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SEMIMICRO QUALITATIVE ANALYSIS

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PREFACE

The first edition of this book was designed for a brief course in qualitative analysis, emphasis being placed upon its use as a laboratory manual and only a minimum of theory being included. Soon after its publication, however, experience in the use of the book led the authors to the belief that the text would be much more usable if the theory portion were expanded. To enhance the value of this expansion, a survey was undertaken, questionnaires being sent to a large number of teachers of qualitative analysis to obtain a consensus as to what subjects should be covered in qualitative analysis and what approach should be used. A gratifying number of replies were obtained from teachers in schools of all sizes and from all parts of the country. Consequently, the suggestions from that survey have been incorporated in this revision.

A number of the changes made and ideas introduced seem especially worthy of mention.

1. The theory portion has been greatly increased, not only to include all subjects commonly treated in qualitative analysis, but also to make use of the educational devices, *repetition and drill.* The theory portion starts with a chapter devoted to the review of important principles of general chemistry; then follow the more involved principles necessary to the proper understanding of qualitative analysis and the theories of solutions. Frequent reference is made to subjects studied in general chemistry to promote the viewpoint that qualitative analysis is an extension of general chemistry and is just the next step in acquiring an understanding of the principles of chemistry.

2. The discussion throughout the book is designed to show the student (*a*) why the principles studied are of use to him, (*b*) how the principles may be used to meet new situations, and (*c*) how the theory and laboratory are related.

To meet these objectives the theory has been illustrated as far as possible by examples taken from actual situations occurring

in the laboratory. The mathematical aspects have been developed through the detailed treatment of many illustrative problems, and many practice exercises have been included at the end of each chapter. These practice exercises make use of material learned not only in the immediate chapter but also in earlier chapters so as to necessitate frequent review of important principles.

3. To avoid the confusion that is likely to develop in the student's mind when much material is covered, each chapter ends in a summary designed to help the student organize his ideas. The summary is in each case followed by a section of review questions whose study serves further to aid in that organization.

4. Modern theories have been treated extensively throughout the book, though the chief approach is more classical than modern. The authors feel that with both viewpoints as prominent as they now are, to exclude either would be detrimental to the best interests of the student. Thus the older conception of hydrogen ion rather than hydronium ion is used predominantly; for *except in those cases where mechanisms* of reactions are being considered, it seems unnecessary to emphasize the hydrated condition of the hydrogen ion when, for example, we still treat the cupric ion in aqueous solution as Cu^{++} rather than write it with the water of hydration that we know it to possess. Where the conceptions of Bronsted and other modern workers seem to make real contributions, however, sections have been devoted to the applications of those theories, the similarities and differences between the concepts being developed. This approach has been used to permit greater freedom to the teacher and yet to provide fairly complete information for the use of the student both now and later.

In the mathematical approach, it has seemed advisable to use concentrations rather than activities; for a thorough understanding of the mathematics involved in a complete treatment of ionic strengths and of activities probably would be too difficult to convey to students of the freshman and sophomore level, and any half measures would be unsatisfactory. The modified classical treatment gives valuable approximations for many cases, and the exercises illustrated are used mostly to help the student understand the simpler principles involved.

Although the book includes many topics that some teachers will feel are nonessential, the organization is such that those topics can be omitted at the discretion of the teacher. In choosing these topics, great use has been made of the results of the questionnaire that was referred to earlier.

In the laboratory portion, a number of improvements based upon experience and upon suggestions obtained from the survey have been incorporated. The main form of the original book has been retained, but improved procedures have been introduced, and convenience has been increased by certain rearrangements of materials. Thus, an unusually successful optional method (Option II) has been included for the analysis of Cation Group III, in addition to the classical method (Option I). The use of a saturated solution of $NaClO_3$ instead of solid $KClO_3$ in the test for manganese has made this test less troublesome; while in Optional Method II, the oxidation of Cr^{+++} to $Cr_2O_7^{=}$ in a nitric acid solution by the action of $NaClO_3$ has lessened the loss of chromium that usually results from the precipitation of $CrO_4^{=}$ with cobalt and nickel in the older sodium hydroxide - peroxide separation. In a similar way the tests for tin and for arsenic have been greatly improved by *seemingly* minor changes in the procedure.

The analysis of the anions has been completely reorganized. By means of preliminary oxidation-reduction elimination tests the time required for the analysis of any unknown is greatly shortened, and at the same time the student acquires an important knowledge of the oxidizing and reducing properties of the anions. In addition, the actual analysis for the anions has been systematized; and especially in Anion Groups II and III, a rather definite precipitation as groups followed by a systematic separation and identification similar to that for cations has been developed.

The notes, which in the first edition were all gathered in one part of the book, have been divided and are placed in groups immediately following the group procedure to which they refer. They are thus much more accessible to the student. The notes have been revised, and much new information has been made available in them. These, together with frequent references to the theory portion, aid greatly in linking the laboratory and lecture portions of the course. In addition, a comprehensive

list of review questions accompanies the work on each group of cations.

It is impossible to list here the names of all those whose suggestions and active assistance made this revision possible, but the authors wish to express their gratitude, especially to all who replied to their questionnaire, and to acknowledge their indebtedness to those people. The authors wish particularly to thank Dr. Otis C. Dermer of this college for having read and criticized the manuscript.

PAUL ARTHUR,
OTTO M. SMITH.

STILLWATER, OKLAHOMA,
September, 1942

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PART I

THEORY

CHAPTER I

INTRODUCTION: REVIEW OF ELEMENTARY PRINCIPLES

One of the first things learned by students in general chemistry is the fact that the chemist identifies and distinguishes among substances by means of differences in their chemical and physical properties. The simpler the substance and the more outstanding its properties the easier the identification becomes. Most of this type of work, however, is done with substances that are by no means simple and with the purpose of learning not only *what* is present in the substance but also *how much* of each component is in a given sample. Such information is obtained by performing an *analysis—qualitative*, to find out *what* is present in the substance, and *quantitative*, to determine *how much* of each component is present in a given sample.

One of the functions of a course in qualitative analysis is to convey a knowledge of the procedures used in determining the composition of ordinary substances. Before any student can realize the full value of the subject, however, he must understand that qualitative analysis involves much more than good technique. The proficient analyst seldom limits himself to acquiring skill in following cookbook types of laboratory procedure, for he knows that the best results come from an understanding of the basic principles that govern the reactions and procedures used. The analyst who does not have such knowledge will find it exceedingly difficult to meet any unusual situations that arise. He may be an excellent technician, but he will seldom be the head man in his work and certainly must depend upon better trained men whenever he is confronted with any new problems. It

behooves each student of analytical chemistry, therefore, to learn *why* each operation is performed as it is rather than to learn a mere routine procedure.

Aside from the analytical training that it furnishes, however, a course in qualitative analysis has a much broader and more important reason for existence. Actually, it is not a new subject —it is *an extension of general chemistry* in which many of the facts learned in the earlier course are treated in greater detail and new facts and many new applications are studied. The principles of general chemistry serve as foundations for analytical chemistry; similarly, a mastery of qualitative analysis is merely the next step in acquiring adequate foundation for the still more specialized branches to be studied later. The material treated in qualitative analysis leads to a better understanding of the laws of chemistry; and this increased knowledge is of a type that is very practical in almost any branch of chemistry with which the student may later find himself occupied.

With these facts in mind, it is quite apparent that a review of some of the more important conceptions studied in general chemistry will be helpful. Some of these points will be discussed in the remainder of this chapter, but it is hoped that the student will refer frequently to his general chemistry text to review topics that must, of necessity, be treated briefly here.

Atomic Structure. In general chemistry we learned that studies of the decomposition products of radioactive elements, of the bombardment of thin metallic films by high-velocity electrons, of artificially produced radioactivity, and of many other similar subjects have made it possible for scientists to identify several subatomic particles and obtain ideas concerning the structure of the atom. Although no accurate picture of the atom can be formulated, a simplified conception as first postulated by the Danish scientist Niels Bohr and later modified in the light of new discoveries can be used to explain many of the facts observed experimentally in the laboratory. At present it may be assumed that three kinds of particles are present in atoms: *electrons*, which are unit negative charges of electricity and which have a mass equal to about $\frac{1}{1850}$ of the weight of a hydrogen atom; *protons*, which are particles possessing a positive charge equivalent in magnitude to that of the electron and a mass equal approximately to one atomic weight unit; and *neutrons*, which are particles

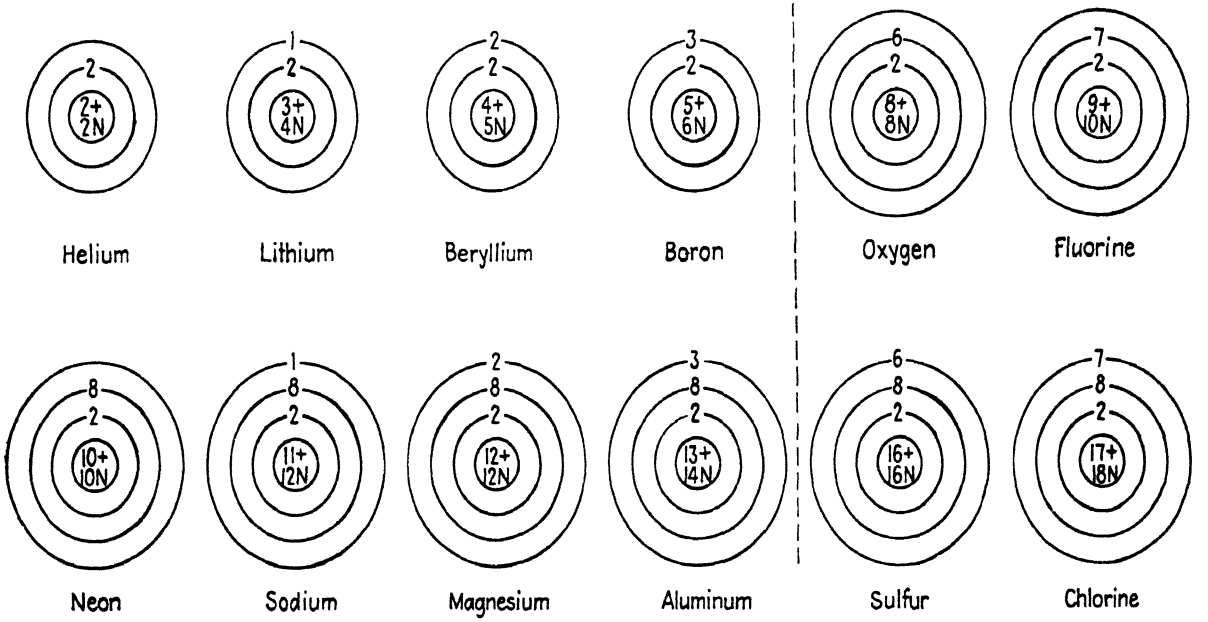


FIG. 1.—Electron distribution in some simple atoms.

having no electrical charge but having a mass equal to that of the proton.*

Early experiments with thin metallic foils pointed to the fact that any atom consists of a compact nucleus surrounded only by electrons. A simple conception of the atom, therefore, is that it consists of a nucleus made up of protons and neutrons and that the electrons, which are systematically arranged in orbits or shells around the nucleus, move around the nucleus of the atom (see Fig. 1). The number of protons in the nucleus is equal to the atomic number of the element. It is obvious that since atoms are electrically neutral, the total number of electrons in the shells around the nucleus must be equal to the number of protons in the nucleus; consequently, the number of electrons also must be equal to the atomic number.

It will be recalled from general chemistry that the valences possible for a given atom are largely controlled by the number of electrons that it has in its outermost electron-containing orbit—sometimes called its *valence orbit*. With the exception of helium which has two, the elements found in the zero group (Group VIII*b*) of the periodic table all have eight electrons in this orbit. None of these elements form compounds or undergo chemical reactions. With certain exceptions,† in the other groups of the

* Two other subatomic particles have been produced and studied; the *alpha particle*, which is a helium atom with two unit positive charges, and the *positron*, a particle having the charge of the proton but a mass equal to that of the electron. It is not known exactly what part each of these plays in the atom. Possibly the proton is merely a close combination of a neutron and a positron. The suggestion has also been made that the neutron is a proton closely associated with an electron. For practical purposes, however, the atom pictured above enables us to explain the simpler reactions and behaviors of atoms.

† The elements from scandium to nickel, from yttrium to palladium, from lanthanum to platinum, and from actinium to uranium do not follow the rule of normally having electrons in the outer orbit equivalent to the number of the periodic group in which they are found. These are the elements in Groups III*a* to VIII*a*, inclusive, in the periodic table. They may exhibit some valences characteristic of the other elements of their group, but they owe this ability to the fact that certain electrons in the shell nearest the valence shell can, under the proper conditions, shift from the inner shell to the outer or valence orbit, thus becoming available to produce the expected valence. For example, iron has two electrons in its outer orbit. When these two electrons are lost, the resultant ion has a valence

periodic table the number of the group is the same as the number of electrons in the valence orbit. For example Group I elements have *one* valence electron; Group II, *two* valence electrons; and so forth, those of Group VII having *seven* valence electrons.

With this simplified picture of the atom in mind we can now consider the question of valence and of the types of compounds formed by different combinations.

Valences and Compound Types. It was mentioned earlier that the elements of Group Zero (Group VIII*b*) are chemically inert, *i.e.*, will not react with other elements. Apparently these atoms have a very stable arrangement of electrons in their outermost electron-occupied shells, the stability of this arrangement being so great that changes in it will not ordinarily occur. If we were to attribute human qualities to atoms, we might say that these atoms are completely "satisfied" with this configuration. To continue the analogy, where the atoms of other elements react, they apparently try *to attain the electronic arrangement of the inert element that comes nearest to having the same number of electrons as they.* In other words, they tend to *lose* electrons or to *gain* or *share* enough of the electrons from another atom to give them eight electrons in the outermost electron-containing orbit.* To illustrate, let us consider some of the elements of the second period, starting with the inert gas neon and considering the typical elements sodium, magnesium, aluminum, silicon, sulfur, and chlorine.

When sodium (a metal) reacts with a nonmetal, the sodium loses its single valence electron to the nonmetal. This leaves the sodium atom with the same number and arrangement of electrons as is found in the neon atom (see Fig. 2). It will be recalled, however, that before reacting, the sodium atom was electrically

---

of +2. If an oxidizing agent of sufficient strength (ordinary oxygen is enough) is brought to act, a third electron will shift outward and be lost by the atom, giving the atom the familiar valence of +3.

* Hydrogen and lithium are exceptions to this rule, the latter tending to lose its valence electron and attain the helium arrangement of two electrons. Hydrogen usually loses its electron to leave only a proton, but in some rare compounds, *e g*, in the formation of metal hydrides, it takes on one electron to attain the helium electronic arrangement. More often it assumes this configuration by sharing electrons with certain nonmetals [as in NH_3, CH_4, PH_3, and SiH_4 (see Fig. 3)].

neutral. The loss of the one electron leaves in the nucleus a proton for which there is no electron in the shells surrounding the nucleus; consequently, the atom of sodium now has an active charge, or *valence*, of +1. Thus, by the loss of an electron, the atom has become what is known as a *cation*, *i.e.*, a *positively charged ion*. If magnesium instead of sodium were to react, it also would attain the electronic configuration of the neon atom. The change in this case, however, would involve the loss of *two*

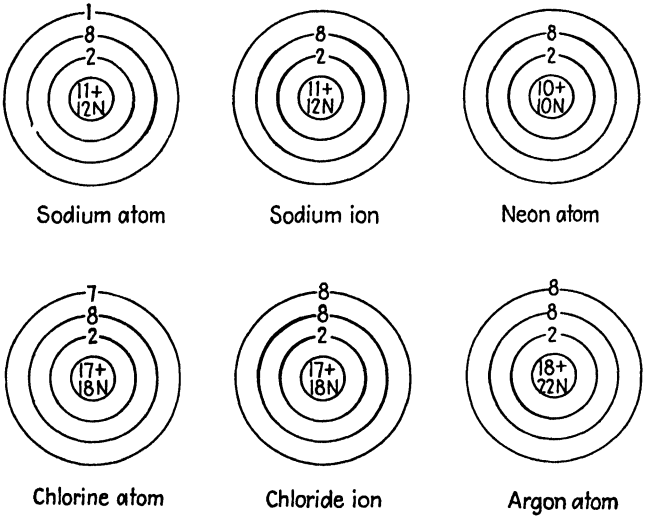


FIG. 2.—Electronic arrangements of atoms, their ions, and the corresponding inert gases.

electrons, and the charge or valence assumed by the atom would be +2. Similarly, aluminum, with three valence electrons, may lose the three electrons and assume a valence, or charge, of +3.

Now, suppose that the nonmetal with which the sodium is reacting is chlorine. Chlorine has seven electrons in its outermost orbit (see Fig. 2). For it to lose all seven electrons in order to assume the neon configuration would be exceedingly difficult. Consequently, in reacting with metals, the chlorine atom tends to *gain* one electron, assuming, thus, the electronic configuration of the much nearer inert gas argon. In so doing, however, the chlorine, which was formerly neutral, takes on the charge of the electron gained and thus assumes a negative valence of 1. Thus

sodium exemplifies those elements which readily lose one electron to attain their most stable electronic patterns, whereas chlorine represents those elements which gain one electron for the same reason. Consequently, when a metal such as sodium reacts with a nonmetal such as chlorine, the atoms of the metal completely give up their valence electrons and the atoms of the nonmetal take on the electrons given up by the metal. The metal is left with one or more excess positive charges; the nonmetal, with excess negative charges; and the resulting ions are held together by the forces of attraction between these unlike charges.

When silicon is considered, a different situation is encountered. To assume the electronic configuration of neon, silicon would have to *lose four* electrons; on the other hand, to attain that of argon, it would be necessary for the silicon atom to *take on four* electrons. To do either of these in the fashion described above would be extremely difficult, and any compounds of silicon that might theoretically be formed in that manner would probably be very unstable * Instead, the silicon atom assumes, when possible, the electronic configuration of the argon atom, doing this by a process of *sharing* the valence electrons possessed by other atoms instead of *taking* the electrons for itself as chlorine did. This may be illustrated by studying the structures of the two compounds of silicon: SiH_4, silane, and $SiCl_4$, silicon tetrachloride (Fig. 3).

In SiH_4 we have a compound of silicon (with four valence electrons) and hydrogen (with one valence electron). Although it is perfectly possible for four hydrogen atoms to yield a total of four electrons to any receptive atom, the silicon cannot retain, without aid, the four additional electrons that it needs. Consequently it may be said that a bargain is struck between the silicon atom and four hydrogen atoms, in which the silicon atom shares its four electrons with four hydrogen atoms, in return for which the hydrogen atoms share their electrons with the silicon—the silicon thus associating itself with the eight required

* The reason for this statement is clear if one remembers that of the elements in the second period, whereas sodium loses its electron readily, magnesium loses its two electrons less readily and, at the other end of this period, whereas chlorine accepts one electron readily, sulfur accepts its two electrons much less readily. Apparently those elements in Group IV (*i.e.*, in the middle of the period) should neither completely lose nor completely take on electrons readily.

to give it a modified argon electronic structure. On the other hand, each atom of hydrogen thus retains a share in its own electron but also gains a share in a second electron. This gives it part interest in a *pair* of electrons, and its electronic structure becomes similar to that of the inert gas helium. The result is that both the silicon atom and the hydrogen atoms are more "satisfied" than they were in the uncombined state and the compound *silane* is formed.

It should be pointed out that these electronic configurations are possible only as long as the silicon and hydrogen remain

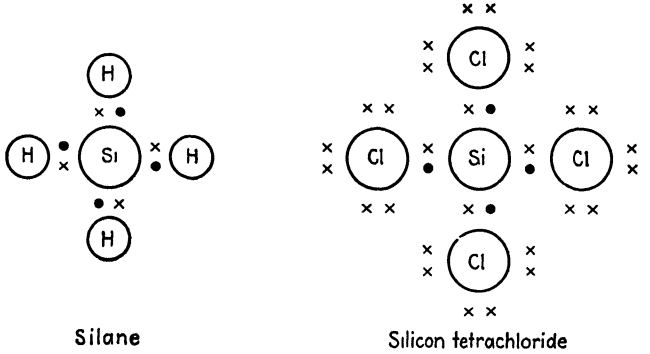


FIG. 3.—Electron sharing in compounds of silicon In this diagram, the dots represent the electrons from the silicon, while the crosses represent those from hydrogen or chlorine.

together, since neither element actually gives up its electron to the other. Consequently, these atoms can separate from each other only if the compound is undergoing decomposition or a reaction with other substances. In this respect the compound is quite different from the product of the reaction of sodium and chlorine. In the latter case the sodium *did not share* its electron—it *gave* the electron to the chlorine atom. Only electrostatic forces hold them together; and if for any reason these forces are weakened sufficiently, the atoms may separate and go their own ways independently, each bearing the charge that it acquired during the original reaction. It will be found later that this accounts, in part at least, for a very important difference between these compounds.

In a similar manner (Fig. 3), when silicon reacts with chlorine, the silicon yields a share in one of its electrons to each chlorine

atom in return for a share in one of the valence electrons of the chlorine atom. By sharing its electrons with four chlorine atoms, each of which in return shares one of its electrons with the silicon atom, the silicon obtains a share in the eight electrons required to give it the electronic configuration of argon. Similarly, the electron that the silicon atom yields to the partnership with each chlorine atom completes the eight electrons needed to give the chlorine the electronic configuration of argon.

It will be noted that in silane each hydrogen atom shares a pair of electrons with the silicon atom and that since there are

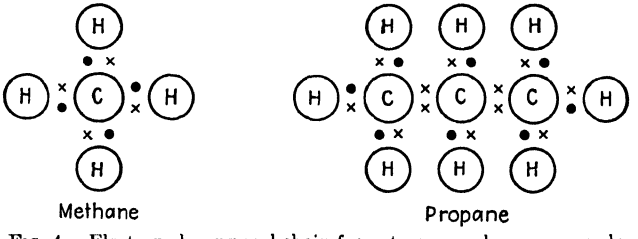


FIG. 4 – Electron sharing and chain formation in carbon compounds.

four such hydrogen atoms, the silicon is sharing four pairs of electrons with the four hydrogen atoms. By the ordinary conception of valence, then, silicon is said to have a valence of 4 and each hydrogen atom a valence of 1.* It obviously is impossible, however, to say that either kind of atom has a positive or a negative valence. To distinguish between this type of valence and the positive and negative valences exhibited in the reaction between sodium and chlorine, it is customary to speak of this type of valence as *covalence* and of the other as *electrovalence*.

As might be expected from the fact that the element carbon also is in Group IV of the periodic table, it is similar to silicon in its behavior. Both elements, but especially carbon, are able to share electrons not only with other kinds of elements but also with atoms of their own kind. Thus, long chains of carbon atoms appear in many carbon compounds, and the whole *large* and *enormously important* field of organic chemistry deals

* In other words, when an element shares electrons, the number of *pairs* of electrons that it *shares* is equal numerically to its valence. It is customary, therefore, to speak of silicon as having a valence of 4, whereas hydrogen and chlorine each have a valence of 1 in compounds with silicon.

with carbon compounds of this type. The electronic arrangements in simple compounds of carbon and hydrogen are illustrated in Fig. 4. From these structures it is easy to see that many compounds of hydrogen and carbon are possible; and if other elements are added also, the possible number of carbon compounds becomes almost endless.

In the case of the compounds of silicon it will be recalled that each atom involved in the reaction contributed one of the electrons of each pair holding the atoms together in the compound. The resulting bonds in these cases were of the purely covalent type. A study of the structure of sulfuric acid, however, shows that such is often not the case. The structure usually suggested as representing the molecule of sulfuric acid shows it as consisting of a sulfur atom surrounded by four oxygen atoms, through two of which two hydrogen atoms are attached to the group. Figure 5 shows the probable manner in which all these atoms are linked. The valence electrons of the sulfur and hydrogen atoms are represented by crosses; those of oxygen, by dots. It will be noticed that two of the atoms of oxygen apparently attach themselves each to a pair of electrons furnished entirely by the sulfur atom. Without contributing any electrons whatsoever to the sulfur, each of these two oxygen atoms appropriates a share in a pair of the electrons of the sulfur, thus completing its own octet and assuming the inert gas configuration needed to give it stability.* On the other hand, each of the

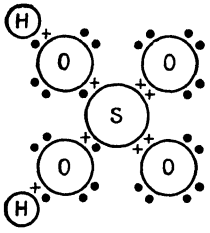


FIG. 5.—Covalent and coordinate bonds in the sulfuric acid molecule.

* Such apparently parasitical behavior is far from uncommon; unattached electron pairs on atoms seemingly are very readily shared with atoms needing one or more pairs of electrons to give them their inert-gas configurations. This type of bond is usually called a *coordinate* bond

For example, in the compound NH_3 the nitrogen atom has one unused pair of electrons. When this substance is brought into contact with an acid, the hydrogen ion from the acid reacts with the ammonia in the following way:

$$\begin{matrix} H \\ :\ddot{N}:H \\ \ddot{H} \end{matrix} + H^+ \rightarrow \left[\begin{matrix} H \\ H:\ddot{N}:H \\ \ddot{H} \end{matrix} \right]^+$$

other two oxygen atoms exchanges a share in one of its electrons for a share in one of the remaining two electrons of the sulfur atom; *i.e.*, each of these two oxygen atoms attaches itself to the sulfur through a shared electron pair. This completes the octet for the sulfur atom but gives each of the two oxygen atoms only seven electrons. The eighth electron for each is obtained from a hydrogen atom, which is thus attached to the oxygen atom through a shared electron pair. An interesting fact is connected with this oxygen-to-hydrogen linkage, however. Although the shared electron pair seems to be similar to that which links this same oxygen atom to the sulfur, actually there is a great difference in the strengths of the two bonds. That between the sulfur and oxygen is very strong; but under the proper conditions the bond between the hydrogen and oxygen can be readily ruptured. When this rupture occurs, however, the electron from the hydrogen is left with the oxygen, the hydrogen assuming under these conditions an electrovalence of $+1$. When both hydrogens are lost by the molecule of sulfuric acid, the SO_4 group remaining is left with an electrovalence of -2 ($SO_4^{=}$). Thus we have an example of a type of valence that is essentially covalence yet under the proper conditions assumes some of the characteristics of electrovalence.

Formerly, compounds in which the atoms were joined by means of electrovalence were known as *polar compounds*, and those held together by covalence were known as *nonpolar*. These two terms, however, are more properly used to distinguish between compounds on the basis of entirely different characteristics. Let us illustrate this by comparing the compounds chloroform, $CHCl_3$, and carbon tetrachloride, CCl_4. The electronic structures of these two compounds are shown in Fig. 6. Although, as has been mentioned in an earlier section, a mechanical picture such as this is not accurate, a study of these diagrams leads to conclusions that have been quite closely verified experimentally. It will be noticed in the diagram for $CHCl_3$ that there is an

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or, as normally written,

$$NH_3 + H^+ \rightarrow NH_4^+$$

Such reactions as these, as well as other illustrations of coordinate valence, will be discussed later in the chapter on complex ions.

unbalance in the arrangement of the electrical charges in the molecule. At one side is the hydrogen atom with its proton, and in the rest of the molecule are accumulated most of the electrons. The result is that one portion of the molecule is slightly negative with respect to the other portion. For all practical purposes this yields a structure with a positive and a negative charge, the two charges being separated by a very small but appreciable distance. Whenever a body has one side nega-

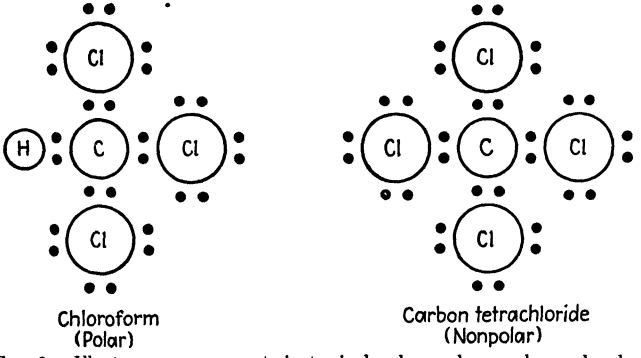


FIG. 6.—Electron arrangements in typical polar and nonpolar molecules

tively charged and the other side positively charged, it is said to be a *dipole*, the strength of the dipole depending upon the distance between the centers of the two charges and upon the magnitude of the charges. A molecule that acts as a dipole is said to possess an *electric moment*, and the molecule is properly classified as a *polar* molecule. Carbon tetrachloride, CCl_4, on the other hand, is entirely symmetrical. Possessing no unbalanced arrangement, it has no electric moment and is classified as a *nonpolar* molecule.

Many molecules that at first glance would seem to be nonpolar are actually quite polar. Water, for example, would be a symmetrical molecule if the hydrogen atoms lay in a straight line with the oxygen atom and on either side of it. Actually, the molecule is angular, the oxygen being at the apex of the angle and the hydrogen atoms lying on the sides of the angle. The result is again an unbalanced arrangement that makes the molecule highly polar. The molecule of sulfur dioxide, SO_2, is similar to that of water in the arrangement of its atoms; con-

sequently, this compound likewise has a high electric moment. Carbon dioxide, on the other hand, is nonpolar.

Solids; Ionic and Molecular Crystals. It will be recalled from general chemistry that studies of the physical characteristics of crystalline solids, particularly of their X-ray diffraction patterns, have given us a fairly clear picture of the arrangement of atoms within the crystal. Just as differences have been found in types of valence bonds, so have differences been found in the types of arrangement of atoms in crystals.

Figure 7 illustrates the arrangement of the ions in a crystal of sodium chloride. It will be noticed that each sodium ion (black

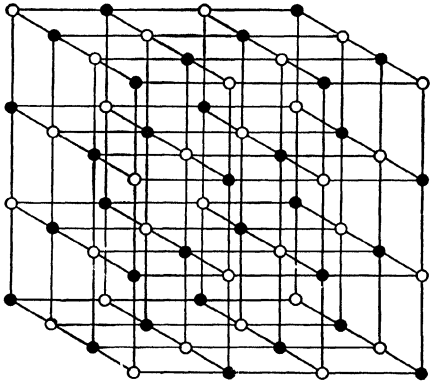


FIG. 7.— Crystal lattice of sodium chloride.

dots) is surrounded by six chloride ions (circles), all equally distant from the sodium ion. Similarly, each chloride ion is surrounded by six sodium ions, all equally distant from the chloride ion. Obviously, no one pair of ions of sodium and chlorine can be differentiated from the group as belonging to one molecule, *i.e.*, as being bound to each other exclusively. The sodium chloride crystal, therefore, has an ionic lattice. Instead of being made up of molecules, it consists of alternate positive and negative ions, the electrostatic valence forces holding the respective ions within the crystal lattice but not holding them together in the form of molecules.

Substances such as carbon tetrachloride have crystalline structures quite different from that of sodium chloride. In carbon tetrachloride the arrangement of atoms in the crystal is

definitely *molecular*. Each carbon atom is closely surrounded by four chlorine atoms, and their arrangement is such that the atoms comprising each molecule are easily identified. In this case, the structural unit of the crystal is the molecule.

Chemical Equilibrium. A review of some of the chemical reactions studied in general chemistry shows that many are of the so-called *reversible* type. For example, in the Haber process for producing ammonia, the reaction

$$N_2 + 3H_2 \rightarrow 2NH_3 \tag{1}$$

is used. On the other hand, one convenient source of hydrogen (contaminated, of course, with nitrogen) is ammonia, which, if passed over a red-hot metallic coil, decomposes to give nitrogen and hydrogen:

$$2NH_3 \rightarrow N_2 + 3H_2 \tag{2}$$

Again, it is possible at high temperatures to have iron react with steam to form iron oxide and hydrogen:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \tag{3}$$

or to have iron oxide react with hydrogen to form iron and steam:

$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O \tag{4}$$

It was pointed out in general chemistry that if any of these reversible reactions are carried out in a closed container so the products of the reaction cannot escape, the resulting mixture soon reaches an *equilibrium*, *i.e.*, a condition in which the relative proportions of the various constituents of the mixture remain unchanged. In other words, if reaction (1) is performed in a sealed container at about 500°C. and the temperature is kept constant, at first ammonia is produced rapidly. As time passes, however, the concentration of ammonia increases more and more slowly, finally becoming constant. Although a large proportion of N_2 and H_2 is still mixed with the ammonia in the container, a longer time will not result in a higher percentage of ammonia in the mixture. The mixture is then said to be at *equilibrium*.

Only reversible reactions can establish equilibriums, and all reversible reactions are capable of so doing. Few chemical reactions are entirely irreversible, though in many cases the equilibrium mixture may contain but a small or even negligible

proportion of the original reactants. For this reason every chemist must understand not only the reasons for the existence of equilibriums but also the factors that influence the point at which equilibrium will be established, *i.e.*, the relative proportions of products and reactants when equilibrium has been established.

Perhaps the broadest rule ever expressed regarding the behavior of equilibriums under changing conditions is the principle of Le Chatelier, which may be stated as follows: *If, to a system at equilibrium, a stress is applied, the equilibrium will shift in such direction as to relieve or partially remove the stress.* In chemical reactions this stress usually takes the form of changes in *concentration*, *temperature*, or *pressure*. The effect of applying these stresses to systems at equilibrium will now be considered in detail.

It becomes obvious that since an equilibrium is set up only by reversible reactions, the relative rates of the two reactions involved must be the controlling factor in the final equilibrium. To illustrate, let us use the reactions

$$H_2 + Br_2 \rightarrow 2HBr \tag{5}$$
$$2HBr \rightarrow H_2 + Br_2 \tag{6}$$

Writing these in the usual way for reversible reactions [reaction (6) is the reverse of reaction (5)], we obtain

$$H_2 + Br_2 \underset{(6)}{\overset{(5)}{\rightleftharpoons}} 2HBr \tag{7}$$

By definition, the conditions necessary for a chemical equilibrium are the existence of two opposing reactions, each undoing what the other is trying to do, and the occurrence of these two reactions at exactly the same rate. In other words, at equilibrium in reaction (7), reaction (5) will be producing HBr at exactly the same rate that reaction (6) is decomposing it.

Obviously, therefore, anything that would affect *unequally* the rates of these reactions would affect the equilibrium point finally established by the mixture. It will be recalled that the principal factors that fix the rate of any chemical reaction are (1) changes in the temperature at which the reaction is taking

place, (2) the use of a catalyst, and (3) changes in the concentration of any of the reactants. Let us consider the probable effect of each of these on the equilibrium point of the foregoing reactions.

The general rule for the effect of temperature on the rate of chemical changes is that an increase of 10°C. will double the rate of any chemical reaction. This is only approximate, however, and the two reactions involved in any one equilibrium are seldom if ever affected to the same extent. In the case of the hydrogen bromide equilibrium, the temperature effect on reaction (6) is greater than that on reaction (5). In other words, although the rates of both reactions are increased when the temperature of the mixture is raised, rate (6) is increased more than rate (5). The net effect, therefore, is that equilibrium will be attained more rapidly at higher temperatures but the yield of HBr will be smaller. On the other hand, in the decomposition of ammonia to form nitrogen and hydrogen,

$$2NH_3 \underset{(1)}{\overset{(2)}{\rightleftharpoons}} N_2 + 3H_2 \tag{8}$$

reaction (2) is more influenced by temperature than reaction (1). Consequently, at higher temperatures equilibrium will be established with less NH_3 and more N_2 and H_2 in the mixture than would be the case at lower temperatures.

If one investigates these reactions more closely, it is found that in the NH_3 equilibrium, reaction (1) is *exothermic* (*i.e.*, gives off heat) whereas reaction (2) is *endothermic* (absorbs heat). Similarly, in the HBr equilibrium, reaction (5) is exothermic and reaction (6) is endothermic. Studies of these and other chemical reactions, therefore, suggest the rule that endothermic reactions are influenced more by changes in temperature than are exothermic reactions. Consequently, the effect of increasing temperature on these reactions would be to shift the equilibriums in the direction of decomposing the NH_3 and HBr, *i.e.*, the direction that would absorb heat. This is exactly what the principle of Le Chatelier would lead one to expect, as the absorption of heat would tend to oppose the rise in temperature.

The effect of *catalysts* on the rate of chemical reactions is well known to every student of chemistry. The characteristics of a

positive catalyst for any reaction are that it speeds up the chemical reaction but that at the end of the reaction the catalyst may be obtained once more. In the case of reversible reactions, however, the effect of a catalyst is peculiar, in that *both reactions are influenced equally.* For example, platinum acts as a catalyst to hasten the decomposition of ammonia to form nitrogen and hydrogen [reaction (2)], but it acts as an equally effective catalyst for the preparation of ammonia from nitrogen and hydrogen [reaction (1)]. The result is that the addition of a positive catalyst shortens the time required for attainment of equilibrium but *has no effect on the relative amounts* of nitrogen, hydrogen, and ammonia in the final equilibrium mixture. The equilibrium point is the same when equilibrium is attained, whether the catalyst was used or not. This generalization applies in the case of all equilibrium reactions, regardless of the nature of the reactants or that of the catalyst used.*

The third factor to be considered is *concentration.* The effect of concentration on the rate of chemical reactions is best summarized in a very important law, the *law of mass action,* which in its simplest form states that the *rate of any chemical reaction is directly proportional to the concentrations of the reacting substances.* Consider the reaction for the production of ammonia from nitrogen and hydrogen:

$$N_2 + 3H_2 \underset{(2)}{\overset{(1)}{\rightleftharpoons}} 2NH_3 \qquad (9)$$

It will be recalled that if the mixture is at equilibrium, the rate r_1 of reaction (1) must be exactly equal to the rate r_2 of reaction (2). Now suppose that at this moment the concentration of nitrogen is suddenly increased. At once, according to the law of mass action, the rate of formation of ammonia [reaction (1)] is increased and thus becomes greater than its rate of decomposition [reaction (2)]. This will result in an increase in the concentration of ammonia. However, as the concentration of

* It must be remembered that when one speaks of the effect produced by changing one factor, it is assumed that all other factors remain constant throughout. To change two factors at once would mean that a qualitative treatment would not be enough unless both factors operated to cause a shift in the same direction.

ammonia increases, the rate of reaction (2) will increase; and as nitrogen and hydrogen are used up to produce the increased amount of ammonia, reaction (1) will slow down until the two rates once more become equal, *i.e.*, equilibrium is once more established. At this new equilibrium point the mixture will contain more ammonia than in the starting equilibrium mixture. It can therefore be said that by increasing the concentration of nitrogen, the equilibrium was shifted to the right, *i.e.*, in the direction of producing ammonia. Similarly it can be shown that increasing the hydrogen concentration or decreasing the concentration of ammonia would shift the equilibrium to the right.*

Although only the qualitative aspects of the law of mass action have been considered above, the law is quantitative as well. Once more using the reaction for the production of ammonia,

$$N_2 + 3H_2 \underset{(2)}{\overset{(1)}{\rightleftharpoons}} 2NH_3 \tag{9}$$

from the law of mass action it can be shown that the rate r_1 of reaction (1) and the rate r_2 of reaction (2) are given, respectively, by the expressions

$$r_1 \propto [N_2][H_2][H_2][H_2]\dagger \tag{10}$$

and

$$r_2 \propto [NH_3][NH_3] \tag{11}$$

where $[N_2]$, $[H_2]$, and $[NH_3]$ represent the concentrations of each of these gases, respectively. It is true that where a propor-

* Frequent use is made of this method of shifting equilibriums to obtain more complete use of a more expensive or otherwise more important reactant. For example, in the production of ammonia, if the concentration of nitrogen is increased, more of the hydrogen will be used up; *i.e.*, when equilibrium is attained, less hydrogen will be left in the mixture than would otherwise be true.

Similarly, if the ammonia is removed from the reaction mixture by liquefying it or by dissolving it in water, the reaction will be more complete.

† It can be shown mathematically than when more than one molecule of the same substance is required in the balanced equation, each molecule must be treated as if it were a different kind of molecule. For an excellent explanation of this fact see "Qualitative Analysis and Chemical Equilibrium," by Hogness and Johnson.

tionality sign ($\propto$) appears in a mathematical expression, there is always a constant that, if properly incorporated in the expression, will convert the expression to an equation. If k_1 and k_2 are used for the respective constants, the expressions for the reaction rates become

$$r_1 = k_1[N_2][H_2]^3 \tag{12}$$
$$r_2 = k_2[NH_3]^2 \tag{13}$$

It will be recalled that at equilibrium, $r_1 = r_2$. It follows then that at equilibrium

$$k_1[N_2][H_2]^3 = k_2[NH_3]^2 \tag{14}$$

Algebraically, this may be rearranged to give

$$\frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{k_1}{k_2} \tag{15}$$

However, the result of dividing one constant by another constant is a third constant. Therefore, letting $K = k_1/k_2$ the expression finally becomes

$$\frac{[NH_3]^2}{[N_2][H_2]^3} = K \tag{16}$$

The constant K is known as an *equilibrium constant.*

Similarly, it can be shown that the application of the law of mass action to the equilibrium set up for the decomposition of HBr

$$2HBr \rightleftharpoons H_2 + Br_2 \tag{17}$$

yields, for the equilibrium constant for this reaction, the mathematical expression

$$\frac{[H_2][Br_2]}{[HBr]^2} = K \tag{18}$$

The facts brought out in these two treatments may readily be formulated into a general expression. If the reaction between two substances, A and B, requires w molecules of A and x molecules of B, and the products are y molecules of C and z molecules of D, *i.e.*,

$$wA + xB \rightleftharpoons yC + zD$$

the equilibrium expression

$$\frac{[C]^v[D]^s}{[A]^w[B]^x} = K^*$$

is obtained. By substitution, this equation may be used to set up the expression for the equilibrium constant for any reaction.

The principle of Le Chatelier, though not quantitative, does indicate *qualitatively* the effect on equilibriums of changes in concentration. In the ammonia equilibrium considered before,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad (9)$$

it was found that increasing the concentration of nitrogen would cause the equilibrium to shift to the right. In this shift, part of the nitrogen is used to produce ammonia. Thus the equilibrium has shifted in such direction as partly to remove the stress—in this case, the increased concentration of nitrogen.

Le Chatelier's principle leads to another interesting generalization in regard to reactions involving substances that are entirely in the gaseous state. By applying Gay-Lussac's law of combining volumes† to the equation for the production of ammonia

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad (1)$$

it will be found that if *one* volume of nitrogen is forced to react *completely* with hydrogen, the reaction will require *three* volumes of hydrogen and the product will be *two* volumes of ammonia, assuming that the volumes of all three gases are measured at the same temperature and pressure. In other words, *four* volumes of gaseous reactants (one of nitrogen and three of hydrogen) will produce *two* volumes of gaseous product. Now suppose that a mixture of the three gases is allowed to come to equilibrium

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* By convention, the substances in the right-hand half of the equation are always placed in the numerator when writing the expression for an equilibrium constant.

† This law states that *in reactions involving two or more gases, the ratio of the volumes of the gases taking part in the reaction is expressible in small whole numbers.* The ratio of the *coefficients* of the formulas of the balanced equation is the same as the ratio of the volumes involved. If this relationship is not remembered clearly, it is suggested that the student review this law in any good general chemistry text.

in a cylindrical container equipped with a piston and that the piston is then moved inward, increasing the pressure on the *whole system.* When equilibrium is once more established, it will be found that the proportion of ammonia has *increased.* This would be expected from Le Chatelier's principle, since the shift from nitrogen and hydrogen to form more ammonia results in a decrease in volume—or in this case in a decrease in pressure to oppose the increase in pressure used to shift the equilibrium.

If, on the other hand, the reaction

$$H_2 + Br_2 \rightleftharpoons 2HBr \qquad (7)$$

is studied, it is found that *two volumes* of gaseous reactants produce *two volumes* of gaseous product. Consequently, changing the pressure has no influence on this equilibrium.

Review Questions

1. Define: (*a*) qualitative analysis, (*b*) quantitative analysis, (*c*) electrovalence, (*d*) covalence, (*e*) coordinate valence, (*f*) atomic number, (*g*) positive catalyst.

2. Of what kinds of particles are atoms believed to be made? Give the known characteristics of each.

3. Show by diagrams what happens when potassium reacts with chlorine to form potassium chloride. Explain, in terms of the apparent stabilities of different electronic arrangements, why such a reaction is believed to occur.

4. What is the difference between a polar and a nonpolar molecule? Give two examples of each.

5. What evidence do we have for the fact that sodium chloride is ionized in the solid state?

6. What are the two chief characteristics of an equilibrium?

7. What factors may be used to change the rate of a chemical reaction?

8. What influence does each of the factors mentioned in Question 7 have upon the point of equilibrium of a reversible reaction?

9. State Le Chatelier's principle. Give several illustrations of the possible applications of this principle.

10. State and explain briefly the law of mass action.

11. In the reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3 + heat$, what would be the effect on the equilibrium of

a. An increase in temperature?

b. A decrease in the concentration of SO_3?

c. Adding a positive catalyst?

d. Adding a negative catalyst?

e. An increase in total pressure?

f. A decrease in the concentration of O_2?

CHAPTER II

SOLUTIONS

Although a knowledge of the laws governing the behavior of solutions is helpful in almost any branch of chemistry, such knowledge is really *essential* in analysis, where most of the operations are performed with unknowns and reagents both of which are in solution. Most of the theories studied in qualitative analysis are, directly or indirectly, theories of solutions. It is well, therefore, to review some of the simpler concepts of solutions learned in earlier work and to extend this review into a study of some of the more advanced theories.

A solution is a mixture of two or more substances in which the interspersed particles are of molecular dimensions.* A true solution appears, even when the eye is aided by optical instruments, to be completely homogeneous. In other words, as far as can be seen, a solution is completely uniform throughout and contains no dissimilar particles. All the components seem to be in the same phase. Consequently, it may be said that a solution is *an optically homogeneous mixture.*

The components of a solution are known as the *solute* and the *solvent.* Although in aqueous solutions water is usually considered the solvent, the actual determination of which component is the solute and which is the solvent depends upon the use to which the solution is to be put. For example, in a solution of sodium hydroxide and water the sodium hydroxide is usually considered the solute and the water the solvent. It will be noticed, however, that when one uses such a solution as a reagent, the sodium hydroxide is the component that enters most directly into any reaction in which such a solution is to take part. A study of this and a number of other solutions, therefore, leads to the conclusion that the solute may be most accurately defined

* To say that the particles are of molecular dimensions does not mean that they are single molecules. They may be single molecules, clusters of a *very few* molecules (*e.g.*, solvated molecules or ions), or parts of molecules (*e.g.*, ions).

as the *chemically more active component* of a solution whereas the solvent is the chemically *less active** *component*.

Let us use the example of sugar dissolving in water and try to develop a mental picture of what happens during the process. At the first instant when the sugar is placed in the water, no dissolved molecules of sugar are present. At once, however, molecules of sugar begin leaving the surface of the solid and passing into the water. Once in solution the molecules move around through the solution in a random manner. Some of the dissolved molecules eventually strike the surface of the solid sugar; and when this happens, a few of these molecules will cling momentarily to the surface of the sugar. Thus, two things are happening during the process of preparing a sugar solution: (1) sugar is dissolving, and (2) sugar is precipitating. These two processes are each the reverse of the other, one undoing what the other is doing. At first the dissolving proceeds much more rapidly than the precipitation; for the concentration of dissolved sugar molecules is low, and relatively few of the molecules are returning to the surface of the original solid sugar. As the concentration of dissolved sugar increases, however, the rate of precipitation increases until eventually, if solid sugar is yet present, the rate of precipitation exactly equals the rate of dissolving. It may be said, therefore, that in this solution the *undissolved solute is in equilibrium with dissolved solute*. Such a solution is a *saturated* solution, and the concentration of solute in such a solution is the *solubility* of that solute.

It is found that solutions can often be prepared in such a way that the concentration of the solute is greater than that in a saturated solution. Such solutions, which are known as *supersaturated* solutions, frequently appear in qualitative analysis and give trouble owing to the fact that the dissolved substance does not precipitate at the desired point in the procedure. The slightly soluble salts of calcium, potassium, sodium, and ammonium and the chloride of lead are especially troublesome in this respect. When such a situation is possible, therefore, special

* It cannot be said generally that the solvent is the *inactive* component As will be seen later in studying the theories of electrolytes, particularly Bronsted's acid-base theory, the solvent often plays an exceedingly important part in the reaction, even though it may not appear in the stoichiometric equation.

precautions to insure precipitation must be taken. Since any supersaturated solution is in an unstable condition, a number of devices may be employed to cause solute to precipitate and the solution to become merely saturated. Some of these are (1) the addition of a small crystal of the solute* to act as a nucleus upon

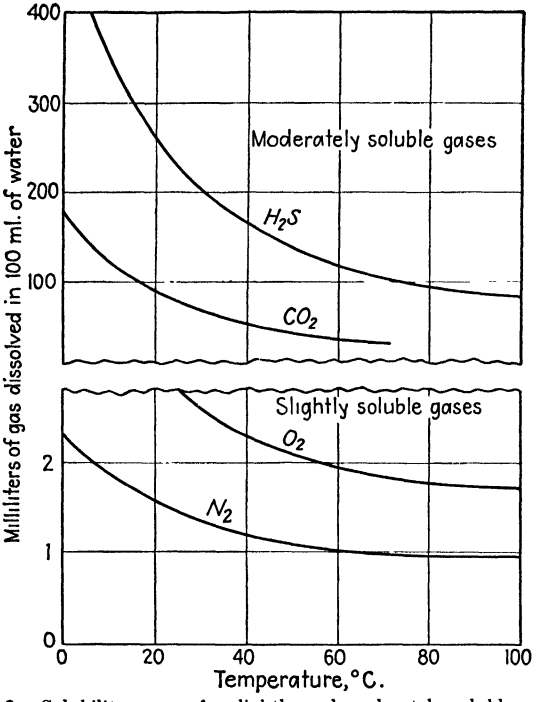


FIG. 8.—Solubility curves for slightly and moderately soluble gases.

which crystallization may occur, (2) vigorous stirring or shaking of the solution, and (3) rubbing the inner wall of the container with the tip of a stirring rod.† If crystallization is started by any of these devices, the first crystals formed will aid in the precipitation of the excess solute.

* This is rarely employed in qualitative analysis, because the addition of such solute introduces that substance into the unknown and makes later confirmation tests for the elements in the solute undependable.

† This apparently removes adsorbed substances from the wall of the vessel and exposes a clean surface upon which crystallization can occur.

Factors Influencing Solubility. It has been found that the solubility of any substance may be influenced by three factors: (1) the nature of the solute and solvent, (2) the temperature, and (3) the pressure.

The first of these factors may be illustrated by comparing water, benzene, and alcohol as solvents and comparing sugar, sulfur, and benzene as solutes. Thus sugar is quite soluble in

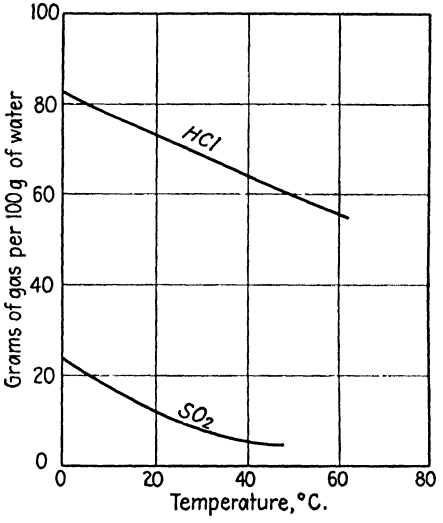


FIG. 9.—Solubility curves for hydrogen chloride and sulfur dioxide.

water but is quite insoluble in benzene; paraffin is insoluble in water but fairly soluble in benzene; and sodium chloride is moderately soluble in water, but its solubility in absolute (anhydrous) ethyl alcohol is very low.

The second factor, *temperature*, influences solubility to an extent and in a manner that vary with both the type of solution and the nature of the solute. When solutions of gases in liquids are considered it may be said, in general, that the solubility of a gas decreases with increased temperature and increases with decreased temperature. This rule is illustrated for slightly and moderately soluble gases in Fig. 8 and for the very soluble gases HCl and SO_2 in Fig. 9.

On the other hand, the solubilities of most solids in water increase with increases in temperature. The extent to which the solubility changes with temperature, however, may be widely different for different solutes, and the solubilities of a few com-

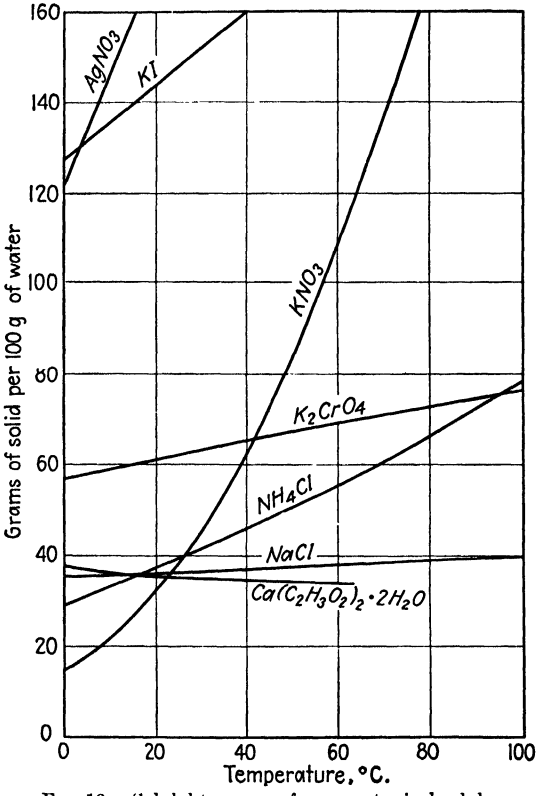


FIG. 10.—Solubility curves for some typical solids.

pounds actually *decrease* with increased temperature. In Fig. 10 the solubility curves for a number of solids are shown. It will be noted that the solubility of NaCl increases only a little with large increases in temperature, that of KNO_3 increases greatly, whereas that of $Ca(C_2H_3O_2)_2$ *decreases* with increases in temperature.

The third factor, *pressure*, has no significant effect on the solubility of solids, but an increase in the pressure of a gaseous

solute increases its solubility in liquids.* The relationship between the partial pressure, p, of the gas, and the solubility, S (in grams per unit quantity of solvent), is quantitative for many gases and is expressed by Henry's law, which states that *the solubility of a gas is directly proportional to the partial pressure of the gas in the free space above the solution.* Mathematically this law is

$$\frac{S}{p} = K, \qquad \text{or} \qquad S = Kp$$

where K is a constant which is characteristic of the solute and solvent, and of the temperature.

Henry's law is fairly accurate for solutions in which there is no reaction between solute and solvent, if the pressures considered are not greater than 1 atm. For greater pressures, however, deviations from this law become much greater; and for aqueous solutions of such gases as NH_3, CO_2, SO_2, and HCl, which react with water, the law is not at all dependable.†

Distribution Ratios. When alcohol and water are mixed, it is found that either will dissolve in the other in all proportions. The same is true of glycerin and water, of benzene and carbon tetrachloride, and of many other combinations of liquids. In such cases the liquids are said to be *miscible* in all proportions. On the other hand, a few drops of ether will dissolve in a much

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* It should be noted that this rule holds only if the solubility of the gas is expressed in terms of the *weight* of solute in a fixed quantity of solvent. Since the volume occupied by a given weight of gas is inversely proportional to the pressure, for those gases which obey Henry's law the *volume* of the gas that will dissolve in a fixed quantity of solvent is independent of pressure.

† It should be remembered that Henry's law expresses the relationship of the concentration of the *dissolved* gas to the pressure of *undissolved* gas. If some of the dissolved gas reacts with the solvent to form a new substance, thus removing the dissolved *solute molecules*, it is a natural consequence of Le Chatelier's principle that more of the gas would dissolve to take the place of those molecules which have been removed. Consequently, gases exhibit unusually high solubilities in solvents with which they react. Sulfur dioxide, which reacts with water as follows,

$$SO_2 + H_2O \rightleftharpoons H_2SO_3$$

is an example of one such gas.

larger volume of water, and a few drops of water will readily dissolve in a much larger volume of ether; however, if anything like equal volumes of the two liquids are mixed, two layers will form, one being ether saturated with water, the other being water saturated with ether.* Such liquids are evidently only partially miscible. Still other pairs of liquids are so insoluble in each other as to be classed as *immiscible.* Among such liquid pairs are benzene and water and carbon tetrachloride and water.

Although a study of all the properties of pairs of immiscible liquids does not come within the scope of this work, one property is so useful that a discussion of it and its application is essential. This property deals with the *distribution* of a solute between two immiscible liquids that are in contact with each other. To illustrate this, suppose that one shakes a solution of iodine in water with an equal volume of CS_2. If the two liquids remain in contact with each other sufficiently long, an equilibrium will be attained between the I_2 in the water and that in the CS_2, *i.e.*,

$$I_{2(\text{water})} \rightleftharpoons I_{2(CS_2)}$$

An application of the law of mass action to this equilibrium yields the following relationship:

$$\frac{\text{Concentration of } I_2 \text{ in } CS_2}{\text{Concentration of } I_2 \text{ in water}} = K$$

In other words, when equilibrium has been attained, the ratio of the concentrations of the solute in the two solvents will equal a constant. The constant for this particular equilibrium is about 400; therefore, when a solution of I_2 in water is shaken with an equal volume of CS_2, most of the I_2 will dissolve into the CS_2, leaving, at equilibrium, only a very small amount of I_2 in the water. By repeated treatments each using small portions of CS_2, all but insignificant quantities of I_2 can be removed from an aqueous solution. Such a process, known as *extraction,* is widely used in chemical processes for the separation of products from other undesirable substances with which they may be in

* At 25°C., 100 g. of ether will dissolve 1.26 g. of water, while 100 g of water will dissolve 6.0 g. of ether.

solution. In qualitative analysis, extractions are often used to make tests for dissolved substances more sensitive and specific.*

The relationship illustrated holds true for any pair of immiscible liquids and for any other solute, provided the solute has the same molecular weight in both solvents. If the solute ionizes, associates, or solvates† in one of the solvents, this simple relationship does not fit the observed facts; more complicated mathematical relationships must be used in such cases.

In those cases where the solubility of the solute in each solvent, taken separately, is very low, the distribution coefficient is equal to the ratio of these solubilities. Thus, if S_1 is the solubility of a given solute in one solvent and S_2 is its solubility in the other,

$$\frac{S_2}{S_1} = \frac{C_2}{C_1} = K$$

Such is not the case, however, where the solubilities in the separate solvents are great; for in more concentrated solutions, other factors destroy the accuracy of this relationship.

Concentration Units. Although frequent mention has been made of the variability of concentrations in solutions, little has thus far been said of the units in which concentrations may be expressed. There are a number of ways of expressing concentrations: in grams per 100 ml. of solvent, in grams per liter of solvent or of solution, in grams per 100 g. of solvent or of solution, in parts per million by weight, in moles per liter (molarity), and in gram-equivalent weights per liter (normality). All these and others are used in different branches of work; but perhaps the most useful of all to the chemist are the *molarities* or the *normalities* of solutions.

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* An example is the use of CCl_4 or CS_2 to extract I_2 or Br_2 from aqueous solutions in testing for iodides or bromides. An oxidizing agent is first added to the aqueous solution to set free the I_2 or Br_2; then the mixture is shaken with a very small volume of either CS_2 or CCl_4. Most of the halogen dissolves in the nonaqueous liquid; and owing to its greater concentration and consequent greater depth of color in this solvent, the halogen is easily seen and recognized.

† Solvation is the term applied to any reaction in which solute molecules combine with one or more solvent molecules. When they are dissolved in water, the molecules of many substances react with water to form hydrates.

A *molar solution* is one that contains 1 *mole* (*a gram-molecular weight*) *of solute* in each *liter* of *solution.** Thus, to prepare a liter of a $1M$ solution of Na_2SO_4 one would dissolve 142 g. of the solid in water and then dilute the resulting solution until the whole had a volume of exactly 1 liter.† If a volume of solution smaller than 1 liter is to be prepared, the proportionate quantity of solute is required. To illustrate, 1 liter of $1M$ sucrose, $C_{12}H_{22}O_{11}$, solution would be prepared by dissolving 342.17 g. of the solute in water and diluting it to a volume of 1 liter. If only 250 ml. of the $1M$ solution were to be prepared, the weight required could be determined by proportion:

$$\frac{\text{Milliliters needed}}{1000 \text{ ml.}} = \frac{\text{weight needed}}{\text{gram-molecular weight}}$$

$$\therefore \frac{250}{1000} = \frac{x}{342.17}$$

$$\therefore x = \frac{250}{1000} \times 342.17 = 85.54 \text{ g. of sucrose needed}$$

This weight of sugar, then, should be dissolved in water, and the solution diluted to a volume of 250 ml. in a 250-ml. volumetric flask.

Concentrations greater or less than those represented by $1M$ solutions are obtained by using more or less of the solute to prepare each liter of solution. A half-molar ($0.5M$) solution contains 0.5 mole of solute in each liter of solution; a $0.23M$ solution contains 0.23 mole per liter of solution; and a $1.42M$ solution contains 1.42 moles per liter of solution.

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* It is true that many substances such as NaCl do not exist in molecular form either in the solid or in the dissolved state. Instead of speaking of the molecular weights of such substances, therefore, it would be more correct to speak of their *formula weight*. For convenience, however, the term *gram-molecular weight* will be used in this book, unless it seems essential to use the other term for special cases.

† In preparing such solutions use is generally made of *volumetric flasks*, which are flasks calibrated to contain a definite volume of liquid when they are filled exactly to a specified level marked by a ring etched around the neck of the flask. For greatest accuracy, the liquid should be measured at the temperature at which the flask was calibrated. This temperature, which is always indicated on the side of the flask, is 20°C. for most apparatus made in the United States.

Problem 1. Suppose that it is desired to prepare 230 ml. of a 0.12*M* solution of $CuSO_4 5H_2O$.

a. Calculate the weight of solute required to make 1 liter of 1*M* solution. This is, by definition, 1 mole of solute, or

Cu = 63 57	10H = 10 08
S = 32 06	5(O) = 80 00
4(O) = 64 00	

The total is 249.71; consequently, for 1 liter of 1*M* solution, 249 71 g of $CuSO_4 5H_2O$ would be required.

b. Next, using the information obtained in (*a*), calculate the weight of solute required to make 230 ml of a 1*M* solution Since only 230 ml. of solution is needed, and since 1 liter (1000 ml) of the solution would contain 249.7 g , the weight of solute required can be calculated from the proportion

$$\frac{230}{1000} = \frac{x}{249.7}$$

$$\therefore x = \frac{230}{1000} \times 249\ 7 = 57.43 \text{ g.}$$

of $CuSO_4 \cdot 5H_2O$ would be needed to prepare 230 ml of a 1*M* solution.

c. Finally, using the information obtained in (*b*), calculate the quantity of solute required to prepare 230 ml of a 0 12*M* solution. Since a 0.12*M* solution is only 0 12 as concentrated as a 1*M* solution, and since 230 ml of a 1*M* solution required 57 43 g. of $CuSO_4 5H_2O$, then 230 ml. of a 0.12*M* solution would require the use of

$$0.12 \times 57\ 43 = 6\ 891 \text{ g}$$

of the salt.*

Problem 2. Suppose that one is given a solution containing 24 g. of Na_2CO_3 in 460 ml. of solution. What is the molar concentration of the solution?

a As in Problem 1, first calculate the weight of Na_2CO_3 required to make 1 liter of 1*M* solution. This is 1 mole, or 106 g

b. Next, calculate what weight of Na_2CO_3 would be present in 1 *liter* (1000 ml.) of a solution of the *given* concentration. This is best solved by proportion:

$$\frac{24}{x} = \frac{460}{1000}$$

$$\therefore x = 52\ 174 \text{ g.}$$

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* Problems of this type may be worked using the logical steps outlined above. Sometimes, however, it may be desirable to use the following formula for such calculations:

$$G = \frac{V \times W \times M}{1000}$$

where G is the weight in grams of solute required to make V ml. of solution of molarity M, and W is the molecular weight of the solute.

c. Finally, calculate the molarity of the solution by dividing the *actual* weight of solute per liter by the weight of solute in 1 liter of a 1*M solution*·

$$52\ 174 \div 106 = 0.492M^*$$

Problem 3. What volume of 1.4*M* $BaCl_2\ 2H_2O$ could be made from 150 g of the salt?

a. As in the earlier problems, first calculate the weight of solute needed to make 1 liter of a 1*M* solution. Again this is 1 mole, or 244 3 g, of $BaCl_2\ 2H_2O$

b. Next, calculate the weight of solute required to make 1 liter of 1.4*M* solution This will be

$$(1.4)(244\ 3) = 342\ 0 \text{ g. for 1 liter of 1 } 4M \text{ solution}$$

c From the answer in *b*, calculate the weight of solute required for *each milliliter* of a 1 4*M* solution.
This is

$$342\ 0 \div 1000 = 0.342 \text{ g per milliliter}$$

d Finally, divide the weight of solute available by the weight of solute required for each milliliter of 1 4*M* solution. This will give as the number of milliliters of solution to be prepared

$$150 \div 0\ 342 = 438\ 6 \text{ ml.}$$

A *normal* (1*N*) solution is a solution that contains 1 *gram-equivalent weight* of solute in each *liter* of *solution.* A 2*N* solution contains 2 gram-equivalent weights of solute per liter of solution, and a 0.2*N* solution contains 0.2 gram-equivalent weight of solute per liter of solution.

The term *gram-equivalent weight* requires discussion. In the first place, it is important to understand that the equivalent weights of many compounds depend upon the use to which the compound is to be put. For example, let us consider the com-

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* The formula mentioned in the earlier footnote may be used here also. By algebraic manipulation, the formula

$$G = \frac{V \times W \times M}{1000}$$

may be rearranged to

$$M = \frac{1000G}{V \times W}$$

By substitution of the values given in this problem, one obtains

$$M = \frac{(1000)(24)}{(460)(106)} = 0.492M$$

pound $NaAl(SO_4)_2$. As a reagent, this substance may be used as a source of sodium, aluminum, or sulfate. If it is being used to supply sodium, the gram-equivalent weight is the same as the gram-molecular weight. On the other hand, as a source of aluminum, the gram-equivalent weight equals one-third of the gram-molecular weight; while as a source of sulfate radicals, the gram-equivalent weight is one-fourth of the gram-molecular weight. In general, for double decomposition reactions, the gram-equivalent weight of a compound is obtained by dividing its gram-molecular weight by the total number of valences represented by the radical of which it is to serve as a source.* Thus in the compound $Fe(NH_4)_2(SO_4)_2$, two valences are furnished by the iron, Fe^{++}; two (one for each) by the ammonium, NH_4^+; and four (two each) by the sulfate radicals, SO_4^{--}. Hence, if the compound is used as a source of either iron or ammonium in a double decomposition reaction, the gram-equivalent weight is half of the gram-molecular weight; if as a source of sulfate radicals, it is one-fourth of the gram-molecular weight.

Problems involving weights of solute, volume, and normality are calculated in a way comparable to the method used in solving corresponding problems involving molarity. The one important difference is that the gram-equivalent weight is used instead of the gram-molecular weight.

Problem 4. What weight of $NaHSO_4$ would be required to prepare 700 ml. of a solution 0.3*N* with respect to sulfate?

a First determine the gram-equivalent weight of $NaHSO_4$ with respect to sulfate. Since the valence of the sulfate radical is 2, the gram-equivalent weight is half the gram-molecular weight:

$$\frac{23 + 1 + 32 + 4(16)}{2} = 60 \text{ g.}$$

* For oxidation-reduction reactions the gram-equivalent weight is obtained by dividing the gram-molecular weight by the *change in valence* undergone by that element in the compound being oxidized or reduced. Thus in the reaction between $KMnO_4$ and HNO_2, the manganese is reduced from a valence of +7 to a valence of +2, and the nitrogen is oxidized from +3 to +5. Consequently the gram-equivalent weight of $KMnO_4$ is one-fifth the gram-molecular weight, while that of HNO_2 is one-half the gram-molecular weight.

A more complete understanding of this will be gained during the study of the chapter on Oxidation-reduction Reactions.

Therefore, if 60 g. of $NaHSO_4$ is dissolved in enough water to make exactly 1 liter of solution, the solution will be $1N$ with respect to sulfate.

b. The concentration desired is, however, not $1N$ but $0.3N$. Consequently, it is necessary to find the weight of solute required for 1 liter of a $0.3N$ solution. This is

$$0.3 \times 60 = 18 \text{ g for 1 liter}$$

c. Finally, since 18 g of solute was required to prepare 1 liter (1000 ml.) of the solution, the weight of solute required for 700 *ml* of $0.3N$ solution may be calculated from the proportion

$$\frac{700}{1000} = \frac{x}{18}$$

$$x = \frac{700}{1000} \times 18 = 12.6 \text{ g.}$$

This and similar problems involving normality, volume, and weight of solute may be solved using a formula similar to that employed for the same type of problems involving molarity. It will be recalled that that equation was

$$G = \frac{V \times W \times M}{1000}$$

Now if in this equation W is changed to E and M is changed to N, there is obtained the equation

$$G = \frac{V \times E \times N}{1000}$$

where G is the weight in grams of solute required to make V ml. of a solution of N normality and E is the gram-equivalent weight of the solute.

A very convenient form of this equation is obtained by using *milliequivalents* (one-thousandth of the gram-equivalent weight) instead of gram-equivalent weights. The milliequivalent weight, e, is found by means of the equation

$$e = \frac{E}{1000}$$

Substituting e in the original expression gives

$$G = VNe$$

This last expression can be rearranged algebraically for use in calculating the normality of a solution when the weight of solute G in V ml. of the solution is given:

$$N = \frac{G}{Ve}$$

or for calculating the number of milliliters V of solution of normality N that can be prepared from G g. of solute:

$$V = \frac{G}{Ne}$$

The expression of concentrations in terms of normality is especially useful to the chemist in quantitative work. If solutions of two substances that are capable of reacting with each other are mixed, the relationship between their normal concentrations and the volumes required of each for the reaction is expressible by the inverse proportion

$$\frac{N_1}{N_2} = \frac{V_2}{V_1}$$

or

$$N_1 \times V_1 = N_2 \times V_2$$

where N_1 and V_1 are the normality and volume, respectively, of one of the solutions and N_2 and V_2 are the normality and volume of the other solution. This same equation may be used to calculate how to dilute a solution of a specified normality to one of a given lower normality. The main types of calculations involving this equation are illustrated in the following problems.

Problem 5 What volume of 0.244N H_2SO_4 would be required to neutralize 65 ml. of 0.52N NaOH?

To solve this problem use the equation

$$N_1 \times V_1 = N_2 \times V_2$$

Let N_1 and V_1 refer to the normality and volume of the acid and N_2 and V_2 refer to the normality and volume of the base. Then by substituting in this expression, obtain

$$0.244V_1 = 0.52 \times 65$$
$$\therefore V_1 = 138.52 \text{ ml.}$$

Problem 6 How should one dilute a 0.35N solution of HCl if it is desired to prepare from it 210 ml. of 0.1N HCl?
To solve this, again use the formula

$$N_1 \times V_1 = N_2 \times V_2$$

this time letting N_1 and V_1 refer to the original acid and N_2 and V_2 refer to the final diluted acid
Then

$$0.35V_1 = 0.1 \times 210$$
$$\therefore V_1 = 60 \text{ ml}$$

Consequently, it would be necessary to take 60 ml. of the 0.35N acid and *dilute it to a volume of* 210 *ml.*

Colligative Properties of Solutions. Some of the physical as well as all the chemical properties of a solution depend upon the *kind* and also the number of particles present in the solution. Certain of the physical properties, however, are dependent only upon the *number* of particles present. Such properties are called *colligative properties.*

If 0.01 mole of any nonvolatile nonelectrolyte* is dissolved in 1000 g. of water,† the resulting solution is found to have a boiling point of 100.0052°C. and a freezing point of −0.0186°C. In other words, by adding 0.01 mole of solute to 1000 g. of water, the boiling point of water is raised 0.0052°C. and its freezing point is lowered 0.0186°C. If a 0.02 molal solution is used instead of the 0.01 molal solution, the indicated changes will be twice as great and, if 0.05 molal, five times as great. If these same relationships exist at all concentrations, the elevation in boiling point produced by dissolving 1 mole of a nonelectrolyte in 1000 g. of water should be 0.52°C. and the corresponding lowering of the freezing point should be 1.86°C. These constants, which are known as the *molal boiling-point constant* and the *molal*

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* For the time being, an *electrolyte* may be identified as any substance whose aqueous solution conducts electricity. Those substances whose solutions conduct well are classed as *strong* electrolytes; those whose solutions conduct but poorly are *weak* electrolytes; and those substances whose aqueous solutions do not conduct electricity are *nonelectrolytes.* A more thorough discussion of these classes will be found in the next chapter.

† A solution made by dissolving 1 mole of solute in 1000 g. of *solvent* is known as a *molal* solution. The distinction between *molar* and *molal* should be carefully noted.

freezing-point constants, respectively, are true for *nonelectrolytes* in general,* in dilute solutions (of the order of 0.01 molal); but in more concentrated solutions, deviations occur, the deviations being greater the higher the concentration.

TABLE I.—MOLAL FREEZING-POINT DEPRESSION FOR AQUEOUS SOLUTIONS OF VARIOUS NONELECTROLYTES

Solute	Molal concentrations of solutions tested		
	0 01	0 1	1 0
Acetone	1 86	1 85	1 79
Glycerin	1 86	1 87	1 89
Sucrose	1 86	1 88	2 06

When dilute solutions of nonelectrolytes in nonaqueous solvents are tested similarly, the same type of regularity is observed. The

* These constants are sufficiently accurate to make the use of alterations in boiling point or freezing point one of the most valuable methods of determining molecular weights As a rule, however, the constants actually used apply to more concentrated solutions, these being for solutions in which 1 mole of solute is dissolved in 100 *g* of solvent instead of 1000 g of solvent In such cases, the boiling-point constant for water is 5 2°C ; and that for benzene, 26 7°C ; while the freezing-point constant for benzene is 49.0°C

As an illustration of the application of these principles to the determination of molecular weights, suppose that a solution of a nonelectrolyte made by dissolving 12 g of the solute in 20 g. of benzene is found to have a freezing point of −3 22°C. Since pure benzene freezes at 5 48°C., the addition of this solute has lowered the freezing point 8 70°C. Now, 12 g of solute in 20 g of benzene would be the same concentration as 60 g of solute in 100 g of benzene One mole of solute in 100 g of benzene would depress the freezing point of the benzene 49 0°C. Substituting in the equation

$$\frac{\text{Measured depression}}{\text{Freezing-point constant}} = \frac{\text{number of grams of solute in 100 g. solvent}}{\text{gram-molecular weight}}$$

one obtains

$$\frac{8\ 70}{49\ 0} = \frac{60}{x}$$

$$\therefore\ x = \frac{(60)(49)}{8.7} = 338 \text{ g.}$$

The approximate molecular weight is, therefore, 338.

constants found, however, vary with the solvent. For example, the molal boiling-point and freezing-point constants for benzene are 2.43 and 5.12°C., respectively, and those for acetic acid are 2.93 and 3.9°C., respectively.

The addition of a solute also affects the vapor pressure of any solvent in which it is dissolved, the effect being to lower the vapor pressure of the solvent. For ideal solutions* the vapor pressure of the solvent is proportional to the mole fraction† of the solvent in the solution. This law, known as *Raoult's law,* may be expressed as

$$P_a = P_b X$$

where P_a and P_b are the vapor pressures of the *solvent* in the solution and in the *pure solvent,* respectively, and X is the *mole fraction of solvent in the solution.*

It has been pointed out frequently that the regular behaviors described apply only to solutions of nonelectrolytes. Solutions of electrolytes exhibit qualitatively the same types of phenomena, but the quantitative relationships do not hold. In general, the

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* An ideal solution would be one in which there is no reaction or tendency toward reaction between the solvent and solute and in which no dissociation or association of the components of the solution occurs. Although such solutions are rare, many exist that approach the ideal closely enough to permit important applications of this law.

† *Mole fraction* is another way of expressing concentrations in solutions. As the term suggests, it represents the *ratio* of the *number of moles of a given component* to the *total number of moles* of all components in the solution. If the number of moles of the solute in a given sample of solution is represented by N_a, then

$$N_a = \frac{\text{weight of solute in the sample}}{\text{gram-molecular weight of solute}}$$

while if the number of moles of solvent in the sample is represented by N_b, then

$$N_b = \frac{\text{weight of solvent in the sample}}{\text{gram-molecular weight of solvent}}$$

From these the mole fraction X of the solvent can be calculated, using the equation

$$X = \frac{N_b}{N_a + N_b}$$

changes in properties produced by adding electrolytes to a solvent are much more pronounced than those obtained by using a nonelectrolyte of equal molal concentration. Table II shows the molal freezing-point lowering constants, ΔT, of water as determined using 0.1 molal solutions of typical electrolytes.

TABLE II.—MOLAL FREEZING-POINT DEPRESSION FOR AQUEOUS SOLUTIONS OF VARIOUS ELECTROLYTES

Solute	ΔT	Solute	ΔT
Acetic acid ..	1 90	Calcium nitrate....	4 58
Hydrochloric acid	3 52	Potassium iodide	3 54
Nitric acid	3 51	Sodium chloride	3 18
Barium nitrate	4 25	Sodium nitrate	3 41
Calcium chloride	4 83	Sodium sulfate	4 34

Although many exceptions make it unsafe to generalize too far,* some interesting relationships may be noted by a study of this table. For instance, those strong electrolytes on this list which contain a total of two radicals in their formulas, namely, HCl, HNO_3, KI, NaCl, and $NaNO_3$, give molal freezing-point depressions within the range 3.41 to 3.54. In other words, strong electrolytes composed of two radicals apparently give molal freezing-point depressions that are close to *twice* as great as those obtained with an equal concentration of a nonelectrolyte. On the other hand, those having three radicals per molecule give depressions that are *between two and three times* that given by nonelectrolytes. The question might well be asked, therefore, whether the number of radicals in the molecule is not related in some way to the unusually high molal freezing-point depression produced by electrolytes. That such a relationship does exist will be shown in the next chapter.

SUMMARY

A *solution* is an optically homogeneous mixture. It is composed of at least two components: the *solute*, which is defined as the chemically active component of the solution, and the *solvent*, which is the chemically less active component,

* Many electrolytes deviate widely from the values shown in this table for apparently similar compounds

A *saturated* solution is a solution in which dissolved solute is in equilibrium with undissolved solute. A *supersaturated* solution is one in which the concentration of solute is greater than at equilibrium conditions. Supersaturation is best overcome by adding a bit of undissolved solute, by vigorous stirring or shaking, or by rubbing the inner side of the container with the tip of a stirring rod to disturb the metastable condition and cause precipitation of the excess solute.

The *solubility* of any solute is defined as its concentration in its saturated solution. The solubility of a gas in a liquid decreases with increased temperature and increases with lower temperatures. *Henry's law* states that the weight of any gas that will dissolve in a given quantity of liquid is *directly proportional* to the pressure at which the gas is supplied. The law is *quantitative* only for pressures less than atmospheric and for solutions in which there is no reaction between the solute and solvent. The *volume* of any gas that dissolves in a given volume of solvent is independent of pressure.

A *molar* solution is one that contains 1 gram-molecular weight of solute per liter of solution. A *molal* solution contains 1 mole of solute per 1000 g. of *solvent*. A *normal* solution contains a gram-equivalent weight of solute in each liter of solution.

For double decomposition reactions, the *gram-equivalent weight* of any substance is calculated by dividing its gram-molecular weight by the number of valences represented in the molecule by the radical to be supplied by the solution when it is used as a reagent.

When two or more liquids are mutually infinitely soluble, they are said to be *miscible;* if neither is soluble in the other, the liquids are said to be *immiscible.*

If a solute is added to two immiscible liquids in contact with each other, it will distribute itself between the two solvents according to its solubility in each. If the solute has the same molecular weight in both solvents, the ratio of its concentrations at equilibrium in the two solvents will equal a constant known as the *distribution coefficient.* The principle is used in *extractions.*

A comparison of dilute solutions of nonelectrolytes shows that with a given solvent, the molal freezing-point depression and the molal boiling-point elevation are essentially the same for all nonelectrolytes. Electrolytes, on the other hand, cause

abnormally great changes in the boiling and freezing points of water, different electrolytes giving widely different changes in such properties. Any electrolyte will produce a greater change in these properties than would any nonelectrolyte.

The addition of a solute to a solvent also causes a lowering of the vapor pressure of the solvent. For ideal solutions, *i.e.*, those in which the components do not ionize, dissociate, associate, or react with each other, the *depression* in vapor pressure of the solvent is proportional to the mole fraction of *solute* in the solution, and the *actual* vapor pressure is proportional to the mole fraction of *solvent.*

Review Questions

1. Define: (*a*) solution, (*b*) solute, (*c*) solvent, (*d*) solubility, (*e*) saturated solution, (*f*) supersaturated solution, (*g*) miscible, (*h*) immiscible, (*i*) solvation, (*j*) molar solution, (*k*) molal solution, (*l*) normal solution, (*m*) gram-equivalent weight, (*n*) milliequivalent

2. What simple test could be used to determine whether a solution of sodium acetate is saturated, supersaturated, or unsaturated?

3. In what ways can the solute be forced to precipitate from a supersaturated solution?

4. What factors influence the solubility of a solid in a liquid? Explain the effect of each.

5. State Henry's law What are the limitations of this law?

6. What effect does temperature have upon the solubilities of gases in liquids?

7. Explain briefly the law regarding the distribution of solutes between two immiscible liquids What limitations does this law have?

8. What relationship exists between the solubilities of a solute in each of two immiscible liquids and the distribution constant of that solute? What limitations does this rule have?

9. What is meant by *extraction?* What practical use is made of extractions?

10. State and briefly explain Raoult's law

11. What is a nonelectrolyte? An electrolyte? Give examples of each

12. What general statements can be made in regard to the molal boiling-point and freezing-point constants of aqueous solutions of nonelectrolytes? Of electrolytes?

13. Of what use are the terms *molal, molar,* and *normal* in qualitative analysis? In quantitative analysis?

Problems

1. What weight of each of the following substances would be required to prepare 240 ml. of 0.18*M* solution?

(*a*) $Ba(NO_3)_2$ (*b*) $FeCl_3$. (*c*) $Na_2SO_4\ 10H_2O$
(*d*) $Pb(C_2H_3O_2)_2\ 3H_2O$. (*e*) $KHCO_3$ (*f*) $NaAl(SO_4)_2$.

Answers: (*a*) 11 29 g (*c*) 13 91 g (*e*) 4 32 g

2. What weight of solute would be present in 150 ml. of a 0 5*M* solution of

(*a*) $BaCl_2\ 2H_2O$? (*b*) Na_2CO_3? (*c*) KNO_3? (*d*) $Cu(NO_3)_2$?

Answer: (*a*) 18.31 g.

3. What volume of 0.1*M* NaCl solution could be prepared from 25 g of NaCl?

Answer: 4 27 liters.

4. What volume of

(*a*) 0 15*M* solution could be made from 10 g. of $Na_2S_2O_3\ 5H_2O$?

(*b*) 3 2*M* solution could be made from 50 g of NH_4Cl?

(*c*) 0 8*M* solution could be made from 100 g of $NiCl_2$?

5. What weight of each of the following would be required to prepare 250 ml. of a solution of

(*a*) K_2CrO_4, which is 0 2*N* with respect to potassium?

(*b*) NaH_2PO_4, which is 0.3*N* with respect to sodium?

(*c*) NaH_2PO_4, which is 1.5*N* with respect to phosphate?

Answer: (*a*) 4 855 g.

6. What is the normality of a solution that contains 40 g. of $BaCl_2\ 2H_2O$ in 200 ml. of solution?

Answer: 1 638*N*

7. What is the normality of a solution that contains 32 g of $FeNH_4(SO_4)_2 \cdot 12H_2O$ in 400 ml. of solution, if the solution is to be used in a double decomposition reaction as a source of

(*a*) Sulfate? (*b*) Iron? (*c*) Ammonium?

8. What is the normality of a solution of $CaCl_2$ that is 10 per cent $CaCl_2$ by weight and whose specific gravity (referred to water at 4°C.) is 1.084?

HINT: What would 1 liter of solution weigh? Then what weight of solute would be present in 1 liter of solution?

Answer: 1 953*N*

9. What is the normality of a solution of HCl if it has a specific gravity of 1.148 and is 29.13 per cent hydrogen chloride by weight?

10. What is (*a*) the molarity and (*b*) the normality of a solution of sulfuric acid if it has a specific gravity of 1.381 and is 48.1 per cent H_2SO_4 by weight?

11. What volume of

(*a*) 1.5*N* H_2SO_4 would be required to neutralize 200 ml. of 0.3*N* NaOH?

(*b*) 0.52*N* H_3PO_4 would be required to neutralize 270 ml. of 0.8*N* KOH?

(*c*) 0.7*N* $BaCl_2$ would be required to precipitate the sulfate in 50 ml. of 0.32*N* Na_2SO_4?

(*d*) 1.2*N* HCl would be required to prepare 500 ml. of 0.55*N* HCl?

(*e*) 4.5*N* NaOH would be required to prepare 3 liters of 0.75*N* NaOH?

Answers: (*a*) 40 ml. (*c*) 22.85 ml.

12. What is the normality of a solution of a base if

(*a*) 65.2 ml. of 0.734*N* H_2SO_4 is required to neutralize 75 ml. of the solution?

(*b*) 34.8 ml. of 0.1224*N* HCl is required to neutralize 50 ml. of the solution?

(*c*) 46.3 ml. of 0.1554*N* HNO_3 is required to neutralize 60 ml. of the solution?

Answer: (*a*) 0.638*N*.

13. What would be the approximate molecular weight of a nonelectrolyte if a solution containing

(*a*) 10 g. of the nonelectrolyte in 200 g. water had a boiling point of 100.2°C.?

(*b*) 15 g. of the nonelectrolyte in 320 g. of benzene had a freezing point of +4.2°C.?

(*c*) 23 g. of the nonelectrolyte in 150 g. of water had a freezing point of −0.55°C.?

Answer: (*a*) 130.

CHAPTER III

THEORIES OF IONIZATION

Electrolytic Conduction. It was explained in the previous chapter that dissolving any one of the class of compounds known as *electrolytes* causes an abnormally large change in the boiling point and the freezing point of water. Solutions of electrolytes differ from those of nonelectrolytes also in that they are able to conduct electricity whereas solutions of nonelectrolytes are nonconductors. For example, suppose that two platinum rods (*electrodes*) are inserted in a beaker filled with very pure water, one of the rods being connected to the positive terminal* and the other being connected through an ammeter to the negative terminal of a battery. The ammeter will show no current flowing through the circuit. If alcohol, sugar, glycerin, or any other nonelectrolyte is added to the water, there will still be no flow of current. If, however, a little NaCl, NaOH, or any other electrolyte is added to the water, a current will flow at once. If 1*N* solutions of different electrolytes are used, it is found that although some, such as NaCl, HCl, and NaOH, allow the passage of a fairly large current of electricity, others, such as NH_4OH, and $HC_2H_3O_2$, conduct electricity much less readily.

The conductivity of a solution may be expressed in terms of its specific, its molar, or its equivalent conductivity. *Specific conductivity* is expressed as the reciprocal of the resistance through a solution between two electrodes each 1 cm. square, parallel to each other and separated by a distance of 1 cm. *Molar conductivity* and *equivalent conductivity*, on the other hand, are measured by placing a solution containing 1 mole or 1 equivalent weight, respectively, of the solute between electrodes of sufficiently large area to permit the *whole* of the solution to be *between* the electrodes, the distance between the electrodes again being 1 cm.

* This electrode is called the *anode;* the electrode connected to the negative terminal of the battery is called the *cathode.*

Faraday's Law. In general chemistry it was learned that the passage of electricity through solutions of electrolytes is always accompanied by chemical reactions at the electrodes. For example, if platinum electrodes connected to a battery are inserted in a concentrated solution of NaCl, it is found that chlorine is given off at the *anode* (the positive electrode), whereas at the *cathode* (the negative electrode) hydrogen is produced. If a solution of H_2SO_4 or of NaOH is used instead of NaCl, the product at the cathode is again hydrogen but that at the anode is oxygen instead of chlorine. If, on the other hand, $CuSO_4$ solution is used, the products are metallic copper and oxygen.

A study of the electrolysis products of solutions such as these and of the quantities of each product produced under different conditions led to the formulation early in the nineteenth century of Faraday's law. In simple words Faraday's law states that *the quantity of material produced at each electrode during the electrolysis of a given solution is directly proportional to the quantity of electricity that passes through the solution.* More precisely, if 96,500 coulombs* (1 faraday) of electricity passes through the solution, 1 *gram-equivalent* weight of product will be produced *at each electrode.* For example, if 96,500 coulombs of electricity is passed through the solution of $CuSO_4$ to which reference was made earlier, 31.785 g. of copper will be deposited at the cathode and 8 g. of oxygen will be given off at the anode.†

Theories of Ionization. It was pointed out in the previous chapter that *different nonelectrolytes* produce the *same* lowering in the freezing point of water if the different solutions tested

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* The coulomb is a unit of *quantity* of electricity, and for practical work the number of coulombs is calculated by multiplying the current (in amperes) by the time (in seconds) that the current is flowing For example, if a steady current of 10 amp. is allowed to flow for exactly 120 sec. (2 min.), 1200 coulombs of electricity will have passed through the circuit.

To get an idea of the magnitude of a faraday, it may be noted that a 100-watt electric light bulb operating on a 110-volt line will allow the passage of 1 faraday (96,500 coulombs) through it if it is operated continuously for 29 hr. 29 min.

† Since the products are in this case elements, a gram-equivalent weight of each element will be formed. It will be recalled that the equivalent weight of an element is obtained by dividing the atomic weight of the element by its valence, *i.e.*, for copper, 63.57 ÷ 2, and for oxygen, 16 ÷ 2.

contain the same number of moles of solute in the same weight of water. Now it will be remembered from beginning chemistry that 1 mole of any molecular substance contains 6.03×10^{23} molecules. Consequently, the solutions mentioned above must contain equal numbers of molecules. Therefore it can be said that equal numbers of molecules, if dissolved in the same weight of water, will produce the same change in the freezing point of the water. The fact that the molecules of different nonelectrolytes are, of course, different leads to an even broader statement; *i.e.*, the magnitude of the freezing-point lowering is dependent upon the *number* of dissolved particles and is *independent of their nature.*

In the previous chapter it was mentioned also that the lowering in freezing point produced by electrolytes is always greater than that produced by an equal number of moles of a nonelectrolyte. If it is considered in the light of the discussion in the preceding paragraph, this seems to indicate just one thing, namely, *any electrolyte produces more particles in its solution than would be produced by the same number of moles of a nonelectrolyte.* This phenomenon would be readily understandable if some of the molecules of the electrolyte broke down into two or more particles. To illustrate this point, let us assume that 100 molecules of a *nonelectrolyte* are dissolved in a very small quantity of water and that the freezing point of the resulting solution is found to be $-0.020°C$. Now suppose also that 100 molecules of an *electrolyte* are dissolved in the same amount of water but that the freezing point of this solution is found to be $-0.030°C$. This phenomenon would be understandable if 50 of the 100 molecules of electrolyte were *to split into two parts;* for then instead of 100 particles dissolved in the water, there would be 50 molecules and 2×50 (or 100) *pieces* of molecules—a total of 150 particles in the solution. Obviously, 150 particles should affect the freezing point half again as much as would 100 particles.

Reasoning of this type, based upon the observed properties of solutions, late in the nineteenth century led the Swedish scientist Arrhenius to present the first workable theory of ionization. Arrhenius's theory consisted essentially of the following points:

1. When any electrolyte is dissolved in water, some of the molecules break down into electrically charged particles or *ions.*

2. The conductivity of any solution is due to these ions and is dependent upon the *number* and *kind* of ions between the electrodes.

3. In solutions of ordinary concentrations some unionized molecules of the electrolyte are in equilibrium with its ions.

4. Not all electrolytes are ionized to the same extent, *weak* electrolytes being only slightly ionized whereas *strong* electrolytes are quite highly ionized.

5. In infinitely dilute solutions, ionization of any electrolyte is complete.

According to Arrhenius's theory, therefore, when acetic acid, $HC_2H_3O_2$, is dissolved in water, some of the molecules break up into ions,

$$HC_2H_3O_2 \rightarrow H^+ + C_2H_3O_2^-$$

an equilibrium quickly being set up between these ions and the unionized molecules in the solution, as represented by the expression

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

This theory can also be used to explain the mechanism of electrolytic conduction. When electrodes are placed in a solution of an electrolyte and the electrodes are connected to a battery, the anions are attracted to the anode and the cations to the cathode. At the electrodes chemical reactions occur that result in electrons being taken from the cathode and supplied to the anode.* Thus, although electrons are not transported from the cathode to the anode by "carriers," the net effect is the same and a current flows in the external metallic circuit.

Since he believed that the equivalent conductance of a particular electrolyte at any given concentration depends upon the number of ions present in that solution, Arrhenius formulated a method of determining what proportion of the molecules are

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* To say that the cathode is negatively charged is just another way of saying that it possesses an excess of electrons; similarly, to say that the anode is positively charged means merely that it is deficient in electrons. Consequently, the cathode will *supply* electrons to anything willing to take them, while the anode will *remove* electrons from anything capable of giving them up. Thus, if concentrated HCl is electrolyzed, the hydrogen ions

ionized in a solution at any given concentration. His method was to divide the actual equivalent conductivity, Λ, of a solution at a known concentration by the equivalent conductivity of the same electrolyte at infinite dilution, Λ_∞. The apparent *degree of ionization*, α, *i.e.*, the ratio of the number of molecules actually ionized to the number originally used in preparing the solution, was then calculated by means of the expression

$$\alpha = \frac{\Lambda}{\Lambda_\infty}*$$

Although Arrhenius's theory of ionization was a definite step in the right direction, it was only to be expected that as new research instruments were developed and new information became available, modifications would have to be made in his theory. Two of the more important modern developments are the Debye-Huckel theory and the theories of Bronsted and his coworkers.

We have learned that many electrolytes, such as sodium chloride, are already ionized even in the solid state. There

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move to the cathode, where they then take on electrons, become neutral atoms, and form hydrogen gas:

$$2H^+ + 2\epsilon \rightarrow H_2$$

On the other hand, chloride ions are attracted to the anode, where they lose electrons and form chlorine gas:

$$2Cl^- - 2\epsilon \rightarrow Cl_2$$

From general chemistry it will be recalled that the taking on of electrons by an atom is known as *reduction*, whereas the loss of electrons is known as *oxidation*. It is easy to see, therefore, that during an electrolysis, the reaction occurring at the *anode* is *always an oxidation* whereas that at the *cathode is always a reduction*.

* For example, the equivalent conductivity of $HC_2H_4O_2$ in a 0.01*N* solution at 18°C. is 14.50 reciprocal ohms. At infinite dilution, its equivalent conductivity is 347 reciprocal ohms. Using the preceding equation, one obtains

$$\alpha = \frac{14.5}{347} = 0.0418$$

In other words apparently 4 18 per cent of the molecules present are, at any given moment, in the ionized state.

is little reason, therefore, to expect these ions to combine in solution to form molecules when the behaviors of other electrolytes indicate that the tendency for ionization should be greater in solution than under other conditions. The chemical activities and the conductivities of concentrated solutions of strong electrolytes, however, are less than would be expected if ionization were complete, and it was for this reason that Arrhenius believed their ionization is incomplete. To explain these apparent anomalies Debye and Hückel formulated the theory whose essential points are as follows:

1. Strong electrolytes, such as sodium chloride and potassium chloride, are completely ionized even in concentrated solutions. Thus, according to this conception, when a crystal of sodium chloride is brought into contact with water, the forces of attraction between the ions on the surface of the crystal and those within the crystal are weakened, allowing the surface ions to pass into the solution. No molecules of solute, therefore, are present in solutions of the strongest electrolytes.

2. Although the force of attraction between the oppositely charged ions of a strong electrolyte is not great enough to hold them together as molecules, the charge on each ion surrounds the ion with a "sphere of influence" that will tend to act upon any ion passing through it. The larger the number of charges on the ion the greater is this sphere of influence.

3. As a given ion moves through the solution, either toward an electrode or by normal processes of diffusion, it passes through the fields of attraction of many other oppositely charged ions, with the result that there is a mutual "dragging" effect which slows the movement of the ions and reduces their activity. This effect is greatest in solutions whose total ion concentrations are great, diminishing with dilution until in very dilute solutions the effect is negligible. This phenomenon and its observed consequences are commonly known as the *salt effect.*

According to the Debye-Hückel theory, therefore, the movements of ions are restrained in solutions of high ion concentration, and the result of this is that the ions act as if their concentrations are lower than they really are. Now it will be noted that there is nothing specific about this effect. Any kind of ion will produce it. Consequently, if a high concentration of a strong electrolyte is added to a solution of a weak electrolyte (whose

ion concentration would ordinarily be low), *the weak electrolyte* will be just as greatly affected by the foreign ions as it would by an equal concentration of its own ions. Thus, any highly ionized electrolyte will produce the salt effect.

The presence of ions in the solutions of any electrolyte in which the solid form has an ionic lattice is easily understood if one assumes that the mechanical picture suggested earlier is correct. Many electrolytes, however, exhibit the properties of an electrolyte only when *dissolved in certain specific solvents.* Since the common acids are of this type, the question as to how these so-called *pseudoelectrolytes* ionize is of some importance. The most probable explanation of the ionization of acids was developed by Bronsted and his coworkers. The contrast between Bronsted's theory and the older theory may be illustrated with acetic acid. It will be recalled that the older theory postulated a simple reversible ionization of acetic acid

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

According to Bronsted's theory, however, the ionization involves a reaction between the solvent and the solute to produce a *solvated* (in water, a *hydrated*) hydrogen ion:

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$

Thus H_3O^+ ($H^+ \cdot H_2O$) (known as *hydronium* or *oxonium* ion) is formed instead of a simple hydrogen ion (or proton), and the energy needed to break the semipolar bond holding the hydrogen to the rest of the acetic acid molecule is furnished by the formation of the H_3O^+.

In line with this theory it is now believed that few, if any, simple hydrogen ions exist in these solutions. Instead, the hydrogen ions, if they exist even momentarily, immediately attach themselves to solvent molecules to form solvated hydrogen ions.

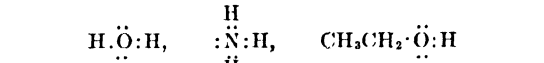
Many cases serve to confirm this theory of solvation in the ionization of pseudoelectrolytes. If hydrogen chloride is dissolved in benzene or toluene, for example, the resulting solution does not conduct electricity. In liquid ammonia, water, or ethyl alcohol, on the other hand, hydrogen chloride acts as a conductor. In other words, although hydrogen chloride does

not ionize in benzene and toluene, in the other solvents mentioned the following reactions occur:*

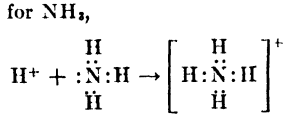
$$HCl + NH_3 \rightarrow NH_4^+ + Cl^-$$
$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$
$$HCl + C_2H_5OH \rightarrow H(C_2H_5OH)^+ + Cl^-$$

Bronsted's Acid-base Theory. In the light of Arrhenius's theory of ionization it has long been customary for chemists to classify electrolytes according to the types of ions that they were believed to supply. Thus acids have long been defined as *substances that yield hydrogen ions* when placed in solution, while bases have been defined as *substances that yield hydroxyl ions* (OH^-) in solution. Now these conceptions of acids and bases work so well for *aqueous* solutions, and aqueous solutions are used so much more frequently than are nonaqueous solutions, that it seems unlikely that the older definitions of acids and bases will ever be completely discarded. Nevertheless there are times when the terms acid and base must be used in another sense, *i.e.*, as defined by Bronsted in his acid-base theory.† According to Bronsted's conception, an acid is *any substance that supplies protons* (*i.e., a proton donor*), whereas a base is *any substance that combines with protons* (*i.e., a proton acceptor*).

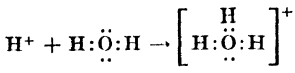
* A study of these ionizing solvents reveals the fact that each of them contains an atom that has at least one unused electron pair:



Apparently the proton attaches itself to one of these electron pairs in forming the solvated ion; thus, for NH_3,



and for water,



† Occasionally certain phenomena will be explained in this book in terms of Bronsted's conceptions. When such is the case, however, it will be made clear.

As an illustration, consider what happens when a solution of sodium hydroxide is added to a solution of hydrochloric acid. Since both these substances are among the strongest electrolytes, their solutions will contain the solute as ions. Any reactions that occur, therefore, will be between ions:*

$$Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + H_2O$$

It will be noticed in this equation† that the only reaction that occurs is that between H^+ and OH^- to form H_2O, for the Na^+ and the Cl^- undergo no change. In this reaction, therefore, the OH^- has accepted a proton (or H^+) to form water. Evidently the OH^- is a base—which, of course, is not entirely out of line with the older conception of bases as *sources* of OH^-.

Now consider the reaction between a solution of sodium acetate, $NaC_2H_3O_2$, and one of hydrochloric acid. The sodium acetate and the hydrochloric acid are both strong electrolytes and may be treated as completely ionized; consequently, the reaction is

$$Na^+ + C_2H_3O_2^- + H^+ + Cl^- \rightleftharpoons Na^+ + Cl^- + HC_2H_3O_2$$

This reaction is an equilibrium reaction, for, as will be recalled from Arrhenius's conception of solutions of weak electrolytes, any ordinary solution of the weak electrolyte $HC_2H_3O_2$ must have some H^+ and some $C_2H_3O_2^-$ present in equilibrium with the $HC_2H_3O_2$ molecules. Some of both the molecules and the simple ions, therefore, must be present in the solution. The formation of $HC_2H_3O_2$ molecules by this reaction, however, illustrates the fact that the $C_2H_3O_2^-$ is capable of accepting protons; consequently, the acetate ion is also considered as a base.

Thus, according to Bronsted's theory, *any anion is a base.* Those anions which are capable of combining with protons to

* In discussions throughout this book, the term *hydrogen ion* will be used rather than hydronium ion. Although there is a modern trend toward the latter term, it seems scarcely justifiable to emphasize the hydrated condition of the hydrogen ions when other hydrated ions, *e.g.*, $Cu(H_2O)_4^{++}$, which exists in aqueous solutions of cupric salts, are usually treated as simple ions in ordinary discussions.

† Equations written in this manner are known as *ionic* equations. They give much more precise pictures of reactions between electrolytes than do the ordinary molecular equations and will be used predominantly throughout this book.

form stable or only slightly dissociated substances are classed as *strong* bases; those which have but slight tendencies to take on protons are classed as *weak* bases. In aqueous solutions, OH^- is still the strongest base; $C_2H_3O_2^-$ would be considered a moderately strong base; and Cl^-, a very weak base. The conception of the hydroxides of metals as bases, therefore, need only to be modified by throwing the emphasis on the OH^- *ion*, rather than on the compound itself, as the base, and then by adding the further fact that bases *other than* OH^- are quite active if conditions are right. In anhydrous acetic acid, for example, $C_2H_3O_2^-$ becomes a very active base; for in such solutions it can accept protons much more readily than in aqueous solutions.

Even neutral molecules may be classed as bases. This is illustrated in the following equations:

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$
$$H_2O + H^+ \rightleftharpoons H_3O^+$$
$$C_2H_5OH + H^+ \rightleftharpoons (HC_2H_5OH)^+$$

The foregoing equations have been written as reversible reactions, which represents the true situation. The products of some such reactions are very stable, but all dissociate to at least a small extent. It can be seen, therefore, that NH_4^+, H_3O^+, $(HC_2H_5OH)^+$, etc., may be classed as *acids*, for each is capable of yielding protons to any sufficiently active proton acceptor. Similarly, it should be noted that those substances which under the older conception were classified as acids are still acids according to Bronsted's definition; for all such substances are capable of furnishing protons. The Bronsted definition is merely more inclusive.

Anions that contain one or more replaceable hydrogen atoms exhibit the properties of both acids and bases. For example, the bicarbonate ion may either accept protons

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3$$

or furnish protons

$$HCO_3^- + OH^- \rightleftharpoons CO_3^= + H_2O$$

SUMMARY

Solutions of *nonelectrolytes* do not conduct electricity, but those of *true electrolytes* do. *Pseudoelectrolytes*, of which the

common acids are examples, conduct electricity only when dissolved in certain so-called *ionizing solvents.* Solutions of strong electrolytes are excellent conductors of electricity; those of weak electrolytes are poor conductors in solutions of ordinary concentration.

Conduction through solutions is always accompanied by *oxidation* at the anode (the positive electrode) and *reduction* at the cathode (the negative electrode). Quantitatively, 96,500 coulombs of electricity (1 faraday) will form 1 gram-equivalent weight of product at each electrode.

Arrhenius explained the abnormal behavior of solutions of electrolytes by stating that (1) some molecules of any electrolyte break down into positively and negatively charged particles which he called *ions;* (2) in solutions of ordinary concentration these electrolytes set up an equilibrium between unionized molecules and their ions; (3) different electrolytes ionize to different extents, the strong electrolytes having the highest percentage of ionized molecules; (4) in infinitely dilute solutions all electrolytes are completely ionized; and (5) the ions between the electrodes are responsible for conduction in solutions of electrolytes.

The modern theories of electrolytes as postulated by Debye and Huckel and others modify Arrhenius's theory chiefly in regard to more concentrated solutions of weak electrolytes and solutions of strong electrolytes. For most practical purposes, strong electrolytes are treated as being *completely ionized.* The increase in conductivity of solutions of strong electrolytes with dilution and certain properties of weak electrolytes in more concentrated solutions are believed due to the dragging effect caused by the attraction between ions of opposite charge. This effect, which is known as the *salt effect,* is less for solutions of low ion concentration than for those of high ion concentration.

Bronsted and others explained the ionization of pseudoelectrolytes as involving a reaction between the molecules of pseudoelectrolytes and those of the solvent. In the case of an acid, one product of ionization in water solution is always hydronium (H_3O^+) ion instead of simple hydrogen ion. From these conceptions also was obtained Bronsted's more general definition of an *acid* as a *proton donor* and of a *base* as a *proton acceptor.* Thus, anions are bases, since they can accept protons. Hydroxyl

ion is the strongest base in aqueous solutions; anions such as acetate and carbonate are moderately strong bases; and those such as Cl^- are very weak bases. Those compounds which were classified under the older conception as acids are still classified as acids, since they are all proton donors. The older conceptions, however, applied only to aqueous solutions, whereas Bronsted's conceptions apply to all solutions.

Anions that contain one or more replaceable hydrogens are both acids and bases.

Review Questions

1. Define: (*a*) anode, (*b*) cathode, (*c*) anion, (*d*) equivalent conductivity, (*e*) hydronium ion, (*f*) pseudoelectrolyte

2. List the chief points of Arrhenius's theory of ionization.

3. State which points of Arrhenius's theory were modified in formulating the modern theories of ionization. Explain what these modifications were.

4. Contrast and compare Bronsted's conception of acids and bases with the older conceptions.

5. By ionic equations, show how the following may act as bases: (*a*) $S^=$, (*b*) $CO_3^=$, (*c*) $SO_4^=$, (*d*) H_2O, (*e*) NH_3, (*f*) $HPO_4^=$

6. By ionic equations, show how the following may act as acids. (*a*) HNO_3, (*b*) H_2O, (*c*) $HPO_4^=$, (*d*) NH_4^+, (*e*) H_3O^+, (*f*) HSO_4^-.

Problems

1. What weight of (*a*) copper and (*b*) oxygen would be formed if 2000 coulombs of electricity were passed through a solution of $CuSO_4$?

Answer (*a*) 0.658 g

2. Assuming the sole gaseous products to be hydrogen and chlorine, (*a*) what volume of hydrogen (at standard conditions), (*b*) what weight of chlorine, and (*c*) what weight of sodium hydroxide would be formed by the passage of a steady current of 200 amp through a concentrated solution of sodium chloride for 5 hr.?

Answers (*a*) 417.7 liters (*c*) 1.492 kg

3. Two cells, one containing silver nitrate and the other sulfuric acid, are connected in series. If 1.4 liters of hydrogen (measured at standard conditions) is collected from the sulfuric acid cell during the electrolysis, what weight (*a*) of oxygen and (*b*) of silver should be formed at the same time? (NOTE: Remember that oxygen will be produced by *both cells.*)

4. What is the apparent degree of ionization of the solute in

a. A 0.01*M* solution of NH_4OH if its equivalent conductivity is 9.66 reciprocal ohms at this concentration and 238 reciprocal ohms at infinite dilution?

b. A 0.01*M* solution of $Ba(OH)_2$ if its conductivity is 207 reciprocal ohms at this concentration and 222 reciprocal ohms at infinite dilution?

c. A 0.01*M* solution of sulfuric acid if its conductivity is 309 reciprocal ohms at this concentration and 383 reciprocal ohms at infinite dilution?

CHAPTER IV

HOMOGENEOUS IONIC EQUILIBRIUMS

Introduction. It was mentioned in an earlier chapter that concentration is an important factor in chemical reactions, both in regard to the rate at which a reaction will occur and, in the case of reversible reactions, in regard to the completeness of reaction. It is evident, therefore, that a knowledge of the concentrations of different *ions* in a mixture where a reaction is occurring between ions is important for predictions of both the rate and the completeness of reaction. Since most of the reactions used in analysis and in many other practical applications of inorganic chemistry are ionic, the quantitative relationships existing in solutions of electrolytes must be thoroughly understood.

For solutions of strong electrolytes* the more fundamental relationships are simple. Such substances may be considered *completely ionized* in solution; consequently, no equilibrium exists between ions and undissociated molecules in solution. If, therefore, the predicted product of reaction between two ions is a strong electrolyte, the reaction will not occur.† Moreover, the concentrations of the different ions in solutions of strong electrolytes can be calculated from the relationships given by the simple chemical

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* In general, salts, with the exception of compounds of lead, mercury, tin, antimony, some zinc compounds, and a few less known types, are strong electrolytes. The hydroxides of the alkali and alkaline earth families and hydrochloric, sulfuric, nitric, hydrobromic, and hydriodic acids are also strong electrolytes. Most of the other bases and acids, however, are weak electrolytes.

† If the ions are present in concentration sufficiently great to exceed the *solubility* of the strong electrolyte, some of the product will precipitate from the solution, thus giving the effect of a reaction. The problem then becomes, however, one of *heterogeneous* equilibrium instead of homogeneous equilibrium. Cases of this kind will be considered in the next chapter.

equation for the ionization of the electrolyte.* If, for example, it is desired to calculate the concentration of Na^+ and Cl^- in a 0.01*M* solution of sodium chloride, from the equation

$$NaCl \rightarrow Na^+ + Cl^-$$

it is found that 1 mole (or more properly, one formula weight) of this salt, if dissolved, will give a solution that contains 1 mole of Na^+ and 1 mole of Cl^-. Consequently, 0.01 mole of the salt will give 0.01 mole of each of these ions; and if that 0.01 mole of salt is dissolved to make a total of 1 liter of solution, the solution will be 0.01*M* with respect to each, Na^+ and Cl^-. Similarly from the equation

$$CaCl_2 \rightarrow Ca^{++} + 2Cl^-$$

it can be deduced that a 0.01*M* solution of calcium chloride would be 0.01*M* with Ca^{++} and 0.02*M* with Cl^-.

Such mathematical treatment of strong electrolytes cannot be used indiscriminately, however, as other factors may lead to error. Neither polybasic acids nor their salts, for example, give correct results by this method; and as will be seen later in the discussion of *hydrolysis*, neither do the salts of weak acids or of weak bases.† Thus, although sulfuric acid is considered a

* Although many of these strong electrolytes are already ionized before they are dissolved, it is convenient to write equations as if ionization occurred only as the solute was dissolving. Actually, such equations merely show the kind and number of ions present in, or produced by, one formula weight of the solute. Too, solution does cause a dissociation of the ions from their orderly arrangement within the crystal lattice, consequently, if one keeps in mind the true picture of what occurs, such a mechanical representation is acceptable.

† Consider, for example, sodium carbonate. According to the equation

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{=}$$

one formula weight of this salt should yield two Na^+ and one $CO_3^{=}$. It actually does yield two Na^+, for these ions undergo no secondary reaction. The $CO_3^{=}$ concentration, however, is much less than would be predicted from the foregoing equation, for $CO_3^{=}$ tends to take on one proton to form the slightly dissociated ion, HCO_3^-:

$$CO_3^{=} + H^+ \rightleftharpoons HCO_3^-$$

As will be seen in a later chapter, water ionizes very slightly to form H^+ and OH^-. In aqueous solutions of Na_2CO_3, therefore, the actual $CO_3^{=}$ con-

strong electrolyte, only one hydrogen ion is completely ionized; the other is reversibly ionized:

$$HSO_4^- \rightleftharpoons H^+ + SO_4^=$$

The ion concentrations in solutions of weak electrolytes cannot be calculated as easily as those in solutions of strong electrolytes. Consider, for example, the ionization of the weak electrolyte, acetic acid, in a 1*M* solution:

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

It is obvious that of the acetic acid used in making the solution, at any given moment some will be in the form of molecules and some in the form of ions. If a solution of sodium hydroxide is added to this solution, the H^+ and OH^- will react to form H_2O; then, as predicted by the principle of Le Chatelier and the law of mass action, the ionization equilibrium for the acetic acid will shift to produce H^+ to replace part of that removed. Eventually, if enough sodium hydroxide is added, no more $HC_2H_3O_2$ will remain; consequently, no more H^+ will be formed, and the acid will have been neutralized. It may be said, therefore, that by the titration of such a solution one measures all the acid in the solution, *i.e.*, the *total acidity*.

On the other hand, many reactions depend not on the total available acid but instead on the *immediate hydrogen ion* concentration. In any equilibrium in which H^+ appears as a reactant or a product, the concentration of the H^+ is important. It is, therefore, often necessary to distinguish between the actual H^+ concentration at a given moment (sometimes called the *momentary acidity*), the *reserve acidity* (the concentration of *molecules* of the acid at a given moment), and the *total acidity*.*

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centration will be less than the original equation suggests, owing to the reaction of some of the $CO_3^=$ with the H^+ of the water.

The possibility of such secondary reactions must always be considered in *highly accurate* work, though in many practical cases they may be disregarded as having a negligible effect

* Two things should be noted here: (1) The total acidity is equal to the sum of the momentary and the reserve acidities (2) In aqueous solutions of any acid that is strong enough to be considered completely ionized, the reserve acidity will be zero and the momentary acidity will equal the total acidity.

If solutions of weak bases are considered, it will be found that a similar situation exists with regard to the momentary and reserve *basicity*. For example, solutions of ammonium hydroxide may be represented by

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

At any one moment, therefore, there will be a certain concentration of OH^- in the solution. If some of this is removed, say by the action of H^+ from an acid, the equilibrium will shift in such a way as to replace some of the OH^-. Again, therefore, one may speak of this solution as having a *momentary*, a *reserve*, and a *total basicity*.

As will be shown later, it is often necessary to have solutions in which the momentary and the reserve acidity or basicity is controlled; when such is the case, *buffer* solutions are usually used. Such solutions and their applications will be discussed later in this chapter.

Monobasic Acids and Monacid Bases.* As was pointed out earlier, the strong acids, such as hydrochloric, nitric, and hydriodic acid, and the strong bases, such as sodium hydroxide and potassium hydroxide, may be considered completely ionized in ordinary solutions. The concentrations of their ions may be easily and simply calculated, therefore, from a knowledge of their formulas and their stoichiometric concentrations.†

* Acids that contain only one hydrogen atom capable of being replaced by a metal are called *monobasic* acids; those with two replaceable hydrogens, *dibasic* acids; and those with three replaceable hydrogens, *tribasic* acids. On the other hand, bases with only one hydroxyl radical are called *monacid* bases; those with two, *diacid* bases; and those with three, *triacid* bases.

† In the preceding chapter it was pointed out that in solutions containing high concentrations of ions, the movement of the ions through the solution is slowed by the dragging effect produced by the mutual attraction of ions of dissimilar charges The rate of any chemical reaction depends partly upon the rate with which the reacting entities can get together; consequently, anything that slows the movement of ions also slows any reaction in which these ions are involved In such solutions, therefore, the rate of any reaction is less than might have been expected from the actual concentrations of the ions involved It is customary to speak of the *activity* or *effective concentration* of each reactant in such cases, this corrected concentration representing the way in which the reactant *actually acts* rather than the way in which it is *supposed* to act.

The high concentration of ions may be furnished by the ionization of the

The concentrations of the ions of weak electrolytes cannot be calculated by methods as simple as those used for strong electrolytes; for in solutions of weak electrolytes there are always at any given moment some unionized molecules of the electrolyte. Consequently, the law of mass action must be applied to obtain the necessary information.

Consider, for example, the ionization of acetic acid.

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

It will be recalled that for any chemical reaction that is at equilibrium, the mathematical product of the concentrations of the products of the reaction divided by the mathematical product of the concentrations of the reactants equals a constant. Applying the law to this equilibrium, one obtains the expression

$$\frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = K_a \qquad (1)$$

where $[H^+]$ is the *molar concentration* of H^+, $[C_2H_3O_2^-]$ is the *molar concentration* of $C_2H_3O_2^-$, $[HC_2H_3O_2]$ is the *molar concentration* of $HC_2H_3O_2$, and K_a is the ionization constant for $HC_2H_3O_2$.* Since this equation is of the familiar algebraic type

$$\frac{ab}{c} = d$$

it will be seen that if *any three* of the four terms involved are known, the fourth may be calculated. For most purposes, however, it is most important to be able to calculate $[H^+]$. For simple solutions of acetic acid in pure water, the problem is much easier than it at first appears to be. If one writes the equation for what happens to *each molecule* of acid that *ionizes*

$$HC_2H_3O_2 \rightarrow H^+ + C_2H_3O_2^-$$

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electrolytes involved in the reaction or may come from a third electrolyte that is not concerned in the reaction. In very dilute HCl solution, for example, the addition of a moderate concentration of $NaNO_3$ reduces the activity of both the H^+ and the Cl^- to a marked extent. For this reason, the effect of this interionic attraction upon the activity of ions is commonly called the *salt effect*.

* The ionization constant for an acid is usually designated as K_a; that for a base, K_b; and that for a salt is usually written K_s.

it is seen that (1) the only important source of H^+ and of $C_2H_3O_2^-$ in the solution is the $HC_2H_3O_2$ itself; (2) for every H^+ produced, one $C_2H_3O_2^-$ is also produced; and (3) for each H^+ produced, one molecule of acetic acid is used up or ionized. Consequently, $[H^+]$ in a solution of acetic acid in pure water equals $[C_2H_3O_2^-]$. Since

$$[H^+] = [C_2H_3O_2^-] \tag{2}$$

$[H^+]$ may be substituted for $[C_2H_3O_2^-]$ in the equation

$$\frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = K_a \tag{1}$$

to give the equation

$$\frac{[H^+][H^+]}{[HC_2H_3O_2]} = K_a \tag{3}$$

or

$$\frac{[H^+]^2}{[HC_2H_3O_2]} = K_a \tag{4}$$

The ionization constants for many weak acids have been determined and can be obtained from tables (see Table III).

TABLE III—IONIZATION CONSTANTS*

Reaction	Temperature, °C.	Constant
$H_3BO_3 = H^+ + H_2BO_3^-$	25	$6\ 5 \times 10^{-10}$
$H_2CO_3 = H^+ + HCO_3^-$	25	$3\ 3 \times 10^{-7}$
$HCO_3^- = H^+ + CO_3^=$	25	$3\ 9 \times 10^{-11}$
$HCN = H^+ + CN^-$	25	$7\ 2 \times 10^{-10}$
$H_3PO_4 = H^+ + H_2PO_4^-$	18	$8\ 3 \times 10^{-3}$
$H_2PO_4^- = H^+ + HPO_4^=$	18	2×10^{-7}
$HPO_4^= = H^+ + PO_4^{\equiv}$	18	4×10^{-13}
$HNO_2 = H^+ + NO_2^-$	18	$4\ 5 \times 10^{-4}$
$HSO_4^- = H^+ + SO_4^=$	25	$1\ 15 \times 10^{-2}$
$H_2S = H^+ + HS^-$	18	9×10^{-8}
$HS^- = H^+ + S^=$	18	1×10^{-15}
$H_2SO_3 = H^+ + HSO_3^-$	25	$1\ 2 \times 10^{-2}$
$HSO_3^- = H^+ + SO_3^=$	25	5×10^{-8}
$HC_2H_3O_2 = H^+ + C_2H_3O_2^-$	25	$1\ 86 \times 10^{-5}$
$NH_4OH = NH_4^+ + OH^-$	25	$1\ 8 \times 10^{-5}$

* Hammett, "Solutions of Electrolytes," 1936.

Thus, the value for K_a for acetic acid at 25°C. is 1.86×10^{-5}. In order to find $[H^+]$, it is necessary only to determine the concentration of the unionized acetic acid in moles per liter, then substitute this for the term $[HC_2H_3O_2]$ in equation (4).

Now if one remembers that only a small fraction of the molecules of a truly weak electrolyte are ionized in solutions of ordinary concentrations, it is readily seen that the number of moles of $HC_2H_3O_2$ actually ionized will be small *compared with the number remaining unionized.* Without significant error, therefore, the concentration of unionized $HC_2H_3O_2$ may be considered as *the same as that added originally.* Applying this assumption to equation (4), the following expression is obtained

$$\frac{[H^+]^2}{M} = K_a \tag{5}$$

$$\therefore [H^+] = \sqrt{MK_a} \tag{6}$$

in which M is the molarity of the acetic acid. This is a general equation which can be applied to solutions of any weak monobasic acid in pure water.*

The concentration of OH^- in solutions of weak bases may be calculated in a similar manner. Suppose, for example, that the concentration of OH^- in a solution of NH_4OH is to be calculated. From the ionization equation

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

one obtains the expression

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = K_b \tag{7}$$

If the same reasoning is used as that applied in considering acetic acid, it can be seen that for every mole of NH_4^+ there is

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* Note that the assumption used here is valid only for quite weak electrolytes in not too dilute solutions. For more highly ionized substances, the number of molecules that ionize will be too great in comparison with the unionized molecules; while as postulated by Arrhenius's theory, in *very dilute* solutions even very weak electrolytes are quite highly ionized.

For solutions in which the electrolyte lost by ionization cannot be disregarded, the H^+ concentration can be calculated by means of the expression

$$[H^+] = \frac{-K_a + \sqrt{K_a^2 + 4MK_a}}{2}$$

1 mole of OH^-; *i.e.*,

$$[NH_4^+] = [OH^-] \tag{8}$$

Substituting OH^- for NH_4^+ in equation (7), one obtains the expression

$$\frac{[OH^-][OH^-]}{[NH_4OH]} = K_b \quad \text{or} \quad \frac{[OH^-]^2}{[NH_4OH]} = K_b \tag{9}$$

Similarly, it can be shown that the concentration of the unionized NH_4OH does not differ significantly from that which it would have if ionization had not occurred; consequently, to calculate the concentration of OH^- it is necessary only to substitute in the *general* equation

$$\frac{[OH^-]^2}{M} = K_b \tag{10}$$

$$[OH^-] = \sqrt{MK_b} \tag{11}$$

Examples of problems and their solution should clarify the ideas discussed above

Problem 1 What is the concentration of H^+ in a 0.01M solution of $HC_2H_3O_2$? First set up the equation for the equilibrium constant for acetic acid.*

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

$$\therefore \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = K_a$$

As pointed out earlier

$$[H^+] = [C_2H_3O_2^-] \tag{2}$$

Also, since acetic acid is a quite weak electrolyte, the molecules lost by ionization may be disregarded and $[HC_2H_3O_2]$ may be considered equal to 0.01M. Substituting, one obtains

$$\frac{[H^+]^2}{0.01} = 1.86 \times 10^{-5}$$

$$\therefore [H^+] = \sqrt{1.86 \times 10^{-5} \times 10^{-2}} = \sqrt{18.6 \times 10^{-8}}$$

$$= 4.3 \times 10^{-4} \text{ mole per liter}$$

Problem 2. What is the H^+ concentration in a 0.1M solution of HCN? Again use the equilibrium expression:†

* Equation (6) may be used directly, if desired In that equation, M is 0.01 and K_a is 1.86×10^{-5} for this problem

† Equation (6) can also be used for this problem, M being 0.1 and K_a being 7.2×10^{-10}.

$$HCN \rightleftharpoons H^+ + CN^-$$
$$\therefore \frac{[H^+][CN^-]}{[HCN]} = K_a$$

As before, $[H^+] = [CN^-]$, and $[HCN] = 0.1M$; also, from Table III,

$$K_a = 7.2 \times 10^{-10}$$
$$\therefore \frac{[H^+][H^+]}{0.1} = 7.2 \times 10^{-10}$$
$$\therefore [H^+]^2 = 0.1 \times 7.2 \times 10^{-10} = 72 \times 10^{-12}$$
$$\therefore [H^+] = \sqrt{72 \times 10^{-12}} = 8.4 \times 10^{-6} \text{ mole per liter}$$

Problem 3 What is the concentration of OH^- in a $0.1M$ solution of NH_4OH?

Set up the expression for the equilibrium constant:*

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = K_b \tag{7}$$

Using the same reasoning as before, $[NH_4^+] = [OH^-]$, and $[NH_4OH] = 0.1M$. From Table III, K_b for NH_4OH is 1.8×10^{-5}. Substituting these values in the foregoing equation, one obtains

$$\frac{[OH^-][OH^-]}{0.1} = 1.8 \times 10^{-5}$$
$$\therefore [OH^-] = \sqrt{1.8 \times 10^{-6}} = 1.3 \times 10^{-3} \text{ mole per liter}$$

When it is desired to calculate $[H^+]$ in a solution of a monobasic weak acid in water, use may also be made of *Ostwald's dilution law*. To derive the equation that expresses this law, let v be the *volume* of solution *that contains* 1 *mole* of acetic acid and let α be the degree of ionization, *i.e.*, the fraction of the total number of moles that are actually ionized. Then from the expression

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$
$$\frac{1-\alpha}{v} \qquad \frac{\alpha}{v} \qquad \frac{\alpha}{v}$$

the number of moles of unionized $HC_2H_3O_2$ will be $1 - \alpha$, that of H^+ will be α, and that of $C_2H_3O_2^-$ will be α. In the solution, therefore, the *concentration* of $HC_2H_3O_2$, of H^+, and of $C_2H_3O_2^-$ will be, respectively, $\frac{1-\alpha}{v}$, $\frac{\alpha}{v}$, and $\frac{\alpha}{v}$. Applying the law of mass action and using these expressions,

$$\frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = K_a \tag{1}$$

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* Equation (11) may be used directly for this type of problem. Thus M will be 0.1, and K_b will be 1.8×10^{-5}, and

$$[H^+] = \sqrt{0.1 \times 1.8 \times 10^{-5}} = 1.3 \times 10^{-3} \text{ mole per liter}$$

becomes

$$\frac{\frac{\alpha}{v}\cdot\frac{\alpha}{v}}{\frac{1-\alpha}{v}} = K_a$$

This may be simplified as follows:

$$\frac{\frac{\alpha^2}{v^2}}{\frac{1-\alpha}{v}} = K_a = \frac{\alpha^2}{v(1-\alpha)} \tag{12}$$

When the electrolyte is very weak, α is very small; consequently, the acetic acid molecules lost by ionization may usually be neglected *in comparison with the* 1 *mole of acid used*, and the expression $v(1-\alpha)$ may be simplified to v. When this is done, the dilution formula becomes

$$\frac{\alpha^2}{v} = K_a \tag{13}$$

Problem 4. Suppose that it is desired to calculate the degree of ionization, α, and the H^+ concentration in a 0.1M solution of acetic acid in pure water. Since the solution is 0.1M, 1 liter contains only 0.1 mole of acetic acid, consequently, the volume needed to furnish *one* mole would be 1/0.1 = 10 liters. Thus, $v = 10$ liters. Substituting in Ostwald's simplified dilution formula

$$\frac{\alpha^2}{v} = K_a \tag{13}$$

$$\therefore \frac{\alpha^2}{10} = 1.86 \times 10^{-5}$$

$$\alpha = \sqrt{1.86 \times 10^{-4}} = 1.36 \times 10^{-2}$$

The degree of ionization, therefore, is 0.0136; *i.e.*, 1.36 per cent of the molecules present in the solution are ionized.

Now each molecule that ionizes thereby produces one H^+. The concentration of H^+, therefore, may be calculated from the equation

$$[H^+] = \alpha \times M \tag{14}$$

$$\therefore [H^+] = 1.36 \times 10^{-2} \times 0.1 = 1.36 \times 10^{-3} \text{ mole per liter}$$

Ostwald's dilution equation has the same form for monacid bases as for monobasic acids; consequently, for weak monacid bases

$$\frac{\alpha^2}{v} = K_b \tag{15}$$

where $v = 1/M$, and

$$[OH^-] = \alpha \times M \tag{16}$$

Problem 5. What is the concentration of OH^- in a 0.1M solution of NH_4OH? Use equation (15); calculate the degree of ionization.

$$\frac{\alpha^2}{v} = K_b \tag{15}$$

$$\therefore \frac{\alpha^2}{1 \div 0\ 1} = 1\ 8 \times 10^{-5}$$

$$\therefore \alpha = \sqrt{1\ 8 \times 10^{-4}} = 1\ 3 \times 10^{-2}$$

Using equation (16), calculate the OH^- concentration.

$$[OH^-] = \alpha \times M = 1.3 \times 10^{-2} \times 0\ 1$$
$$= 1\ 3 \times 10^{-3} \text{ mole per liter}$$

Thus far, only solutions containing a single acid or a single base have been considered. It is not at all unusual, however, to be dealing with solutions containing a mixture of acids or of bases. Although any accurate calculation of the concentrations of the different ions in such solutions is difficult, often valuable approximations can be made with relative ease.

Suppose that two monobasic acids of formulas HA and HB are present in the same solution. If the *concentrations of the two acids are the same*, and if the ionization constant for HA is of the order of ten thousand or more times as great as that for HB, the H^+ from the HB may usually be disregarded. If the concentration of HA is less than that of HB, the differences between the constants must be greater before the H^+ from the weaker acid, HB, can be neglected.

Similarly, if HA is a strong electrolyte such as HCl, and HB is a weak electrolyte such as $HC_2H_3O_2$, the H^+ from the weak acid may be disregarded and only that from the strong acid considered.

For bases, similar reasoning applies. The OH^- in an approximately equivalent mixture of two bases may be considered as coming exclusively from the stronger base, if the ionization constant of the latter is enough larger than that of the weaker base. Thus, in a solution that contains equal concentrations of sodium hydroxide and ammonium hydroxide, the latter may be regarded as contributing only insignificant quantities of OH^-.*

* By calculation it may be shown that in a solution that is 0 1M with sodium hydroxide and 0.1M with ammonium hydroxide, the $[OH^-]$ from the sodium hydroxide will be approximately 550 times that from the ammonium hydroxide. On the other hand, in a solution that is 0 001M with each of these bases, the $[OH^-]$ from the sodium hydroxide will be only about 51 times that from the NH_4OH. This is to be expected, since the ionization

This is true, since the OH^- from the stronger base represses the ionization of the weaker base and thus reduces its contribution of OH^- to the solution.

Buffer Solutions. Since the solution of any weak electrolyte contains molecules of the electrolyte in equilibrium with its ions, an increase in the concentration of one of the ions will cause a decrease in the concentration of the other. Thus, if any soluble, highly ionized acetate is added to a solution of acetic acid, the ionization of the acetic acid will be repressed. In other words, in the reaction

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

an increase in the concentration of $C_2H_3O_2^-$ will cause the reaction to shift in a direction to form more unionized $HC_2H_3O_2$. In doing so, however, H^+ reacts with $C_2H_3O_2^-$; consequently, the net effect is to *decrease* the concentration of H^+ while *increasing* the concentration of $HC_2H_3O_2$ molecules. The *momentary* acidity is *decreased*, but the *reserve* acidity is *increased*. Now suppose that a solution of a strong acid is used instead of the acetic acid but a salt of a weak acid is added to the solution. It will be recalled that the anions of weak acids (*e.g.*, $C_2H_3O_2^-$, $CO_3^=$, etc.) are capable of combining with H^+ to form molecules of the weak acid. If the acid formed is a sufficiently weak electrolyte, the reaction between the H^+ and the anion gives a moderately good yield of the undissociated molecules of the acid; at the same time the concentration of H^+ is reduced. If, therefore, a salt of a weak acid, such as sodium acetate, is added to a solution of a strong acid, such as hydrochloric acid, a reaction of the following type will occur:

$$H^+ + Cl^- + Na^+ + C_2H_3O_2^- \rightleftharpoons Na^+ + Cl^- + HC_2H_3O_2$$

or, eliminating the Na^+ and Cl^-, since they do not actually undergo any change,

$$H^+ + C_2H_3O_2^- \rightleftharpoons HC_2H_3O_2$$

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of any weak electrolyte is much more extensive the more dilute the solution. Consequently, for solutions of mixtures of strong and weak bases, it is found that in more dilute solutions the OH^- from the weak base can no longer be neglected, unless the ionization constant of the weak base is much smaller. The same is true of the H^+ mixtures of strong and weak acids. The accurate mathematical treatment of such solutions, however, will not be considered here.

In other words, if any acetate is added to a solution of any strong acid, a reaction will occur between the H^+ and $C_2H_3O_2^-$ to form $HC_2H_3O_2$.

Now if the concentration of the strong acid is *more than equivalent* to that of the salt, reaction will occur resulting in a *mixture* of the *strong* acid and the *weak* acid. If the concentrations of the salt and the strong acid are *exactly equivalent* to each other, the solution will be one of a *weak acid alone;* but if the *salt* of the weak acid is present in concentration *greater than that of the acid,* the resulting solution will be essentially the same as one prepared by adding the salt of the weak acid to a solution of the weak acid. Referring again to the mixture of sodium acetate and hydrochloric acid, if the number of moles of hydrochloric acid exceeds the number of moles of sodium acetate, the mixture will, when equilibrium is attained, be essentially a solution of hydrochloric acid (due to the excess used), acetic acid, and sodium chloride.* The concentration of the H^+ in such a solution as this, therefore, can be calculated using the method described for mixtures of acids. If, on the other hand, the number of moles of hydrochloric acid are the same as the number of moles of sodium acetate, neither will be in excess and the solution may be treated as a solution of acetic acid in pure water. However, if the sodium acetate is in excess, the equilibrium mixture will contain acetic acid and its ions and the ions furnished by the excess of sodium acetate used will be present in addition. Since all the sodium acetate is in the form of ions,† and since the $C_2H_3O_2^-$ that it furnishes is of the same kind as one of the ions furnished by the acetic acid, the ionization of the acid will be repressed and the calculation of the $[H^+]$ must be approached by a different method.

With mixtures of bases with salts of weak bases, similar reasoning applies. The addition of a salt of a weak base to a

* The Na^+ and Cl^- in these solutions may be disregarded unless it is necessary to consider the *salt effect.* Therefore only the ions furnished by any unreacted HCl or $NaC_2H_3O_2$ and the molecules and ions of the $HC_2H_3O_2$ need be considered.

† It will be remembered that most salts are strong electrolytes and may be considered as completely ionized. Even though the salt was formed from a weak acid or, as in the case of ammonium salts, from a weak base, it is still completely ionized and the ions are therefore readily available for reaction with other substances that may be in solution.

solution of a base causes a decrease in the concentration of the OH^- and an increase in the reserve base. Thus, if an ammonium salt such as ammonium chloride is added to a solution of ammonium hydroxide, the NH_4^+ from the ammonium salt represses the ionization of the NH_4OH, thereby decreasing the concentration of the OH^- and increasing the concentration of NH_4OH. If, on the other hand, an ammonium salt such as NH_4Cl is added to a solution of a strong base such as NaOH, the following type of reaction will occur:

$$NH_4^+ + Cl^- + Na^+ + OH^- \rightleftharpoons Na^+ + Cl^- + NH_4OH$$

If the NaOH is in excess, the final mixture may be regarded as a mixture of a strong base and a weak base in calculating the OH^- concentration; if the NaOH and NH_4Cl are present in equivalent concentrations, the solution should be treated as that of a simple weak base in water; while if the NH_4Cl is in excess, the final mixture must be considered as a mixture of a weak base and a salt of a weak base. In any of these cases, however, the effect of adding the salt of a weak base is to reduce the OH^- concentration and increase the concentration of reserve (unionized) base.

A solution of an acid containing an excess of a salt of a weak acid or of a base containing excess salt of a weak base is said to be a *buffer solution.* Any salt used to produce such a solution is called a *buffering agent.* Buffer solutions have characteristics that make them very valuable for many purposes. The concentration of H^+ in a buffered acid or of OH^- in buffered base is often very low but is resistant to changes, owing to the fact that the ionization of the weak acid or base is repressed and the reserve acidity or basicity is increased. If, for example, a solution of ammonium hydroxide buffered with ammonium nitrate is considered, in the equilibrium

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

the ammonium nitrate furnishes NH_4^+ to increase the concentration of that ion in the solution. This causes the NH_4OH equilibrium to shift to the left. As it does so, some of the OH^- is thereby removed to form unionized NH_4OH, the amount of the latter, therefore, being increased. Now suppose that a very small quantity of an acid is added to this buffered mixture.

Some of the OH^- will be removed by reacting with the H^+ from the acid to form water. However, as the OH^- concentration is reduced by this reaction, the equilibrium will shift, some of the reserve base ionizing to replace most of the OH^- lost. Thus, the buffered solution resists changes in its OH^- concentration.

Suppose that instead of an acid one adds a little of a strong base such as sodium hydroxide. As was illustrated before, some of the NH_4^+ from the buffering agent would react with a large portion of the OH^- from the sodium hydroxide to form NH_4OH. Consequently, the reserve base would be markedly increased, but the OH^- concentration would be increased but slightly. Thus, small quantities of either acids or bases can be added to buffered solutions with little change in the H^+ or OH^- concentrations* of the buffered solutions.

Mathematically it can be shown that buffered solutions also resist changes in H^+ or OH^- concentration on dilution with water.

Mathematical Treatment of Buffer Solutions. The calculation of the H^+ or OH^- concentration in buffered solutions requires the use of equations obtained by the application of the law of mass action to the ionic equilibriums involved. Examples of such problems and their solutions will be considered in the following problems.

Problem 6. A solution is made by adding 0.1 mole of $NaC_2H_3O_2$ and 0.01 mole of $HC_2H_3O_2$ to enough water to make 1 liter of solution. What is the H^+ concentration of the resulting solution at 25°C?

a. From the ionization equation of the weak electrolyte present—in this problem, the $HC_2H_3O_2$—obtain the expression for its ionization constant:

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

$$\therefore \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = K_a$$

b. Since $NaC_2H_3O_2$ is completely ionized, and since each mole of it furnishes 1 mole of $C_2H_3O_2^-$, the 0.1 mole of $NaC_2H_3O_2$ in each liter of solution will give a solution 0.1*M* with respect to $C_2H_3O_2^-$. This enables us to neglect the relatively small amount of $C_2H_3O_2^-$ produced by ionization

* As will be explained later, both the H^+ and OH^- concentrations of a solution may be expressed in terms of what is known as the pH of the solution. A better way of describing the properties of any buffered solution, therefore, regardless of whether it is basic or acidic, is to say that *the* pH *of such a solution resists changes.*

of the $HC_2H_3O_2$ and likewise the similarly small amount of $HC_2H_3O_2$ lost by ionization. Consequently, $[C_2H_3O_2^-]$ will be 0.1 *M*, and $[HC_2H_3O_2]$ will be 0.01 *M*.

The constant K_a as obtained from ionization tables is 1.86×10^{-5} at 25°C. Substituting these values in the preceding equation, one obtains

$$\frac{[H^+](0.1)}{(0.01)} = 1.86 \times 10^{-5}$$

$$\therefore \frac{[H^+]}{0.1} = 1.86 \times 10^{-5}$$

$$\therefore [H^+] = 1.86 \times 10^{-5}\,(0.1) = 1.86 \times 10^{-6} \text{ mole per liter}$$

Problem 7 A solution is made by dissolving 0.1 mole of NH_4Cl and 0.01 mole of NaOH in enough water to make 1 liter of solution. What is the OH^- concentration of the solution?

a Consider the stoichiometric equation for the reaction that will occur; and disregarding for the moment any reversibility in the reaction,

$$NaOH + NH_4Cl \rightarrow NaCl + NH_4OH$$

note that 1 mole of NaOH reacts with 1 mole of NH_4Cl to form 1 mole of NH_4OH. However, though the solution considered contained 0.1 mole of NH_4Cl, it contained only 0.01 mole of NaOH. The latter will therefore be used up, and the final solution will be the same as would have been obtained using 0.09 mole (the original 0.1 mole less the 0.01 mole that reacted) of NH_4Cl, 0.01 mole (the amount produced by the reaction of the NH_4Cl with the NaOH) of NH_4OH, and no NaOH. Mathematically these quantities may be obtained as follows:

	NaOH	+	NH_4Cl	→	NaCl	+	NH_4OH
Given	= 0.01 mole		0.1 mole				
Used or produced	= 0.01 mole		0.01 mole		0.01 mole		0.01 mole
Left	= 0.00 mole		0.09 mole		0.01 mole		0.01 mole

b From (*a*) it is found that the final solution is 0.09 *M* with NH_4Cl and 0.01 *M* with NH_4OH. The weak electrolyte that controls the OH^- concentration is NH_4OH. From its ionization equation, by application of the law of mass action, one obtains the equation:

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = K_b$$

where K_b is 1.8×10^{-5}.

If the same reasoning is used as was applied to Problem 6, it can be shown that with only insignificant error, the NH_4^+ may be considered as coming only from the completely ionized NH_4Cl while the amount of NH_4OH may be assumed as equal to that which was theoretically produced in the reaction between the NaOH and NH_4Cl. Therefore the NH_4^+ concentration is 0.09 *M*, and the NH_4OH concentration is 0.01 *M*. Substituting these

values in the preceding equation, one obtains the expression

$$\frac{(0.09)[OH^-]}{(0.01)} = 1.8 \times 10^{-5}$$
$$\therefore [OH^-] = 1/9 \times 1.8 \times 10^{-5} = 0.2 \times 10^{-5} = 2.0 \times 10^{-6} M$$

Problem 8. Suppose that a solution is made by dissolving 0.15 mole of $NaC_2H_3O_2$ and 0.05 mole of HNO_3 in enough water to make the volume exactly 1 liter. What is the H^+ concentration of the solution?

a. Consider the quantitative aspects of the reaction between the $NaC_2H_3O_2$ and HNO_3, as was done for the NaOH and NH_4Cl in Problem 2:

	$NaC_2H_3O_2$	+ HNO_3	→ $NaNO_3$	+ $HC_2H_3O_2$
Given	= 0.15 mole	0.05 mole		
Used or produced	= 0.05 mole	0.05 mole	0.05 mole	0.05 mole
Left	= 0.10 mole	0.00 mole	0.05 mole	0.05 mole

b From (*a*) it is found that the final solution is 0.1*M* with $NaC_2H_3O_2$ and 0.05*M* with $HC_2H_3O_2$. Again, the $C_2H_3O_2^-$ may be considered as coming only from the $NaC_2H_3O_2$, and the loss of $HC_2H_3O_2$ molecules by ionization may be disregarded. Consequently, the concentration of $C_2H_3O_2^-$ is 0.1*M*, and that of $HC_2H_3O_2$ is 0.05*M*. Substituting these values and the value of K_a in the equation

$$\frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = K_a$$

one obtains

$$\frac{[H^+](0.1)}{(0.05)} = 1.86 \times 10^{-5}$$
$$\therefore [H^+] = 1/2 \times 1.86 \times 10^{-5} = 0.93 \times 10^{-5} = 9.3 \times 10^{-6} M$$

Polybasic (Polyprotic) Acids. Polybasic (*polyprotic*) acids ionize in steps, each successive stage occurring to a less extent than the previous one. Thus, H_2CO_3 first loses one hydrogen to form HCO_3^-, and then the HCO_3^- ionizes to form $CO_3^=$:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^=$$

For each step in the ionization an expression for an ionization constant can be derived:

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3]} = K_1$$
$$\frac{[H^+][CO_3^=]}{[HCO_3^-]} = K_2$$

The constant for the first stage in the ionization of a polybasic acid is always larger than that for the second stage; the constant for the second stage is larger than the third; etc. For example, in the case of H_2CO_3 at 25°C., K_1 is 3.3×10^{-7}, while K_2 is 3.9×10^{-11}.

Similarly, H_3PO_4 ionizes in three steps, and corresponding expressions for ionization constants may be obtained:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$

$$\therefore \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = K_1$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{--}$$

$$\therefore \frac{[H^+][HPO_4^{--}]}{[H_2PO_4^-]} = K_2$$

$$HPO_4^{--} \rightleftharpoons H^+ + PO_4^{---}$$

$$\therefore \frac{[H^+][PO_4^{---}]}{[HPO_4^{--}]} = K_3$$

For H_3PO_4 at 18°C. K_1 is 8.3×10^{-3}, K_2 is 2×10^{-7}, and K_3 is 4×10^{-13}.

It is obvious that any accurate calculation of the H^+ concentrations in solutions of polybasic acids would be by no means simple. Fortunately, however, usable approximations can often be made. If, as is usually the case, K_1 for the acid is much greater than K_2, and if the solution is not too dilute, the H^+ in a solution containing only the acid and water may be considered as all coming from the first step in the ionization. In other words, the acid may be treated as a monobasic acid with an ionization constant equal to K_1. Naturally, however, the accuracy of such calculations is not great when K_1 is not much larger than K_2 or where the concentration is low; for in either of these cases the proportion of H^+ furnished by the later steps in the ionization becomes much greater.

A more extensive treatment of polybasic acids would be too involved for an elementary course; however, one such acid, hydrosulfuric acid, H_2S, will be considered more fully in a later chapter.

SUMMARY

On the assumption that the ionization of strong electrolytes is complete, it is possible to calculate the ion concentrations in

solutions of strong electrolytes from the simple ionization equation. Secondary reactions of the ions with the solvent, *e.g.*, as in hydrolysis, may, however, lead to lower concentration of a given ion.

The *activity* (effective concentration) of an ion will be less than its actual concentration in solutions where the total ion concentration is moderately great. This is due to the so-called *salt effect.* If solutions containing ions whose only possible reaction products are strong electrolytes are mixed, no reaction will occur between those ions as long as everything remains in solution.

Solutions of weak acids contain an equilibrium mixture of H^+, the anion of the acid, and undissociated molecules of the acid. The H^+ concentration is known as the *momentary acidity*, the concentration of undissociated acid is known as the *reserve acidity*, and their sum is known as the *total acidity.* In solutions of strong acids the reserve acidity is zero. Solutions of weak bases have *momentary basicity* (the OH^- concentration), *reserve basicity* (the concentration of undissociated molecules of the base), and *total basicity.*

The ion concentrations in solutions of monobasic weak acids or monacid weak bases may be calculated either by using the expressions for their respective ionization constants or by using *Ostwald's dilution formula.* The latter can be also be used to calculate the degree of ionization in solutions of these acids or bases.

In mixtures of two monobasic acids, if the ionization constants of the two are sufficiently different, the H^+ concentration may be approximated by disregarding the weaker acid and assuming that all the H^+ comes from the stronger acid. The assumption is not valid, however, if the solution is *very dilute* or if the degrees of ionization are too near the same value. The same situation exists in regard to mixtures of bases.

Buffer solutions are solutions of weak acids containing a salt of a weak acid or of weak bases containing a salt of a weak base. Strong acids may be buffered by adding an excess of a salt of a weak acid; strong bases may be buffered by adding an excess of a salt of a weak base. The concentration of H^+ or of OH^- in buffer solutions is calculated by means of the expression for the ionization constant for the weak acid or weak base used or

formed in the buffer solution. In a buffered acid solution the H^+ concentration is usually low but resists changes, whether those changes are attempted by adding more acid, by adding a base, or by diluting the solution. The OH^- concentration in the buffered solution of a base is similarly low but constant.

Polybasic (or polyprotic) acids ionize in steps. The ionization constant, K_1, for the first stage in the ionization of the acid is always greater than that for the second, K_2, etc. The H^+ concentration in solutions of such acids may be approximated by disregarding the later steps in the ionization and treating the acid as a *monobasic* acid whose ionization constant is equal to K_1. Such an approximation is valid, however, only if K_1 is very much larger than K_2 and if the solution is not too dilute.

Review Questions

1. Why must the theory of complete ionization be used with caution in predicting ion concentrations in solutions of strong electrolytes?

2. What is meant by *momentary*, *reserve*, and *total* acidity? Illustrate.

3. What is meant by momentary, reserve, and total basicity?

4. Define the terms: (*a*) monobasic acid, (*b*) monacid base, (*c*) polyprotic acid, (*d*) buffered solution

5. Using the simplified Ostwald dilution formula, predict the effect produced on the degree of ionization of a weak electrolyte by (*a*) diluting the solution, (*b*) increasing the ionization constant by a change in temperature.

6. State briefly how the *approximate* H^+ concentration in a solution that contains two acids may be calculated. Under what conditions would such an approximation be invalid?

7. List the chief characteristics of a buffered solution.

8. How can the approximate H^+ concentration in a solution of a dibasic acid be calculated? How are approximations of this type restricted?

9. Write the expressions for the ionization constants of the following

(*a*) H_2SO_3	(*b*) NH_4OH	(*c*) H_3PO_4
(*d*) H_4SiO_4	(*e*) H_3BO_3	(*f*) H_2S

Problems

1. What is the concentration of H^+ in each of the following solutions?

(*a*) 0.03M $HC_2H_3O_2$.	(*b*) 0.02M HCN.	(*c*) 0.002M $HC_2H_3O_2$
(*d*) 0.3M HCl.	(*e*) 0.001M HNO_3	(*f*) 0.001M H_2CO_3.
(*g*) 0.05M H_2SO_3.		

Answers: (*a*) $7.4 \times 10^{-4}M$. (*b*) $3.8 \times 10^{-6}M$. (*c*) $1.9 \times 10^{-4}M$. (*d*) 0.3M. (*e*) 0.001M.

2. What is the OH^- concentration in (*a*) 0.05M NH_4OH? (*b*) 0.001M NH_4OH?

Answer: (*b*) $1.3 \times 10^{-4}M$.

3. What is the degree of ionization in each of the solutions in Problem 1?

4. What is the degree of ionization in each of the solutions in Problem 2?

5. A solution is prepared by adding 1 mole of NH_4Cl and 0.4 mole of NaOH to enough water to make 1 liter of solution.

a. What is the equation for the reaction that occurs?

b. What concentration of NH_4Cl will be left?

c. Of NaOH?

d. What concentration of NH_4OH will be formed?

e. Of NaCl?

Answers: (*b*) $0.6M$. (*c*) None. (*d*) $0.4M$. (*e*) $0.4M$.

6. A solution is made up to contain 0.01 mole of sodium acetate and 0.002 mole of HCl per liter.

a. What reaction occurs while the mixture is being made?

b. What concentration of each of the products is produced?

c What concentration of each of the original substances is left?

7. If 200 ml. of $0.8M$ NH_4NO_3 is mixed with 600 ml of $0.08M$ KOH, what will be the concentration in the mixture after equilibrium is established (*a*) of NH_4OH? (*b*) of KOH? (*c*) of KNO_3? (*d*) of NH_4NO_3?

Answers: (*a*) $0.06M$. (*c*) $0.06M$.

8. If a solution is made by *mixing equal volumes* of $0.1M$ $NH_4C_2H_3O_2$ and $0.5M$ HCl, what is the concentration of (*a*) HCl, (*b*) $NH_4C_2H_3O_2$ (*c*) $HC_2H_3O_2$, and (*d*) NH_4Cl in the final solution after all reactions have occurred?

Answers: (*a*) $0.2M$. (*b*) None. (*c*) $0.05M$. (*d*) $0.05M$.

9. A certain solution is made by dissolving 0.30 mole of NaOH and 0.15 mole of $(NH_4)_2SO_4$ in water and diluting the whole to 2 liters volume. What is the concentration in the resulting mixture (*a*) of $(NH_4)_2SO_4$? (*b*) of NaOH? (*c*) of NH_4OH? (*d*) of Na_2SO_4?

Answers: (*a*) None. (*b*) None. (*c*) 0.15 mole per liter. (*d*) 0.075 mole per liter.

10. What is the concentration of H^+ in each of these solutions:

(*a*) $0.1M$ $HC_2H_3O_2$ containing 0.3 mole per liter of $NH_4C_2H_3O_2$?

(*b*) $0.01M$ $HC_2H_3O_2$ containing 0.03 mole per liter of $NH_4C_2H_3O_2$? (Note that this would be solution (*a*) diluted to one-tenth its former concentration.)

(*c*) The solution in Problem 6?

(*d*) The solution in Problem 8?

(*e*) A solution made by dissolving 0.5 mole HNO_3 and 1 mole $Ca(C_2H_3O_2)_2$ in water and diluting to 5 liters?

(*f*) A solution made by dissolving 0.05 mole of H_2SO_4 and 0.5 mole of $NaC_2H_3O_2$ in water and diluting to 1 liter?

Answers: (*a*) $6.2 \times 10^{-6}M$. (*b*) Same as *a*. (*c*) $4.65 \times 10^{-6}M$. (*d*) $0.2M$. (*e*) $6.2 \times 10^{-6}M$. (*f*) $4.65 \times 10^{-6}M$.

11. What is the OH^- concentration in the following solutions:

a. A solution that is $0.5M$ with NH_4Cl and $0.5M$ with NH_4OH?

b. A solution that is $0.1M$ with NH_4OH and $0.25M$ with $(NH_4)_2SO_4$?

c. The mixture in Problem 5?

Answers: (*a*) $1.8 \times 10^{-5}M$. (*b*) $3.6 \times 10^{-6}M$. (*c*) $1.2 \times 10^{-5}M$.

12. *a.* What would be the H^+ concentration in a solution that was $0.05M$ with $HC_2H_3O_2$ and $0.1M$ with $NaC_2H_3O_2$?

b. What would the H^+ concentration be in (*a*) if 0.01 mole of NaOH were added to this solution? (HINT: What reaction occurs?)

c. Repeat *b*, using 0.02 mole of NaOH?

d. What is the H^+ concentration in a solution that is $0.05M$ with HCl?

e. What would be the concentration of H^+ in *d* if 0.01 mole of NaOH were added to the solution? If 0.02 mole of NaOH were added?

Answers: (*a*) $9.3 \times 10^{-6}M$. (*b*) $6.7 \times 10^{-6}M$. (*c*) $4.65 \times 10^{-6}M$. (*d*) $0.05M$. (*e*) $0.04M$. $0.03M$.

13. What concentration of

(*a*) $HC_2H_3O_2$ would be required to give a solution that is $0.002M$ with H^+?

(*b*) HCN would be required to give a solution that is 3×10^{-5} with H^+?

(*c*) NH_4OH would be required to give a solution that is $0.003M$ with OH^-?

(*d*) NH_4OH would be required to give a solution that is $0.0004M$ with OH^-?

Answers: (*a*) $0.215M$. (*c*) $0.5M$.

14. What concentration of the indicated salt would be required to give a solution of the ion concentration specified:

(*a*) $NaC_2H_3O_2$ in $0.1M$ $HC_2H_3O_2$, to give an H^+ concentration of 3×10^{-6} mole per liter?

(*b*) $Ca(C_2H_3O_2)_2$ in $0.05M$ $HC_2H_3O_2$, to give an H^+ concentration of 4.5×10^{-5} mole per liter?

(*c*) NH_4Cl in $0.02M$ NH_4OH, to give an OH^- concentration of 3×10^{-5} mole per liter?

(*d*) $(NH_4)_2SO_4$ in $0.1M$ NH_4OH, to give an OH^- concentration of 4×10^{-3} mole per liter?

Answers: (*a*) $0.62M$. (*d*) $2.25 \times 10^{-4}M$.

CHAPTER V

HETEROGENEOUS REACTIONS: SOLUBILITY PRODUCT

The preceding chapter was devoted to ionic equilibriums of the type in which all the active components are in solution in a *single* phase. As would be expected, reactions between substances in *different* phases* are influenced by all those factors which affect homogeneous reactions and equilibriums; in addition, however, other factors brought into existence through the necessity for the transfer of reactant at the surface between the phases must be considered.

Suppose that a zinc rod is inserted into a dilute solution of sulfuric acid. Bubbles of hydrogen will quickly form at the surface of the metal and rise to the surface of the liquid, the reaction being

$$Zn + 2H^+ \rightarrow Zn^{++} + H_2 \qquad (1)$$

Just as in the case of homogeneous reactions, if the sulfuric acid is made *more concentrated,* the rate of the reaction will increase. Similarly, if the *temperature* is raised, or if a positive *catalyst*† is added, the rate of formation of hydrogen will increase.

Obviously, this reaction occurs at the surface of the metal; so if the area of exposed surface is increased, the rate of the reaction will also increase. Thus, if the same rod were ground to a fine powder, the enormous new surface that would then be in contact with the solution would result in much more rapid reaction. If this illustration is typical, therefore, the rate of any heterogeneous reaction is proportional to the *surface* acted upon.

The rate of diffusion is another important factor in changes occurring in heterogeneous systems. Since the reaction between

* By reactions between substances in *different phases* are meant such things as reactions between a liquid and a solid, two immiscible liquids, a gas and a liquid—in other words, between substances that are separated by a boundary surface.

† It should be recalled from general chemistry that if a metal low in the electrochemical series is dipped into the acid and brought into contact with the zinc, the rate of the reaction will increase.

H^+ and metallic zinc occurs at the surface of the metal, it is obvious that the H^+ must move from wherever it may be in the solution to the surface of the metal before reaction can occur. Similarly, when a solid undergoes simple solution, the dissolved particles must diffuse *away* from the region near the surface of the solid; otherwise the adjacent solution becomes saturated, and the solution farther away remains unsaturated. For this reason the rate of any heterogeneous reaction is increased by stirring; for by stirring, the concentration of dissolved reactants at the surface is kept the same as that in other parts of the solution.

Heterogeneous Equilibriums. The heterogeneous reactions of greatest interest to the analytical chemist are those between liquids and solids or liquids and gases. Most of these reactions are of the reversible type; if conditions are right, therefore, these reactions may reach a condition of equilibrium. Such an equilibrium, like others, may be shifted by changes in temperature, concentration, or pressure. Consider, for example, a solution of sodium chloride in water. It will be recalled from the chapter on solutions that solid solute and dissolved solute are in equilibrium with each other only in a *saturated solution.* Consequently, the processes defining a saturated solution of sodium chloride may be represented by the equation

$$NaCl_{solid} \rightleftharpoons NaCl_{dissolved} \tag{2}$$

In the chapter on ionization, however, it was pointed out that the dissolved NaCl is *completely ionized.* To be accurate, therefore, the equilibrium must be represented as follows:

$$NaCl^*_{solid} \rightleftharpoons Na^+ + Cl^- \tag{3}$$

Now suppose that the *temperature* of this mixture is increased. The heat of solution† of sodium chloride is small but negative;

* As was explained in an earlier footnote, solids are represented throughout this book by their formulas without regard to the question as to whether the crystal lattice is ionic or molecular.

† When any solid is dissolved, heat is either absorbed or evolved. The quantity of heat evolved when 1 mole of the solid is dissolved is known as the *heat of solution* for that substance. The values given in handbooks may be either for solutions consisting of a stated number of moles of solvent to one formula weight of solute or for infinitely dilute solutions, since the dilution markedly affects the observed heat of solution.

When the dissolving process is accompanied by the *absorption* of heat, the heat of solution is said to be *negative.*

consequently, an increase in temperature will cause the equilibrium to shift somewhat to the right; *i.e.*, more of the solid will dissolve. This is in harmony with the information that a solubility chart gives (see Fig. 10)—the solubility of NaCl increases very slightly with an increase in temperature.

Suppose that the concentration of one of the ions, either Na^+ or Cl^-, is increased. This could be done by adding a highly soluble compound that has *an ion in common* with sodium chloride. For example, sodium hydroxide would furnish Na^+, or hydrochloric acid would furnish Cl^-. If a high concentration of either of these compounds is added to a saturated solution of sodium chloride, the equilibrium between the solid and its ions shifts to the left and some solid sodium chloride precipitates. The shifting of an equilibrium upon the addition of a compound furnishing ions of a type that are a part of the equilibrium is a very useful phenomenon known as the *common ion effect.* It should be noted that the addition of hydrochloric acid to this equilibrium mixture causes not only an *increase* in the *quantity of solid sodium chloride* but also a *decrease in the concentration of the second ion, i.e.*, the Na^+, since the solid sodium chloride can be formed only at the expense of the Na^+ in the solution. As will be seen later, the common ion effect is used very frequently when it is desired either to make a precipitation more complete or to reduce the concentration of a given ion.

Now suppose that instead of increasing the concentration of either the Na^+ or Cl^-, one *decreases* the concentration of one of these ions. In that case more NaCl must dissolve partially to replace the ions removed. In general, therefore, one can dissolve more of any solid electrolyte by adding a reagent that will reduce the concentration of any kind of ion produced by the solid.

In an earlier chapter it was explained that anything influencing the forward and reverse reactions of an equilibrium *unequally* will cause a shift in the equilibrium. In discussing heterogeneous reactions it was pointed out that the rate of reaction between substances in different phases is dependent upon the amount of surface exposed; consequently, the question as to the effect of surface upon the point of equilibrium of a reversible reaction must be considered. If saturated sodium chloride solution is used as an example, the two reactions involved are

$$NaCl_{(solid)} \rightarrow Na^+ + Cl^- \quad (4)$$
$$Na^+ + Cl^- \rightarrow NaCl_{(solid)} \quad (5)$$

Now, both of these reactions occur at the surface of the solid NaCl. In other words, the dissolving of NaCl is a process of ions *leaving* the surface of the solid, whereas crystallization is a process of ions *returning to* that surface. If, then, the surface is increased, the rate of dissolving will increase; but the rate of crystallization will increase to exactly the same extent, since there is just that much more surface to which the ions can return. It becomes obvious, therefore, that the amount of surface has no effect upon the point of equilibrium. Applied to saturated solutions of solids in general, this means that the solubility of a solid is *independent* of the *surface area* of the solid in contact with the solution. The amount of surface affects only the *rapidity with which equilibrium is attained.**

Although only systems of liquids and solids have been considered thus far, gases and liquids behave similarly. Discussion of such heterogeneous equilibriums will be reserved, however, for the chapter on Hydrogen Sulfide.

Heterogeneous Equilibriums and Dissolution. It was suggested earlier that in a saturated solution of a solid electrolyte if the concentration of any one of the ions of the electrolyte could be reduced, more of the solid would dissolve. Actually this is a general principle which may be applied to any electrolyte of limited solubility, regardless of state. Frequently the principle can be used only if one kind of ion yielded by the electrolyte is unimportant and can be destroyed or lost without defeating the purpose at hand; sometimes, however, the same thing can be accomplished by a reversible process which will permit later recovery of the ion removed.

Although it is customary to speak of certain substances as being *insoluble*, actually none is *completely* insoluble. The solubilities of many substances such as silver chloride, calcium carbonate, barium sulfate, and ferrous sulfide are very low. Yet each is soluble to a very slight extent (see Fig. 11), *e.g.*, a saturated solution of silver chloride being about 0.00001*M* at 25°C. Con-

* It has been found that *very fine* particles of some solids are somewhat more soluble than coarser particles. The particles ordinarily used or obtained, however, are not sufficiently small to show this effect.

sequently, the saturated solution of any salt, no matter how low its solubility, contains some dissolved material in equilibrium with the excess solid, and such compounds should be described as *slightly* soluble rather than as insoluble. As to the nature of the dissolved substances, two facts should be recalled: (1) According to the modern conception, most salts are completely ionized even in concentrated solutions; and (2) according to accepted theory, ionization is always complete in infinitely dilute solutions. Many of the slightly soluble compounds considered in qualitative analysis are salts, and the saturated solutions of these slightly soluble salts are, naturally, extremely dilute. Consequently it may be assumed that all the dissolved electrolyte is completely ionized and that the saturated solution of any slightly soluble electrolyte represents an equilibrium between the undissolved solid and its ions in solution, *e.g.*, for AgCl

$$AgCl_{(solid)} \rightleftarrows Ag^+ + Cl^- \qquad (6)$$

On this basis, the problem of dissolving any slightly soluble electrolyte resolves itself into one of reducing the concentration of *either* the cation or the anion or *both*.

Reduction in the concentrations of cations is usually effected by the action of reagents which react with the cations to form either (1) *complex ions* or (2) *weak electrolytes*. The first of these methods is best illustrated by the dissolving of silver chloride in ammonium hydroxide in the analysis of Cation Group I. As just pointed out, if silver chloride is allowed to remain in contact with water, an equilibrium will eventually be established between the undissolved solid and Ag^+ and Cl^- in the solution. If some ammonium hydroxide is added to this solution, the following equilibrium will be established:

$$Ag^+ + 2NH_3 \rightleftarrows Ag(NH_3)_2^+ * \qquad (7)$$

* Although it is customary to write the formula for ammonium hydroxide as NH_4OH, actually a large proportion of the dissolved material is in the form of NH_3 molecules. It is more truly representative of the nature of ammonium hydroxide solutions to assume the existence of the following equilibrium mixture:

$$NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows NH_4^+ + OH^-$$

which shows ammonium hydroxide to be a source of NH_3 molecules as well

Since the complex ion* $Ag(NH_3)_2^+$ is entirely different from the simple silver ion in properties, this reaction reduces the concentration of simple Ag^+ in the solution. The equilibrium

$$AgCl_{(solid)} \rightleftharpoons Ag^+ + Cl^- \tag{6}$$

must therefore shift to the right; and if sufficient reagent has been used, the solid will dissolve.†

In a similar way, $Cu(OH)_2$ and $Cd(OH)_2$ in Group II are dissolved in excess ammonium hydroxide to form $Cu(NH_3)_4^{++}$ and $Cd(NH_3)_4^{++}$, respectively; while $Zn(OH)_2$, $Co(OH)_2$, and $Ni(OH)_2$ in Group III are dissolved in ammonium hydroxide ammonium salt mixtures to form $Zn(NH_3)_4^{++}$, $Co(NH_3)_6^{++}$, and $Ni(NH_3)_4^{++}$, respectively. The equilibriums involved may be illustrated by those for the dissolving of $Cu(OH)_2$ in an *excess* of ammonium hydroxide:

$$Cu(OH)_{2\,(solid)} \rightleftharpoons Cu^{++} + 2(OH^-) \tag{8}$$

$$Cu^{++} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{++} \tag{9}$$

The reaction of Cu^{++} with NH_3 to form $Cu(NH_3)_4^{++}$ reduces the concentration of simple Cu^{++}; consequently, equilibrium (8) shifts to the right, and some of the solid $Cu(OH)_2$ dissolves. As this shift produces more Cu^{++}, the NH_3 still remaining (remember that an excess was used) reacts with nearly all of these to form

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as of NH_4^+ and OH^-. Indeed, there is excellent evidence to support the belief that few or no NH_4OH molecules exist and that the equilibrium existing in a solution of ammonium hydroxide is more accurately represented by the equation

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

* Ammonia forms complex ions with many metals, examples of these being the diammine silver ion, $Ag(NH_3)_2^+$, the tetrammine cupric ion, $Cu(NH_3)_4^{++}$, the hexammine cobalt ion, $Co(NH_3)_6^{++}$, the tetrammine zinc ion, $Zn(NH_3)_4^{++}$, and many others.

The ammonia and other complex ions will be discussed much more fully in a later chapter.

† The dissolving of a solid is often quite rapid, but the disappearance of solid is slow because the dissolving is partly offset by recrystallization. If, however, one or more of the types of ions produced are removed or changed *as rapidly as they appear in the solution*, the dissolving will take place almost as quickly as if it were irreversible. Consequently, if even *dry* AgCl is treated with an aqueous solution of ammonium hydroxide, the solid will usually dissolve quite rapidly.

more $Cu(NH_3)_4^{++}$. In other words, reaction (9) keeps reducing the Cu^{++} concentration, while reaction (8) replenishes it. Eventually, therefore, if enough ammonium hydroxide is added, all the solid disappears.*

The dissolving of mercuric iodide, if an *excess* of potassium iodide is added in testing for mercury in Group I or Group II, is another illustration of dissolution caused by complex ion formation. If a limited quantity of I^- is added to a solution of Hg^{++}, the reaction

$$Hg^{++} + 2I^- \rightleftharpoons HgI_{2(solid)} \tag{10}$$

occurs; but if an excess of I^- is used, the reaction goes further:

$$HgI_{2(solid)} + 2I^- \rightleftharpoons HgI_4^= \tag{11}$$

The sulfides of copper and of silver can be dissolved readily in solutions of sodium or potassium cyanide. The reactions for silver are

$$Ag_2S_{(solid)} \rightleftharpoons 2Ag^+ + S^= \tag{12}$$
$$Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^- \tag{13}$$

* It will be noticed that the equations for the formation of complex ions are written as reversible reactions. This means that not all the Cu^{++} and not all the NH_3 are removed from the solution by reaction (9). If, therefore, a reagent is added that is capable of effectively reducing the concentration of either Cu^{++} or NH_3, reaction (9) will be shifted to the left once more.

This principle is used in the procedure for Cation Group I, in which AgCl is first dissolved in NH_4OH to separate it from Hg_2Cl_2 and then, after filtering, the solution containing $Ag(NH_3)_2^+$ and Cl^- is acidified with nitric acid to reprecipitate the AgCl. The reactions involved are

$$AgCl_{(solid)} \rightleftharpoons Ag^+ + Cl^- \tag{6}$$
$$Ag^+ + Cl^- + NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^- \tag{6a}$$
$$NH_3 + H^+ \rightleftharpoons NH_4^+ \tag{6b}$$

Note that reaction (6) goes to completion to the right because reaction (6*a*) removes Ag^+ as fast as AgCl goes into solution. The resulting solution contains $Ag(NH_3)_2^+$ and Cl^-. When nitric acid is added to this mixture, the H^+ from the acid reacts with the NH_3 molecules, which, with a very low concentration of Ag^+, are in equilibrium with the complex ions. Thus, in reaction (6*b*) the NH_3 is removed by reaction with H^+ to form NH_4^+. Reaction (6*a*) must therefore shift to the left, resulting in an increase in the concentration of Ag^+. This, in turn, causes reaction (6) to shift to the left, producing solid AgCl.

Still another way of reducing the cation concentration can be used for the compounds of certain metals. The hydroxides of these particular metals not only are able to undergo normal neutralization reactions with strong acids but also are able to react with very active bases. Such hydroxides, known as *amphoteric hydroxides*, are exemplified by the hydroxides of lead, tin, antimony, zinc, chromium, and aluminum. Although there is some question as to exactly what happens when the hydroxides of any of these metals dissolve in an active base, their behavior is most simply illustrated by assuming that these hydroxides are capable of ionizing to form not only the simple cation and hydroxyl ions but also *hydrogen ions* and *anions* containing the metal. For example, $Zn(OH)_2$ might be considered as ionizing in the following two ways:

$$Zn(OH)_{2(solid)} \rightleftharpoons Zn^{++} + 2(OH^-) \qquad (14)$$

$$Zn(OH)_{2(solid)} \rightleftharpoons H^+ + HZnO_2^- \qquad (15)$$

According to this conception,* any mixture of $Zn(OH)_2$ and water will contain the following equilibrium mixture:

$$Zn^{++} + 2(OH^-) \rightleftharpoons \begin{bmatrix} Zn(OH)_2 \\ H_2ZnO_2 \end{bmatrix}_{(solid)} \rightleftharpoons H^+ + HZnO_2^- \qquad (14, 15)$$

If a base is added, the OH^- from the base will react with the H^+ in this mixture to form water. The reaction will shift to the right, therefore, and the solid will dissolve, yielding a solution containing hydrogen zincate ions, $HZnO_2^-$.

Slightly soluble salts of those metals whose hydroxides are amphoteric will often dissolve in solutions of active bases. In Cation Group II, for example, the presence of lead is confirmed by the solubility of its chromate in NaOH solution. The reactions involved are

$$PbCrO_{4(solid)} \rightleftharpoons Pb^{++} + CrO_4^= \qquad (16)$$

$$Pb^{++} + 3(OH^-) \rightleftharpoons HPbO_2^- + H_2O \qquad (17)$$

The second method used to reduce the concentration of a cation, *i.e.*, by the formation of a weak electrolyte, is best illustrated by

* One theory postulates the formation of *complex ions* in reactions between the cation and OH^-. This will be treated in the more detailed discussion of amphoterism in Chap. VIII.

the dissolving of lead sulfate in concentrated ammonium acetate or sodium acetate solution (see the Cation Group II procedure). Lead acetate is *very soluble* but *only slightly ionized;* consequently, if a warm, concentrated solution of ammonium acetate is added to solid lead sulfate, the reaction

$$PbSO_{4(solid)} \rightleftharpoons Pb^{++} + SO_4^{=} \tag{18}$$

is shifted toward the right, owing to the removal of Pb^{++} by the reaction

$$Pb^{++} + 2C_2H_3O_2^{-} \rightleftharpoons Pb(C_2H_3O_2)_{2(slightly\ ionized)} \tag{19}$$

The law of mass action is applied effectively by the use of a high concentration of the acetate to force the last reaction well toward completion.

Thus far we have considered the removal of only cations as a method of dissolving precipitates. Even more widely used, however, are reactions that reduce the concentration of the anions. Since the methods used depend upon the nature of the anion, these anions are best considered individually. The more common of those used in analysis to produce slightly soluble compounds are OH^-, $S^=$, $CO_3^=$, $CrO_4^=$, and $PO_4^{\equiv}$; consequently, these anions will be considered here.

Hydroxyl ions can be removed most effectively by the addition of acids, the OH^- reacting with H^+ from the acid to form water. The dissolving of slightly soluble hydroxides in acids can be illustrated by the reaction between lead hydroxide and nitric acid:*

$$Pb(OH)_{2(solid)} \rightleftharpoons Pb^{++} + 2(OH^-) \tag{20}$$

$$OH^- + H^+ \rightleftharpoons H_2O \tag{21}$$

Sulfides are dissolved by (1) the addition of H^+ to form the very slightly ionized and only moderately soluble compound, hydrogen sulfide; (2) the oxidation of $S^=$ to elementary sulfur or to $SO_4^=$; or (3) the reaction of the cation with excess $S^=$ to form *anions* in which the metal is combined with sulfur—such as thioar-

* It should be apparent that any reagent used to *dissolve* a solid must be chosen with proper consideration for any effect that the second ion may have. For example, though H_2SO_4 would furnish the necessary H^+ for this reaction, the $SO_4^=$ would immediately reprecipitate the Pb^{++} as the very slightly soluble $PbSO_4$. This would naturally defeat the purpose for which the reaction was being performed.

senite, AsS_3^-, and thiostannate, $SnS_3^=$, ions. As a complete discussion of these relationships is given in the chapter on Hydrogen Sulfide, the subject will not be treated here.

Carbonates are readily dissolved in acids owing to the formation of slightly ionized HCO_3^- and H_2CO_3, and the decomposition of the latter to form H_2O and CO_2. In Cation Group IV, for example, the metals are first precipitated as carbonates, and then the carbonates are dissolved in acid. If barium carbonate is used for an example, the steps in the dissolving of these carbonates are as follows;

$$BaCO_{3(solid)} \rightleftharpoons Ba^{++} + CO_3^= \quad (22)$$

$$CO_3^= + 2H^+ \rightleftharpoons H_2CO_3 \quad (23)$$

$$H_2CO_3 \rightleftharpoons H_2O + CO_2\uparrow \quad (24)$$

The gas, CO_2, whose solubility is not great even in cold water, is readily driven from the mixture by heat. This causes equilibrium (24) to shift to the right and thereby removes H_2CO_3. In turn, equilibrium (23) must shift to the right, and the concentration of $CO_3^=$ is consequently reduced. This causes equilibrium (22) to shift to the right, and the solid dissolves because the removal of $CO_3^=$ prevents the attainment of equilibrium between the solid and its ions.

Chromates may be dissolved either (1) by reducing $CrO_4^=$ to Cr^{+++}, or (2) by the addition of H^+ to convert the chromate, $CrO_4^=$, to dichromate, $Cr_2O_7^=$.* Thus, one of the most effective ways to dissolve $BaCrO_4$ is to add hydrochloric acid and warm the mixture:

$$BaCrO_{4(solid)} \rightleftharpoons Ba^{++} + CrO_4^= \quad (25)$$

$$2CrO_4^= + 2H^+ \rightleftharpoons Cr_2O_7^= + H_2O \quad (26)$$

$$Cr_2O_7^= + 14H^+ + 6Cl^- \rightleftharpoons 2Cr^{+++} + 7H_2O + 3Cl_2\uparrow \quad (27)$$

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* The dichromate ion is really an *acid chromate*, two ions of which have, between them, lost one molecule of water. A chromate can be readily converted to a dichromate simply by acidifying the solution·

$$CrO_4^= + H^+ \rightleftharpoons HCrO_4^-$$

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^= + H_2O$$

As indicated in these equations, the process is reversible; consequently, any solution that contains $CrO_4^=$ also contains some $Cr_2O_7^=$, and any solution that contains $Cr_2O_7^=$ also contains some $CrO_4^=$. Also, dichromates can be readily converted to chromates simply by addition of a base, since the OH^- of the base will remove H^+ by reacting with it to form H_2O.

If the concentration of H^+ is high, reaction (26) alone will cause much of the $BaCrO_4$ to dissolve, as is evidenced by the fact that nitric acid, which is incapable of reducing $Cr_2O_7^=$, is a moderately good reagent to use for dissolving $BaCrO_4$. Indeed, many chromates, such as Ag_2CrO_4 and $SrCrO_4$, are readily dissolved via reaction (26), even such weak acids as acetic acid yielding sufficient H^+ to accomplish this.

The salts of weak acids in general dissolve in—or at least react with—strong acids. Phosphates, for example, usually are soluble in nitric acid. The reactions involved may be illustrated by using $Ca_3(PO_4)_2$:

$$Ca_3(PO_4)_{2(solid)} \rightleftharpoons 3Ca^{++} + 2PO_4^{\equiv} \quad (28)$$

$$PO_4^{\equiv} + H^+ \rightleftharpoons HPO_4^{=} \quad (29)$$

$$HPO_4^{=} + H^+ \rightleftharpoons H_2PO_4^- \quad (30)$$

$$H_2PO_4^- + H^+ \rightleftharpoons H_3PO_4 \quad (31)$$

Heterogeneous Equilibriums and Precipitation. The application of equilibrium principles to the dissolving of slightly soluble electrolytes has been discussed in some detail in the preceding pages. Now, however, it is necessary to consider how these slightly soluble substances can be *formed.* It has been pointed out repeatedly that, under identical conditions, the same equilibrium mixture will be obtained regardless of which of the two opposing reactions of the system may be used at the beginning. If, for example, water is saturated with AgCl, the equilibrium

$$AgCl_{(solid)} \rightleftharpoons Ag^+ + Cl^- \quad (6)$$

will be produced. On the other hand, if a solution containing Ag^+ (*e.g.*, silver nitrate solution) is added to a solution containing an *equivalent quantity* of Cl^- (*e.g.*, hydrochloric acid or sodium chloride solution), some AgCl will precipitate* and the equilibrium will again be set up. If, therefore, it is desired to precipitate AgCl from a solution containing Ag^+, it is necessary only to add

* Sometimes the precipitation of slightly soluble compounds is delayed by formation of a supersaturated solution. The relationships illustrated here naturally do not apply to supersaturated solutions, since the solid and the ions in solution are not in equilibrium under those conditions. The same is true if there is not sufficient Ag^+ and Cl^- to cause any solid AgCl to form, *i.e.*, if the solution is unsaturated.

to it a solution containing Cl^- and the reaction

$$Ag^+ + Cl^- \rightleftharpoons AgCl_{(solid)} \tag{32}$$

will take place

In general, to cause a precipitate of a given slightly soluble electrolyte to form, it is necessary only to add a sufficiently concentrated solution of the desired cation to a solution of the desired anion. Thus, to precipitate $BaSO_4$ from a solution containing Ba^{++}, add a solution containing $SO_4^{=}$ (*e.g.*, K_2SO_4 or H_2SO_4 solution):

$$Ba^{++} + SO_4^{=} \rightleftharpoons BaSO_{4(solid)} \tag{33}$$

To precipitate a slightly soluble sulfide such as CdS from a solution containing Cd^{++}, add a source of S^- such as H_2S:

$$Cd^{++} + S^- \rightleftharpoons CdS_{(solid)} \tag{34}$$

while to precipitate a slightly soluble hydroxide such as $Cu(OH)_2$ from a solution containing Cu^{++}, add a solution of a base:

$$Cu^{++} + 2(OH^-) \rightleftharpoons Cu(OH)_{2(solid)} \tag{35}$$

In each case, however, it is necessary to consider other possible factors in choosing the reagent and in determining conditions. For example, ammonium hydroxide would be a poor choice of bases to use to precipitate $Cu(OH)_2$, since care would be required to prevent part or all the $Cu(OH)_2$ from being redissolved owing to the formation of $Cu(NH_3)_4^{++}$.

Similarly, it would be difficult if not impossible to precipitate a given metal sulfide from a solution containing reagents in which that sulfide is soluble. Thus, CuS is soluble in KCN solution:

$$CuS_{(solid)} \rightleftharpoons Cu^{++} + S^{=} \tag{36}$$

$$2Cu^{++} + 8CN^- \rightleftharpoons 2Cu(CN)_3^{=} + C_2N_2 \tag{37}$$

Consequently, if a sufficiently great excess of KCN is added to a solution containing Cu^{++}, the concentration of the Cu^{++} is reduced to such a low value that it is impossible to precipitate CuS from the solution by adding hydrogen sulfide.

Likewise, solids that are soluble in acids cannot be precipitated from solutions of high H^+ concentration. Many examples of this type of phenomenon will be found during the study of the analytical procedure.

Solubility Products. Thus far the relationships between solid electrolytes and solutions containing their ions have been considered only qualitatively. For more accurate work and for use in *accurately predicting the dissolution or precipitation* of given substances under specified conditions, quantitative relationships are essential.

Again consider, for example, a solution in which Ag^+ and Cl^- are in equilibrium with solid AgCl. Regardless of whether the equilibrium mixture was prepared by mixing solutions containing Ag^+ and Cl^- to form solid AgCl or by saturating water by shaking it with solid AgCl, the equilibrium mixture may be represented by the equation

$$AgCl_{(solid)} \rightleftharpoons Ag^+ + Cl^- \tag{6}$$

Since this is a true equilibrium, the law of mass action may be applied to it quantitatively; consequently, the relationship

$$\frac{[Ag^+][Cl^-]}{[AgCl_{(solid)}]} = K \tag{38}$$

holds true. Now it will be recalled from the earlier discussion of factors influencing heterogeneous equilibriums that the point of equilibrium of a heterogeneous system is independent of the amount of surface or the total quantity of any solid taking part in the reaction. In other words, *as long as some solid is present,* its effect on the point of equilibrium is the same, whether there is little or much solid. Consequently, the effective "concentration" of the solid is constant. If, then, the preceding equation is rearranged algebraically,

$$[Ag^+][Cl^-] = K[AgCl_{(solid)}] \tag{39}$$

and if it is recalled that in mathematics, the product of two constants is equal to a third constant, one can obtain the simplified expression

$$[Ag^+][Cl^-] = K_{s.p.} \tag{40}$$

in which $K_{s.p.}$, which is known as the *solubility-product constant,* is substituted for the product of the two constants K and $[AgCl_{(solid)}]$.

It will be noted that during the derivation of this equation, no restrictions were made as to the method by which equilibrium was attained—it was necessary only that *the system be at equilibrium.*

Consequently, this equation means that regardless of how the system was formed, at equilibrium the product obtained by multiplying the molar concentration of Ag^+ in the solution by that of the Cl^- (in other words, the *ion product*) must equal a constant. If therefore, any two of the three terms involved in this equation can be evaluated, the third term can be calculated just as in any

TABLE IV.—SOLUBILITY-PRODUCT CONSTANTS*

Salt	Temperature, °C	Constant
AgBr	25	7.7×10^{-13}
AgCl	25	1.6×10^{-10}
AgCN	20	2.7×10^{-12}
Ag_2CO_3	25	8.2×10^{-12}
Ag_2CrO_4	25	3.3×10^{-12}
AgI	25	1.5×10^{-16}
AgSCN	18	5×10^{-13}
$BaCO_3$	25	8×10^{-9}
$BaCrO_4$	25	2.2×10^{-10}
$BaSO_4$	25	1.0×10^{-10}
$CaCO_3$	25	8×10^{-8}
CaC_2O_4	25	2.6×10^{-9}
CaF_2	25	3.8×10^{-11}
$CaSO_4$	25	2.3×10^{-4}
$Fe(OH)_2$	18	1.6×10^{-14}
$Fe(OH)_3$	18	1.1×10^{-36}
$MgCO_3$	12	1.9×10^{-4}
$Mg(OH)_2$	18	2×10^{-11}
$PbCO_3$	18	3.3×10^{-14}
$PbCrO_4$	18	1.8×10^{-14}
$PbSO_4$	18	1.0×10^{-8}
$SrCO_3$	25	1.6×10^{-9}
$SrCrO_4$	25	3.6×10^{-5}
$SrSO_4$	25	2.8×10^{-7}
Ag_2S		10^{-50}
CdS		10^{-29}
CuS		10^{-42}
FeS		10^{-19}
HgS		10^{-54}
MnS		10^{-15}
NiS		10^{-24}
PbS		10^{-28}
ZnS		1.2×10^{-23}

* Most of these constants were obtained from Hammett's "Solutions of Electrolytes, 1936.

other algebraic equation. For all slightly soluble electrolytes in which the cation and anions have equal valences, *i.e.*, uni-univalent, bi-bivalent, etc., compounds,* a similar expression can be derived. The numerical value of the solubility-product constant, however, will be different for each substance (see Table IV). Thus, the solubility-product expressions for $BaSO_4$ and for $CaCO_3$ are, respectively,

$$[Ba^{++}][SO_4^{=}] = K_{s.p.} = 1 \times 10^{-10} \tag{41}$$

$$[Ca^{++}][CO_3^{=}] = K_{s.p} = 8 \times 10^{-8} \tag{42}$$

For salts of other types, the solubility-product expressions are slightly more complicated, that for the uni-bivalent salt Ag_2CrO_4 being

$$[Ag^{+}][Ag^{+}][CrO_4^{=}] = K_{s.p}$$

or

$$[Ag^{+}]^2[CrO_4^{=}] = K_{s.p} \tag{43}$$

while that for the bi-univalent compound $Mg(OH)_2$ is

$$[Mg^{++}][OH^{-}][OH^{-}] = K_{s.p}$$

or

$$[Mg^{++}][OH^{-}]^2 = K_{s.p} \tag{44}$$

and that for SnS_2 is

$$[Sn^{++++}][S^{=}][S^{=}] = K_{s.p}$$

or

$$[Sn^{++++}][S^{=}]^2 = K_{s.p.} \tag{45}$$

It can be seen from these illustrations that the solubility-product constant of any slightly soluble compound is equal to the mathematical product of the molar concentrations of the ions that it forms, the concentration of each ion being raised to a power equal to the number of that kind of ions in the formula. For

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* Electrolytes are sometimes classified according to the valence types represented in their formulas The first part of the classification applies to the cation, whereas the latter part refers to the anion For example, in Na_2SO_4 the cation, Na^{+}, has a valence of 1, while the anion, $SO_4^{=}$, has a valence of 2. This compound is therefore a uni-bivalent compound. Similarly, NaCl is uni-univalent; $CaCO_3$ is bi-bivalent; $Ca(OH)_2$ is bi-univalent; etc.

example, in Sb_2S_3 there are *two* Sb^{+++} and *three* $S^{=}$ in the formula. The solubility-product expression is, therefore,

$$[Sb^{+++}]^2[S^{=}]^3 = K_{sp} \tag{46}$$

A general formula for the solubility-product expression for any slightly soluble electrolyte, M_yX_z, would therefore be

$$[M]^y[X]^z = K_{sp}. \tag{47}$$

With these principles in mind it is now possible to define much more accurately the conditions necessary to cause a slightly soluble electrolyte to precipitate or to dissolve. Before such a compound will precipitate from a solution, the ion product must, momentarily at least, *exceed* the value for the solubility-product constant for the compound. On the other hand, for a slightly soluble electrolyte to dissolve, the ion product must be *less* than the solubility-product constant. For example, consider a solution containing Ag^+ and $CrO_4^{=}$ in contact with solid Ag_2CrO_4. If the ion product $[Ag^+]^2[CrO_4^{=}]$ is made *greater* than the solubility-product constant for Ag_2CrO_4, more solid will form. On the other hand, if this ion product is *less* than the solubility-product constant, some of the solid will disappear. If the ion product *exactly equals* the solubility-product constant, the amount of solid in contact with the solution will not change.

Although the K_{sp} for any given compound is, in general, a true constant, it will vary if certain factors are changed. The factors that cause such changes are as follows:

1. *Changes in Temperature.* It will be noted that the values given in Table IV are at specified temperatures.* As was pointed out in the chapter on Solutions, the solubilities of most substances vary widely with changes in temperature (see Fig. 11). Since the solubilities of solids generally increase with increases in temperature, the solubility-product constants for most solids also increase with increases in temperature.

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* The temperatures are not specified for the metal sulfides, for unusual difficulties in determining the solubility-product constants for sulfides make the values as given only approximations. The error involved in disregarding the temperature effect for sulfides is no greater than are the errors in determining the value of these constants.

2. *Changes in Solvent.* The solubility-product constants given in such tables are for solutions of the slightly soluble substance in *water.* For other solvents or even for mixtures of water and other liquids, the constants depart widely from these values. This fact is sometimes used in analysis to precipitate certain compounds more completely. Most salts are much less soluble in ethyl alcohol or mixtures of ethyl alcohol and water than they are in pure water—in other words, their solubility-product constants are much smaller in alcohol or alcohol-water mixtures than in water alone. Thus, in Cation Group IV the precipitation of

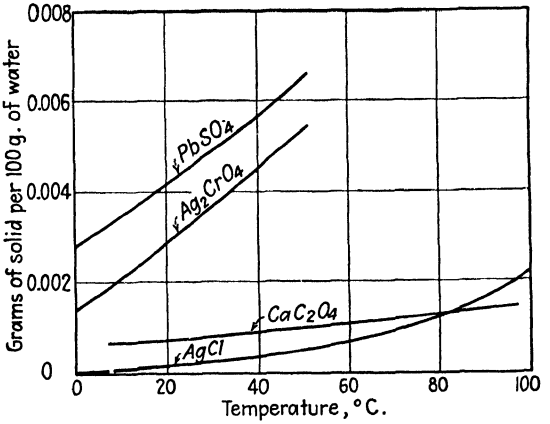


FIG. 11.—Solubility-temperature curves for some slightly soluble salts.

$SrCrO_4$ is made much more nearly complete by the addition of ethyl alcohol to the mixture

3. *Solutions of High Ion Concentration.* It was pointed out in the discussion of the modern theories of electrolytes that when the total concentration of ions in a solution is great, the ions interfere with one another and thus slow their movement through the solution. Since the rate of crystallization in a saturated solution is dependent upon the rate at which ions can diffuse through the solution, obviously if the total ion concentration is great, the rate of crystallization will be less than would be expected if such a "dragging" effect did not exist. In the equilibrium representing a saturated solution of thallous chloride,

$$TlCl_{(solid)} \rightleftharpoons Tl^+ + Cl^- \qquad (48)$$

anything that retards the reverse reaction will cause more TlCl to go into solution. That high ion concentrations produce such an effect was shown by Bray and Winninghoff, who found that TlCl has a solubility of 0.016 mole per liter in pure water while in 0.01*M* KNO_3 solution, which contains no ions in common with those from TlCl, it has a solubility of 0.019 mole per liter. Evidently, then, the solubility-product constant for a given substance will change if the total ion concentration becomes great. This phenomenon, which is another illustration of the *salt effect*, is produced by even moderate concentrations of any strong electrolyte.

It should be pointed out also that owing to the fact that a saturated solution of any fairly soluble salt has a high ion concentration, the salt effect produced by the substance itself in such a solution is so great that a solubility-product expression for it could have no usable quantitative meaning. Consequently, solubility-product expressions are never applied to any but *slightly soluble electrolytes.*

Although the salt effect of the usually rather high concentration of ions used in qualitative analysis* materially decreases the mathematical accuracy of the solubility-product relationship, this relationship may be used for many useful estimations. Examples of such problems will be considered now.

Problem 1. A dilute solution of HCl is added, a little at a time with stirring, to a Cation Group I unknown which contains only $AgNO_3$. When the precipitation seems complete, the solution is found to be 0.01*M* with Cl^-. If the ions in the solution are at equilibrium with solid AgCl, what is the concentration of Ag^+ left in the solution?

a. Since the equilibrium is between Ag^+ and Cl^- and solid AgCl, the solubility-product relationship for AgCl must be satisfied. This relationship is

$$[Ag^+][Cl^-] = K_{sp} \tag{40}$$

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* If *activities*, *i.e.*, concentrations corrected for the salt effect, are used instead of actual concentrations, the range of usefulness of the solubility product is greatly increased and these relationships may be applied accurately to solutions in which the salt effect is quite pronounced. The relationship for AgCl would then be expressed

$$a_{Ag^+} \times a_{Cl^-} = K_{sp}$$

where a_{Ag^+} is the activity (or effective concentration) of Ag^+ and a_{Cl^-} is the activity of Cl^-.

b. In Table IV it is found that the solubility-product constant for AgCl is 1.6×10^{-10},* also, the original problem stated that the concentration of Cl^- was $0.01M$ when equilibrium was finally established. Substituting these values in the foregoing equation, one obtains the expression

$$[Ag^+](0.01) = 1.6 \times 10^{-10}$$

$$[Ag^+] = \frac{1.6 \times 10^{-10}}{0.01} = \frac{1.6 \times 10^{-10}}{1 \times 10^{-2}} = 1.6 \times 10^{-8}M$$

Problem 2. If a certain solution is $0.1M$ with Mg^{++}, what concentration of OH^- will be required to cause $Mg(OH)_2$ just to start precipitating?

a. First, the solubility-product expression for the slightly soluble compound, $Mg(OH)_2$, must be formulated. This is

$$[Mg^{++}][OH^-]^2 = K_{sp} \tag{44}$$

b. The K_{sp} for $Mg(OH)_2$, as obtained from Table IV, is 2×10^{-11}; the concentration of Mg^{++} as given in the statement of the problem is $0.1M$. By substituting these values in the preceding equation, one obtains

$$(0.1)[OH^-]^2 = 2 \times 10^{-11}$$

$$\therefore [OH^-]^2 = \frac{2 \times 10^{-11}}{0.1} = 2 \times 10^{-10}$$

$$\therefore [OH^-] = \sqrt{2 \times 10^{-10}} = 1.4 \times 10^{-5}M$$

Problem 3. If the solubility-product constant for $Fe(OH)_2$ is 1.64×10^{-14}, (*a*) what is its solubility in moles per liter and (*b*) what is the concentration of OH^- in its saturated solution?

a. Again the solubility product expression must be formulated:

$$[Fe^{++}][OH^-]^2 = K_{sp} = 1.64 \times 10^{-14}$$

b. Now let the solubility of this compound, in moles per liter, be represented by S. This means, therefore, that 1 liter of the saturated solution of $Fe(OH)_2$ contains S moles of the solute. It will be remembered, however, that the dissolved solute is considered completely ionized. So the S *moles* in each liter will give S moles of Fe^{++} and $2S$ moles of OH^- per liter of saturated solution. Therefore, in the saturated solution the concentrations of the ions are

$$[Fe^{++}] = S \text{ moles per liter}$$
$$[OH^-] = 2S \text{ moles per liter}$$

Substituting these values in the equation for the solubility-product constant gives

$$(S)(2S)^2 = 1.64 \times 10^{-14}$$

$$\therefore 4S^3 = 1.64 \times 10^{-14}$$

$$S = \sqrt[3]{\frac{1.64 \times 10^{-14}}{4}} = \sqrt[3]{4.1 \times 10^{-15}} = 1.6 \times 10^{-5}M$$

* In these problems it will be assumed that the data are given for a temperature that does not differ significantly from those for which the required constants are given in Table IV.

c. As was explained earlier, the concentration of OH^- in a saturated solution of $Fe(OH)_2$ is twice the solubility of this compound; *i.e.*,

$$[OH^-] = 2S$$
$$\therefore [OH^-] = 2(1.6 \times 10^{-5}) = 3.2 \times 10^{-5} \text{ mole per liter}$$

Problem 4. If the solubility of Sb_2S_3 is 1.75×10^{-3} g. per liter, what is the solubility-product constant for this compound?

a. The expression for the solubility product of this compound is

$$[Sb^{+++}]^2[S^-]^3 = K_{sp} \tag{46}$$

b Let S be the solubility, in *moles* per liter, of Sb_2S_3. Then the concentration of ions in the saturated solution will be

$$[Sb^{+++}] = 2S$$
$$[S^-] = 3S$$

Substituting these equivalents in the preceding expression, one obtains

$$(2S)^2(3S)^3 = K_{sp}$$
$$\therefore (4S^2)(27S^3) = K_{sp}$$
$$\therefore 108S^5 = K_{sp}$$

c. In the problem, the solubility of Sb_2S_3 was stated as 1.75×10^{-3} g. per liter, S, however, represents this solubility in *moles* per liter. Consequently, S must be evaluated by dividing 1.75×10^{-3} by the gram-molecular weight of Sb_2S_3, or

$$S = 1.75 \times 10^{-3} \div 339.7 = 5.1 \times 10^{-6} \text{ mole per liter of } Sb_2S_3$$

d. Substituting this value for S in the expression

$$108S^5 = K_{sp}$$

derived above, one obtains

$$108(5.1 \times 10^{-6})^5$$
$$\therefore K_{sp} = 108(3.45 \times 10^{-27})$$
$$= 3.72 \times 10^{-25}$$

Selective Precipitation. If a solution containing $S^=$ is added to a solution containing Cu^{++} and Na^+, the only precipitate that will form is CuS—for CuS is only slightly soluble, while Na_2S is extremely soluble. When the possible products differ as widely in solubility as do these two compounds, such phenomena can be easily predicted. However, suppose the solution contained Cu^{++} and Cd^{++}. The addition of $S^=$ might result in the formation of CuS, of CdS, or of both. for each of these compounds is only slightly soluble. The questions arise, then, "If $S^=$ were added to such a mixture, which would precipitate first, CuS or CdS?" and

"How much (in terms of concentration) of the ion that precipitated first would be left when the other began to precipitate?" The answers to such questions serve as the basis for many separations in qualitative analysis. For example, the Group II cations are precipitated as sulfides, leaving Groups III, IV, and V in solution. Yet later some of the Group III cations are *precipitated as sulfides*, in spite of the fact that these same metals remained in solution while Group II cations were being precipitated from that same solution! Similarly, though $Mg(OH)_2$ is only slightly soluble in water, the solution can be made basic during the precipitation of Groups III and IV without precipitating any $Mg(OH)_2$!

The success of these procedures depends upon differences in the solubility-product relationships and constants for the slightly soluble compounds involved. For example, consider a solution that is 0.1*M* with Cu^{++}, Cd^{++}, Fe^{++}, and Zn^{++}. Of these, the Cu^{++} requires the lowest concentration of $S^{=}$ for precipitation to start; the Cd^{++} is next; and the Zn^{++}, next; while the Fe^{++} requires the highest concentration of $S^{=}$ to initiate precipitation. Consequently, if a solution containing $S^{=}$ were added, little by little, to this solution (the mixture being stirred, allowed to stand until equilibrium was attained, and filtered after each addition), black CuS ($K_{sp} = 10^{-42}$) would be the only product at first; then when the concentration of Cu^{++} became sufficiently low, yellow CdS ($K_{sp} = 10^{-29}$) would form. When the Cd^{++}, in turn, was reduced to a sufficiently low concentration, white ZnS ($K_{sp} = 1.2 \times 10^{-23}$) would form; and finally, when much of the Zn^{++} was gone, black FeS ($K_{sp} = 10^{-19}$) would precipitate.

Such differences in the concentration of $S^{=}$ required to precipitate the sulfides of the different metals make it possible to precipitate certain metals and leave others in solution. This is essentially what is done in precipitating Group II while leaving Group III in solution. The method of control of the $S^{=}$ concentration will be discussed in the chapter on Hydrogen Sulfide, but typical mathematical relationships among representative cations and anions can be considered here.

Problem 5. Suppose that a solution of $AgNO_3$ were added to a solution that is 0.1*M* with $CrO_4^{=}$ and 0.1*M* with Cl^{-}. (*a*) Which would precipitate first, Ag_2CrO_4 or AgCl? (*b*) What would be the concentration of the first anion which precipitated, at the moment the other anion starts to precipitate?

a. If the concentration of Ag^+ needed to make the ion product, $[Ag^+][Cl^-]$, equal to the K_{sp} for AgCl is compared with the concentration of Ag^+ needed to make the ion product, $[Ag^+]^2[CrO_4^=]$, equal to the K_{sp} for Ag_2CrO_4, the *smaller value obtained* will be for the compound that will precipitate first. Since the concentration of $CrO_4^=$ is $0.1M$, the necessary concentration of Ag^+ for the Ag_2CrO_4 can be calculated as follows:

$$[Ag^+]^2[CrO_4^=] = K_{sp} \tag{43}$$
$$\therefore [Ag^+]^2(0.1) = 3.3 \times 10^{-12}$$
$$\therefore [Ag^+] = \sqrt{\frac{3.3 \times 10^{-12}}{10^{-1}}} = \sqrt{33 \times 10^{-12}} = 5.74 \times 10^{-6}M$$

The Ag^+ needed for the AgCl is calculated as follows:

$$[Ag^+][Cl^-] = K_{sp} \tag{40}$$
$$\therefore [Ag^+](0.1) = 1.6 \times 10^{-10}$$
$$\therefore [Ag^+] = \frac{1.6 \times 10^{-10}}{10^{-1}} = 1.6 \times 10^{-9}M$$

Since only 1.6×10^{-9} mole per liter of Ag^+ is required to make the solution saturated with respect to Ag^+ and Cl^-, whereas 5.7×10^{-6} mole per liter would be required to saturated it with respect to Ag^+ and $CrO_4^=$, the AgCl will precipitate first.

b. The calculations given above showed that the first substance to precipitate is AgCl. As more Ag^+ is added, more AgCl will precipitate, but as this happens, the concentration of Cl^- will decrease and that of Ag^+ will increase. Eventually, the Ag^+ will have increased until the ion product, $[Ag^+]^2[CrO_4^=]$, very slightly exceeds the K_{sp} for Ag_2CrO_4. Part (*b*) of this problem asks what the concentration of Cl^- will be at this moment. Now when both compounds are precipitating, *the solubility-product relationships for both must be satisfied*, for the solution is saturated with respect to both. However, only an insignificant quantity of the $CrO_4^=$ has yet been precipitated, consequently, its concentration may still be considered $0.1M$. The concentration of Cl^- remaining can be calculated, then, in either of two ways:

(1) The concentration of Ag^+ needed for the solution to be saturated with respect to Ag^+ and $CrO_4^=$ was calculated in (*a*) and was found to be $5.7 \times 10^{-6}M$. But this same Ag^+ controls the Cl^- concentration. Therefore, the latter may be calculated by substituting this concentration for the Ag^+ in the expression

$$[Ag^+][Cl^-] = K_{sp}$$
$$\therefore (5.74 \times 10^{-6})[Cl^-] = 1.6 \times 10^{-10}$$
$$\therefore [Cl^-] = \frac{1.6 \times 10^{-10}}{5.47 \times 10^{-6}} = 2.75 \times 10^{-5}M$$

(2) Since the solution is saturated with respect to the ions of both compounds, both of the following hold true:

$$[Ag^+]^2[CrO_4^=] = K_{sp} = 3.3 \times 10^{-12}$$
$$[Ag^+][Cl^-] = K_{sp} = 1.6 \times 10^{-10}$$

Now since *both are in the same solution*, $[Ag^+]$ *is exactly the same for both expressions.* Consequently, it may be eliminated from consideration as follows:

$$[Ag^+][Cl^-] = 1.6 \times 10^{-10}$$

$$\therefore [Ag^+]^2[Cl^-]^2 = (1.6 \times 10^{-10})^2 = 2.56 \times 10^{-20}$$

$$\therefore \frac{[Ag^+]^2[Cl^-]^2}{[Ag^+]^2[CrO_4^-]} = \frac{2.56 \times 10^{-20}}{3.3 \times 10^{-12}} = 7.7 \times 10^{-9}$$

$$\therefore \frac{[Cl^-]^2}{[CrO_4^-]} = 7.7 \times 10^{-9}$$

But the CrO_4^- has a concentration of 0.1 mole per liter. Substituting this in the foregoing, one obtains

$$\frac{[Cl^-]^2}{0.1} = 7.7 \times 10^{-9}$$

$$\therefore [Cl^-] = \sqrt{7.7 \times 10^{-10}} = 2.7 \times 10^{-5} \text{ mole per liter}$$

SUMMARY

Heterogeneous reactions are those between substances in different phases. The rates of such reactions are dependent upon temperature, catalysts, and concentration, as are other reactions, and also upon the *amount of surface* and the *rate of diffusion.*

Heterogeneous equilibriums are affected by the same factors as are other chemical equilibriums. The point of equilibrium is independent of surface, since both reactions are affected equally by the amount of surface.

Saturated solutions of electrolytes of limited solubility are examples of heterogeneous equilibriums. Some of the solute can be forced from such solutions by adding *a high concentration* of any very soluble strong electrolyte that has an ion in common with the solute. As this precipitation occurs, the concentration of the second ion is thereby diminished. This phenomenon is an example of the *common ion effect.*

As is predicted from Le Chatelier's principle, increasing the temperature increases the solubilities of those substances whose heats of solution are negative, *i.e.*, which absorb heat while dissolving. Similarly, diminishing the concentration of either the cation or the anion of any electrolyte in its saturated solution will cause some of any excess solute to dissolve. Slightly soluble electrolytes may thus be dissolved by reducing the concentration of the *cations* in their aqueous solution by forming either *complex ions* or weak electrolytes, or they may be dissolved by reducing

the concentration of the *anions*. Some metals form hydroxides that are only slightly soluble in water but are soluble in either acids or strong bases Such hydroxides are said to be *amphoteric*. These and other slightly soluble *hydroxides* may be dissolved in acids, owing to the formation of water. *Carbonates* are soluble in acids, owing to the formation of slightly ionized bicarbonate ions and carbonic acid and owing to the decomposition of the latter to form carbon dioxide gas. Some *sulfides* are soluble in strong acids with the formation of hydrogen sulfide; for others, the $S^{=}$ must be oxidized. *Chromates* dissolve in acids, owing to the formation of $Cr_2O_7^{=}$ from the $CrO_4^{=}$, or they may dissolve by the action of reducing agents which convert $CrO_4^{=}$ to Cr^{+++}. The *salts of weak acids* may often be dissolved by the action of strong acids, the concentration of the anion being reduced by the formation of molecules of the weak acid.

The concentrations of the ions in a saturated solution of any slightly soluble electrolyte are related to each other mathematically by means of the *solubility-product* expression for the compound involved. For any slightly soluble electrolyte, M_yX_z, the solubility-product relationship states that the ion product $[M]^y[X]^z$ equals the solubility-product constant for the compound when the solution is saturated with respect to its ions. The constant for any given compound varies with changes in (1) temperature, (2) solvent, and (3) total ion concentration. The last effect is another illustration of the *salt effect*.

Solubility-product relationships enable one to make many predictions. To *precipitate* a given slightly soluble electrolyte, the ion concentrations must be increased until the ion product is greater, momentarily at least, than the solubility-product constant for the compound. *To dissolve* such a compound, the ion product must be reduced to a value less than that of the solubility-product constant.

When two kinds of ions are present in the same solution, and a reagent is added that is capable of precipitating both, that compound which will reduce the concentration of the reagent the most completely will be the first to precipitate.

Review Questions

1. Explain what is meant by: (*a*) heterogeneous reactions, (*b*) phases, (*c*) common ion effect, (*d*) amphoteric hydroxides (illustrate by equations).

2. What factors affect the rate of heterogeneous reaction?

3. What influence does each of the factors mentioned in (2) have upon the point of equilibrium in a heterogeneous system?

4. Explain in detail what would be expected to happen if a saturated solution of calcium sulfate were treated with a saturated solution of (*a*) potassium sulfate or (*b*) calcium chloride. Give reasons for each prediction.

5. What general methods may be employed to dissolve slightly soluble electrolytes? Illustrate by means of ionic equations.

6. What methods may be used to reduce the concentration of a cation in the solution of a salt of that cation?

7. By means of equations explain how slightly soluble compounds of the following anions may be dissolved: (*a*) hydroxides, (*b*) carbonates, (*c*) chromates, (*d*) sulfides, (*e*) phosphates.

8. Using ionic equilibrium equations as aids, explain why

(*a*) $CaCO_3$ dissolves in dilute acetic acid.

(*b*) ZnS dissolves in dilute HCl.

(*c*) CaC_2O_4 dissolves in HNO_3. (HINT: $H_2C_2O_4$ is a weak electrolyte.)

(*d*) $Cu(OH)_2$ dissolves in excess NH_4OH.

(*e*) $PbSO_4$ dissolves in saturated ammonium acetate.

9. List six metals whose hydroxides are amphoteric.

10. List six metals capable of forming complex ions with ammonia, and give the formulas for these complex ions.

11. Give equations showing the formation of three complex *anions* in which metals appear.

12. Write the solubility-product expressions for the following:

(*a*) Ag_2CO_3.	(*b*) $Mg_3(PO_4)_2$.	(*c*) As_2S_5.
(*d*) $MgNH_4PO_4$.	(*e*) $ZnCO_3$.	(*f*) $AlPO_4$.

13. What conditions are necessary for the precipitation of any slightly soluble electrolyte from solution? For the dissolving of any slightly soluble electrolyte?

14. In terms of the relative magnitudes of the ion product and the solubility product, explain why

(*a*) AgCl precipitates when $0.01M$ $AgNO_3$ is added to a $0.001M$ HCl solution.

(*b*) AgCl does not precipitate when just enough $AgNO_3$ and HCl are added to water to give a solution that is $10^{-5}M$ with Ag^+ and $10^{-7}M$ with Cl^-.

(*c*) Ag_2CrO_4 does not precipitate when a solution is made $10^{-3}M$ with Ag^+ and 10^{-7} with $CrO_4^=$.

(*d*) $Fe(OH)_2$ is soluble in HCl.

15. Explain why AgI precipitates before AgCl does if $AgNO_3$ solution is added little by little to a solution that is $0.1M$ with Cl^- and $0.1M$ with I^-.

Problems

1. A solution is $0.1M$ with $Pb(NO_3)_2$, $0.2M$ with $Fe(NO_3)_2$, and $0.1M$ with $Mn(NO_3)_2$. If H_2S is passed into the solution until no more precipi-

tate forms and until the sulfide ion concentration in the solution at the end is 10^{-22} mole per liter, which of the metal sulfides will have precipitated? What will be the concentration of each metal ion in the final solution?

2. The solubility of $CaCrO_4$ is 14.1 g. per liter. Calculate its solubility-product constant.

Answer: 8.1×10^{-4}

3. The solubility of SrC_2O_4 is 0.05 g per liter. Calculate its solubility-product constant

4. The solubility of $Ca_3(PO_4)_2$ is 0 03 g. per liter. What is its solubility-product constant?

5. The solubility of $MgNH_4PO_4$ is 0.52 g. per liter. What is its solubility-product constant?

6. From the solubility-product constants of the following substances, calculate their solubilities in (1) moles per liter, (2) grams per liter, and (3) grams per 100 ml :

(*a*) $BaCO_3$ (*b*) CaF_2. (*c*) $PbSO_4$.
(*d*) Ag_2S. (*e*) $Mg(OH)_2$. (*f*) Ag_2CrO_4.

Answers: (*a*) $9 \times 10^{-5}M$; $1\ 8 \times 10^{-2}$ g per liter; 1.8×10^{-3} g. per 100 ml (*b*) $2\ 1 \times 10^{-4}M$, $1\ 6 \times 10^{-2}$ g per liter; 1.6×10^{-3} g per 100 ml

7. From calculations using the solubility-product constants of AgI, AgBr, Ag_2CO_3, Ag_2CrO_4, and AgCN, list these compounds in the order of decreasing concentrations of Ag^+ needed to precipitate the compounds from 0 $1M$ solutions of I^-, Br^-, $CO_3^=$, $CrO_4^=$, and CN^-.

8. What is the minimum concentration of

(*a*) Ag^+ that would precipitate Ag_2CO_3 from a solution that is 0 $002M$ with $CO_3^=$?

(*b*) $CO_3^=$ that would precipitate $MgCO_3$ from a solution that is $0.0003M$ with Mg^{++}?

(*c*) OH^- that would precipitate $Fe(OH)_3$ from a solution that is $0.005M$ with Fe^{+++}?

Answer. (*a*) $6\ 4 \times 10^{-5}M$.

9. What is the concentration of

(*a*) $S^=$ in a saturated solution of CuS in water?

(*b*) $S^=$ in a saturated solution of PbS?

(*c*) OH^- in a saturated solution of $Mg(OH)_2$?

(*d*) $CrO_4^=$ in a saturated solution of Ag_2CrO_4?

Answers: (*a*) 10^{-21} mole per liter. (*c*) $3\ 4 \times 10^{-4}$ mole per liter.

10. What concentration of NH_4OH would be required just to begin to precipitate:

(*a*) $Mg(OH)_2$ from $0.01M$ $MgCl_2$?

(*b*) $Fe(OH)_3$ from 0 $005M$ $FeCl_3$?

(*c*) $Fe(OH)_2$ from $0.005M$ $FeSO_4$?

Answer. (*a*) $1.1 \times 10^{-5}M$.

11. What concentration of NH_4Cl would be needed just to prevent the precipitation of·

(*a*) $Mg(OH)_2$ from a solution that is $0.01M$ with Mg^{++} and $0.1M$ with NH_4OH?

(*b*) $Fe(OH)_2$ from a solution that is $0.05M$ with Fe^{++} and $0.02M$ with NH_4OH?

(*c*) $Fe(OH)_3$ from a solution that is $0.001M$ with Fe^{+++} and $0.01M$ with NH_4OH?

Answer: (*a*) $4.02 \times 10^{-2}M$.

CHAPTER VI

HYDROGEN SULFIDE AND METAL SULFIDES

Although there are procedures for qualitative analysis that make no use of hydrogen sulfide, in those which are most frequently employed this substances is one of the most important reagents. Since the intelligent use of any substance depends upon a thorough understanding of its properties, it is well to review some of the properties of hydrogen sulfide and of its aqueous solution, *hydrosulfuric acid*, as well as of its salts.

Hydrogen sulfide is a colorless gas, of very disagreeable odor, and of only moderate solubility in water (its saturated solution is about 0.1*M*, at 1 atm. pressure). The gas is very poisonous, being fatal even in dilutions of 1 part in 2000 by weight. Hydrogen sulfide is a powerful reducing agent, whether in the gaseous state or in aqueous solution. Solutions of hydrogen sulfide are readily oxidized by oxygen of the air to form sulfur:

$$2H_2S + O_2 \rightarrow 2H_2O + 2S$$

With more powerful oxidizing agents such as nitric acid or aqua regia, sulfur or sulfuric acid is formed. Typical reactions are

$$3H_2S + 2H^+ + 2NO_3^- \rightarrow 3S + 2NO + 4H_2O$$
$$3H_2S + 2H^+ + 8NO_3^- \rightarrow 3SO_4^{=} + 8NO + 4H_2O$$

Besides its action as a reducing agent, hydrosulfuric acid is a very weak acid. Being dibasic, it ionizes in two steps:

$$H_2S \rightleftharpoons H^+ + HS^-$$
$$HS^- \rightleftharpoons H^+ + S^=$$

Although the concentration of $S^=$ furnished by H_2S in aqueous solutions is very low, this $S^=$ is important, since many cations are capable of reacting with it to form only slightly soluble sulfides; consequently, hydrogen sulfide is important in analysis as a precipitating reagent.

Since aqueous solutions of hydrogen sulfide are acidic, hydrogen sulfide reacts with bases to form salts. Thus in Cation Group III when hydrogen sulfide is passed into the buffered ammoniacal solution, the following reaction occurs:

$$H_2S + 2NH_4OH \rightleftharpoons 2NH_4^+ + S^= + 2H_2O$$

The resulting solution is the same as a solution of ammonium monosulfide, $(NH_4)_2S$.

Mathematical Relationships. Hydrogen sulfide is unique in that its low solubility permits its treatment as a slightly soluble electrolyte to which solubility-product principles may, within limits, be applied, while it may also be treated in the usual way as a weak electrolyte. To treat hydrosulfuric acid as a weak electrolyte, use is made of the equilibrium relationships

$$\frac{[H^+][HS^-]}{[H_2S]} = K_1 \tag{1}$$

$$\frac{[H^+][S^=]}{[HS^-]} = K_2 \tag{2}$$

in which K_1 is 9×10^{-8} and K_2 is 1×10^{-15} at 18°C. Since both these equilibriums must be satisfied in any solution of hydrosulfuric acid, $[HS^-]$, which is the most difficult term to evaluate, is the same for both. Rearranging the expression for K_2, one obtains

$$[HS^-] = \frac{[H^+][S^=]}{K_2} \tag{3}$$

By substituting this value for HS^- in the expression for K_1, and rearranging, the following may be obtained:

$$\frac{[H^+][H^+][S^=]}{[H_2S](K_2)} = K_1$$

$$\therefore \frac{[H^+]^2[S^=]}{[H_2S]} = K_1 \times K_2 \tag{4}$$

Now for solutions in which the concentrations of any two of the terms, $[H^+]$, $[S^=]$, and $[H_2S]$, are known, the concentration of the third term can readily be calculated from equation (4). Since the second step in the ionization is much more difficult than the first, however, the concentration of H^+ in hydrosulfuric acid is *not*

twice that of the $S^=$ as would be true if the H_2S were completely ionized. Consequently, the concentration of H^+ or of $S^=$ in a solution of H_2S in pure water cannot be calculated directly from equation (4). An approximate value for $[H^+]$ can be derived from equation (1), however, by assuming that the second step in the ionization, *i.e.*, the ionization of HS^-, is so slight in comparison to the first that it may be disregarded. The H_2S may then be treated as a monobasic acid ionizing according to the equation

$$H_2S \rightleftharpoons H^+ + HS^-$$

in which case, with no other sources of H^+ or HS^- present, $[H^+]$ and $[HS^-]$ may be considered equal to each other. Mathematically, equation (1) would then become

$$\frac{[H^+][H^+]}{[H_2S]} = K_1$$

$$\frac{[H^+]^2}{[H_2S]} = 9 \times 10^{-8} \tag{5}$$

Then if the concentration of H_2S is known, $[H^+]$ can be calculated. By calculating the approximate value of $[H^+]$ in this way, and then substituting this value for $[H^+]$ in equation (4), a useful approximation of the concentration of $S^=$ can be calculated for solutions of H_2S in pure water.

Problem 1. What is the H^+ concentration in a solution that is $0.03M$ with H_2S?

To solve this equation, disregard the secondary ionization and treat the solution as if H_2S were a monobasic acid. The following equation [equation (1)] will then apply:

$$\frac{[H^+][HS^-]}{[H_2S]} = 9 \times 10^{-8}$$

Since no other significant source of either H^+ or HS^- is present, $[H^+]$ equals $[HS^-]$; consequently,

$$\frac{[H^+][H^+]}{[H_2S]} = 9 \times 10^{-8}$$

$$\therefore \frac{[H^+]^2}{0.03} = 9 \times 10^{-8}$$

$$\therefore [H^+] = \sqrt{0.27 \times 10^{-8}} = \sqrt{27 \times 10^{-10}} = 5.2 \times 10^{-5} M$$

Problem 2. What is the $S^=$ concentration in a solution that is $0.02M$ with H_2S?

a. First calculate the approximate $[H^+]$ as was done in Problem 1.

$$\frac{[H^+]^2}{0.02} = 9 \times 10^{-8}$$

$$\therefore [H^+] = \sqrt{0.18 \times 10^{-8}} = \sqrt{18 \times 10^{-10}} = 4.24 \times 10^{-5} M$$

b. Since $[H^+]$, $[H_2S]$, and K_1 and K_2 are now known, $[S^=]$ can be calculated using equation (4):

$$\frac{[H^+]^2[S^=]}{[H_2S]} = (9 \times 10^{-8})(1 \times 10^{-15})$$

$$\frac{(4.23 \times 10^{-5})^2[S^=]}{0.02} = 9 \times 10^{-23}$$

$$\therefore [S^=] = \frac{0.18 \times 10^{-23}}{18 \times 10^{-10}} = \frac{18 \times 10^{-25}}{18 \times 10^{-10}} = 1 \times 10^{-15} M^*$$

As mentioned earlier, if a solution is saturated with H_2S, it can be treated, within limits, as a solution of a slightly soluble substance. In the equation

$$\frac{[H^+]^2[S^=]}{[H_2S]} = K_1 \times K_2 \tag{4}$$

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* Note that the number of moles of $S^=$ per liter in this solution is numerically equal to K_2 for the ionization of H_2S. This is not by chance, because it can be shown that for any dibasic acid whose K_2 is sufficiently small, the molar concentration of the normal anion of the acid is approximately numerically equal to K_2 for the acid. The reasoning is as follows:

Consider the dibasic acid, H_2CO_3, as typical. The ionization of this acid will occur in two steps,

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^=$$

from which are obtained the equations

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3]} = K_1 \tag{a}$$

$$\frac{[H^+][CO_3^=]}{[HCO_3^-]} = K_2 \tag{b}$$

Mathematically, then, the following will be true:

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3]} \times \frac{[H^+][CO_3^=]}{[HCO_3^-]} = K_1 \times K_2 \tag{c}$$

$$\therefore \frac{[H^+]^2[CO_3^=]}{[H_2CO_3]} = K_1K_2$$

In deriving this equation, no assumptions were made; the equation will, therefore, apply to any solution containing $CO_3^=$, H^+, and H_2CO_3. Now, in solutions containing nothing but this equilibrium mixture in pure water, if

for a solution that is saturated with hydrogen sulfide at a pressure of 1 atm., $[H_2S]$ is very close to $0.1M$. For most solutions this value does not change markedly, even though small quantities of other electrolytes are present, as long as equilibrium has been established between the gaseous and the dissolved H_2S. Consequently, for such solutions the expression may be modified as follows:

$$\frac{[H^+]^2[S^=]}{0.1} = (9 \times 10^{-8})(1 \times 10^{-15})$$

$$\therefore [H^+]^2[S^=] = 0.9 \times 10^{-23} \qquad (6)$$

For most purposes it is sufficiently accurate to use 1×10^{-23} for this constant instead of 0.9×10^{-23}.

The last equation is subject to the same limitations as equation (4), except that in addition equation (6) *applies only to saturated solutions* and the term $[H_2S]$ does not appear in it.

Problem 3. A $0.3N$ solution of HCl is saturated with H_2S at 1 atm. pressure. What is the $S^=$ concentration in the solution?

a. Since HCl is completely ionized, the minute quantity of H^+ from the H_2S may be disregarded and all the H^+ may be considered as coming from the HCl. $[H^+]$ will, therefore, be $0.3M$.

b Since $[H^+]$ is now known and the constants for H_2S are known, $[S^=]$ may be calculated from equation (6):

$$[H^+]^2[S^=] = 9 \times 10^{-24}$$

$$\therefore (0.3)^2[S^=] = 9 \times 10^{-24}$$

$$\therefore [S^=] = \frac{9 \times 10^{-24}}{9 \times 10^{-2}} = 1 \times 10^{-22} \text{ mole per liter}$$

Applications to Analysis. In qualitative analysis, the precipitation of the cations of Group II and some of Group III depends

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it is assumed that the secondary ionization is negligible, $[H^+]$ will equal $[HCO_3^-]$ and equation (*a*) can be simplified to

$$\frac{[H^+]^2}{[H_2CO_3]} = K_1 \qquad (d)$$

Finally, by dividing equation (*d*) into equation (*c*), one obtains the expression

$$\frac{\cancel{[H^+]^2}[CO_3^=]}{\cancel{[H_2CO_3]}} \times \frac{\cancel{[H_2CO_3]}}{\cancel{[H^+]^2}} = \frac{K_1K_2}{K_1}$$

$$\therefore [CO_3^=] = K_2$$

Similar results are obtained with other dibasic acids whose K_1 and K_2 are of the proper relative magnitudes.

upon the low solubilities of their sulfides. To precipitate the members of Group II, the solution is adjusted to a concentration of H^+ equivalent to that of $0.3N$ hydrochloric acid and then the solution is saturated with hydrogen sulfide. This brings down the sulfides of only Group II, leaving the Group III cations in solution. Next, the solution is made basic with a buffered solution of ammonium hydroxide, and again it is saturated with hydrogen sulfide to precipitate Group III cations.

The reason can readily be shown why the sulfides of the Group II cations will precipitate from a solution $0.3N$ with hydrochloric acid whereas those of Group III will not. In Problem 3 given above, the $S^=$ concentration in a solution $0.3N$ with hydrochloric acid and saturated with H_2S was shown to be $1 \times 10^{-22}M$. Now, one of the most soluble—and, therefore, the most difficult to precipitate—sulfides of the Group II cations is that of cadmium. The solubility-product expression for CdS is

$$[Cd^{++}][S^=] = 1 \times 10^{-29}$$

If the $S^=$ is 1×10^{-22} molar when precipitation is complete, *i.e.*, when the solution is *saturated* with hydrogen sulfide, the concentration of the Cd^{++} left in the solution will be

$$[Cd^{++}](1 \times 10^{-22}) = 1 \times 10^{-29}$$
$$\therefore [Cd^{++}] = 1 \times 10^{-7} \text{ mole per liter}$$

On the other hand, consider manganese, which is in Group III. Substituting the same value for $[S^=]$ in the solubility-product expression for MnS yields

$$[Mn^{++}](1 \times 10^{-22}) = 1 \times 10^{-15}$$
$$\therefore [Mn^{++}] = 1 \times 10^{+7} = 10{,}000{,}000M$$

Since this is an impossibly high concentration, it is obvious that MnS cannot be precipitated from any obtainable solution in which the H^+ concentration is as great as $0.3N$.

However, let us consider a *basic* solution saturated with H_2S. As will be seen in the next chapter, even basic solutions contain some H^+; and according to equation (6), the H^+ concentration controls the $S^=$ concentration. In a solution that is $10^{-5}M$ with OH^-, the concentration of H^+ is 10^{-9} mole per liter. If this value

is used, the concentration of $S^{=}$ in such a basic solution is obtainable from the equation

$$[H^+]^2[S^{=}] = 9 \times 10^{-24}$$

$$\therefore [S^{=}] = \frac{9 \times 10^{-24}}{1 \times 10^{-18}} = 9 \times 10^{-6} \text{ mole per liter}$$

Now suppose that one calculates the maximum concentration of Mn^{++} that could remain, at equilibrium, in such a solvent:

$$[Mn^{++}][S^{=}] = 1 \times 10^{-15}$$

$$\therefore [Mn^{++}](9 \times 10^{-6}) = 1 \times 10^{-15}$$

$$\therefore [Mn^{++}] = \frac{1 \times 10^{-15}}{9 \times 10^{-6}} = 1.1 \times 10^{-10} \text{ mole per liter}$$

Consequently, MnS can be precipitated satisfactorily from even slightly basic solutions.

It will be noted, therefore, that an *increase* in $[H^+]$ *decreases* $[S^{=}]$ markedly whereas a decrease in $[H^+]$ increases $[S^{=}]$ in any solution saturated with hydrogen sulfide. In other words, a basic solution saturated with hydrogen sulfide will have a much higher concentration of $S^{=}$. Since cations vary as to the concentration of $S^{=}$ needed for their effective precipitation as sulfides, it is possible selectively to precipitate less soluble sulfides and leave the more soluble ones in solution, by careful adjustment of the H^+ concentration followed by saturation with H_2S.

These same principles can be applied to the dissolving of precipitates consisting of the metal sulfides. Suppose that a solution $0.1M$ with hydrochloric acid is added to a precipitate of ferrous sulfide. In contact with any aqueous solution, some ferrous sulfide dissolves, as represented by the equilibrium

$$FeS_{(solid)} \rightleftharpoons Fe^{++} + S^{=}$$

Some of the H^+ from the HCl, however, reacts with some of the $S^{=}$ to establish the equilibrium

$$2H^+ + S^{=} \rightleftharpoons H_2S$$

If the $[H^+]$ from the HCl is maintained at 0.1 mole per liter, this last equilibrium permits a *maximum* $S^{=}$ concentration of

$$[H^+]^2[S^{=}] = 9 \times 10^{-24}$$

$$\therefore (0.1)^2[S^{=}] = 9 \times 10^{-24}$$

$$\therefore [S^{=}] = \frac{9 \times 10^{-24}}{10^{-2}} = 9 \times 10^{-22} \text{ mole per liter}$$

Now substituting this value for $S^{=}$ in the solubility-product expression for FeS,

$$[Fe^{++}][S^{=}] = 1 \times 10^{-19}$$
$$\therefore [Fe^{++}] = \frac{1 \times 10^{-19}}{9 \times 10^{-22}} = 0.111 \times 10^{3} = 111M$$

This means that, with $[H^{+}]$ as great as $0.1M$, the $S^{=}$ concentration will be so low that the ion product, $[Fe^{++}][S^{=}]$, must be well below the value for the K_{sp} for this compound. Consequently, solid ferrous sulfide will dissolve* in $0.1N$ hydrochloric acid.

Applying the same values for H^{+}—and therefore, for $S^{=}$—to a precipitate of cadmium sulfide, one finds that

$$[Cd^{++}][S^{=}] = 1 \times 10^{-29}$$
$$\therefore [Cd^{++}](9 \times 10^{-22}) = 1 \times 10^{-29}$$
$$[Cd^{++}] = 1.1 \times 10^{-8} \text{ mole per liter}$$

In other words, cadmium sulfide will dissolve only until the concentration of Cd^{++} equals $1.1 \times 10^{-8}M$. Consequently, cadmium sulfide will not dissolve to any significant extent† in cold $0.1M$ HCl.

When the solubility-product constant for a metal sulfide is too small to permit the dissolving of the sulfide by adding H^{+}, other

* There are some sulfides, such as NiS and CoS, that, if properly prepared, dissolve but slowly in even $1N$ HCl, though these sulfides are really soluble in such a solution and cannot be precipitated from it. The question is one of *rate* of solution rather than of actual solubility, since in time such precipitates will finally dissolve. This difference in rates of solution is sometimes used as an analytical device in separating nickel and cobalt from more rapidly dissolved sulfides such as those of manganese and zinc.

† It is possible to dissolve CdS in $3N$ HCl, however, especially when the solution is heated. This cannot be shown accurately by calculations using actual ion concentrations, however, as other factors such as the salt effect and complex ion formation are far too pronounced to permit useful approximations in such calculations. Even in $0.1M$ HCl the actual solubility of CdS is somewhat greater than that calculated above.

Some sulfides, such as that of copper, are soluble in concentrated solutions of HCl, even though their solubility-product constants are so small that the removal of $S^{=}$ by the action of H^{+} could not possibly account for such an occurrence. This is usually due to the fact that the *cation* is also being reduced in concentration by the formation of complex ions such as $CuCl_4^{=}$. The binary halogen acids are notable for their ability to form complex ions with many metals.

devices are used. Most of such sulfides are readily soluble in nitric acid owing to oxidation of the $S^=$ to S^0 or $SO_4^=$. For example, cupric sulfide, in contact with any aqueous solution, tends to establish the equilibrium

$$CuS_{(solid)} \rightleftharpoons Cu^{++} + S^=$$

Nitric acid, however, is a powerful oxidizing agent. With a solution containing $S^=$, therefore, dilute nitric acid reacts chiefly as shown in the following two equations:

$$3S^= + 8H^+ + 2NO_3^- \rightarrow 3S^0 + 4H_2O + 2NO$$
$$3S^= + 8H^+ + 8NO_3^- \rightarrow 3SO_4^= + 4H_2O + 8NO$$

With more concentrated HNO_3, the following two reactions probably predominate, though some of the action is as given above:

$$S^= + 4H^+ + 2NO_3^- \rightarrow S^0 + 2H_2O + 2NO_2$$
$$S^= + 8H^+ + 8NO_3^- \rightarrow SO_4^= + 4H_2O + 8NO_2$$

Since any of these reactions reduce the $S^=$ concentration very effectively, most sulfides will dissolve in HNO_3.

Mercuric sulfide, which is one of the least soluble of the sulfides, is attacked but slowly by nitric acid, even when the latter is hot and concentrated. The reaction first produces a white double salt, $Hg(NO_3)_2 \cdot 2HgS$, which slowly dissolves to yield a solution of mercuric nitrate.

Mercuric sulfide is best dissolved by aqua regia,* which is made by mixing nitric and hydrochloric acids and owes most of its activity to the presence of chlorine formed by the reaction

$$3HCl + HNO_3 \rightarrow 2H_2O + NOCl + Cl_2\dagger$$

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* HgS is also readily dissolved by concentrated hydriodic acid, HI. Although this acid is not an oxidizing acid and therefore does not remove $S^=$ effectively enough to dissolve HgS, the Hg^{++} reacts with I^- to form the unusually stable and slightly ionized complex ion, $HgI_4^=$. This reduces the concentration of Hg^{++} and causes the HgS to dissolve. As HgS dissolves, the concentration of $S^=$ increases until it is sufficiently great to cause H_2S to escape from the solution By this reaction the concentration of $S^=$ is not permitted to become greater.

† At the moment it is formed, the chlorine is in the form of *single atoms; i e*, it is *nascent* chlorine. The activity of atomic chlorine is much greater than that of molecular chlorine; consequently, the activity of aqua regia

The action of aqua regia on mercuric sulfide is dual; it not only oxidizes $S^{=}$ to S^0 and to $SO_4^{=}$ but also supplies Cl^- to combine with the Hg^{++} to form the slightly dissociated complex ion, $HgCl_4^{=}$.

The separation of the *subgroups* of Cation Group II depends upon the reaction of certain cations with $S^{=}$ in high concentration to form thio complex ions. Sb^{+++}, for example, reacts with $S^{=}$ in limited concentrations to form slightly soluble Sb_2S_3:

$$2Sb^{+++} + 3S^{=} \rightleftharpoons Sb_2S_{3(solid)}$$

At the higher concentrations of $S^{=}$ present in ammonium sulfide, however, the reaction goes further to form a soluble product:

$$Sb^{+++} + 3S^{=} \rightleftharpoons SbS_3^{\equiv}$$

These reactions will be discussed in greater detail in the chapter on Complex Ions.

Solutions of soluble sulfides such as $(NH_4)_2S$ and Na_2S are capable of reacting with elementary sulfur to form polysulfides:

$$(NH_4)_2S + S \rightarrow (NH_4)_2S_x$$

Such reagents not only exhibit most of the reactions of the monosulfides but also oxidize many readily oxidized cations to higher valence states. For example, stannous sulfide, which is not soluble in ammonium monosulfide, dissolves readily in the polysulfide owing to oxidation of the tin to the stannic state, followed by the formation of the thio complex:

$$SnS + S_x^{=} \rightleftharpoons SnS_3^{=} + S^0$$

SUMMARY

From the standpoint of analytical chemistry, the chief uses of hydrogen sulfide are based on the facts that (1) it is a powerful reducing agent; (2) it is a very weak electrolyte, dissociating in water solution to give $S^{=}$; and (3) it is a gas that is only moderately soluble.

When hydrogen sulfide or hydrosulfuric acid is oxidized by mild oxidizing agents, the $S^{=}$ is converted to free sulfur; with strong oxidizing agents, such as nitric acid or aqua regia, $SO_4^{=}$ as well as free sulfur is formed.

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exceeds that of chlorine water and of many other strong oxidizing agents. For obvious reasons, however, the reagent loses its activity on standing and must be prepared fresh at the time it is used.

Hydrogen sulfide equilibriums may be treated mathematically either as for a *weak dibasic acid* or, within limitations, as for a *slightly soluble electrolyte.* For the latter the solution considered must be saturated. As the H^+ concentration in a solution containing H_2S is decreased, the $S^=$ concentration increases. In basic solutions, the concentration of H^+ is less than it is in acidic or neutral solutions; consequently, although the sulfides of the Group III cations do not precipitate with those of Group II, they *do* precipitate when the solution is made alkaline.

The slightly soluble sulfides are usually dissolved (1) by the addition of acids to remove $S^=$ by forming H_2S, (2) by the use of oxidizing agents to oxidize $S^=$ to free sulfur or to $SO_4^=$, or (3) by the addition of ammonium or sodium sulfide to form thio complex ions in which the metal appears in the anion. The sulfides of those metals which form thio complexes may also be dissolved in polysulfides, the reaction in some cases involving oxidation of the metal to a higher valence by the action of the polysulfide.

Review Questions

1. List the chief properties of hydrogen sulfide and hydrosulfuric acid.

2. What effect would be produced upon the hydrogen ion concentration of a solution by the addition of a soluble sulfide to it?

3. What effect would be produced upon the sulfide ion concentration of a solution by the addition of

a. A strong acid such as HCl or H_2SO_4?

b A base such as NH_4OH or NaOH?

c. A solution containing Cu^{++}?

d. A solution containing Na^+?

4. According to Bronsted's theory of acids and bases, how would $S^=$ be classified? H_2S? HS^-?

5. In terms of the ion product and solubility-product constant, what conditions must be brought about if it is desired to (*a*) precipitate some HgS, (*b*) dissolve some CdS, (*c*) make a solution that is saturated with respect to Ag^+ and $S^=$?

6. By means of ionic equations explain why:

(*a*) PbS dissolves in dilute HNO_3 but HgS does not.

(*b*) CuS dissolves in KCN solution.

(*c*) CoS does not precipitate with Cation Group II, though it does precipitate in Group III

7. What methods may be used to dissolve slightly soluble sulfides? Illustrate by means of ionic equations.

8. Complete the following equations, and indicate by reverse arrows which reactions are appreciably reversible:

(*a*) $Cu^{++} + H_2S \rightarrow$ (*b*) $Bi^{+++} + H_2S \rightarrow$ (*c*) $Fe^{+++} + H_2S \rightarrow$
(*d*) $Cd(NH_3)_4^{++} + H_2S \rightarrow$ (*e*) $S^{=} + HNO_3 \rightarrow$ (*f*) $Sb_2S_3 + S^{=} \rightarrow$

9. From the results of the first three reactions in Question 8 what would you predict as likely to happen to the H^+ concentration in any solution from which metal sulfides are being precipitated by the action of H_2S? Would this cause any difficulty in the precipitation of Cation Groups II and III? Explain.

Problems

1. What is the concentration of $S^=$ in:
a. A saturated solution of H_2S in pure water?
b. A solution that is $0.005M$ with H_2S?
c. A solution that is $0.0025M$ with H_2S?
2. What is the concentration of $S^=$ in a solution:
a. That is $0.1M$ with respect to HCl and saturated with H_2S?
b. That is $10^{-8}M$ with H^+ and saturated with H_2S?
c. That is $0.004M$ with H^+ and saturated with H_2S?
Answer: (*a*) 1×10^{-21} mole per liter.
3. What is the maximum equilibrium concentration of each of the following ions in a solution whose $S^=$ concentration is $10^{-22}M$ (note that this is the approximate concentration of $S^=$ in the solution at the end of the precipitation of Cation Group II):

(*a*) Cu^{++}. (*b*) Ag^+. (*c*) Pb^{++}.
(*d*) Hg^{++}. (*e*) Zn^{++}. (*f*) Ni^{++}.

Answer: (*a*) 10^{-20} mole per liter
4. From the results obtained in Problem 3, under what conditions would it be possible to precipitate ZnS in Group II? Would any Zn^{++} be left in the solution? How much?
5. If a $0.1M$ solution of acetic acid buffered with 0.1 mole per liter of ammonium acetate contains Zn^{++}, Ni^{++}, and Mn^{++}, what is the maximum concentration of each of these three cations that can remain in the solution after it is saturated with H_2S? Could the sulfides of these metals possibly be precipitated from such a solution?
Answer: $[Zn^{++}] = 4.3 \times 10^{-10}$ mole per liter.

CHAPTER VII

IONIZATION OF WATER; HYDROLYSIS

Water and Its Ions. Thus far, water has been regarded largely as a solvent that contributed little in the way of ions to any solutions in which it was the solvent. It has been pointed out a number of times, however, that although water is almost a nonelectrolyte, it does ionize to a very slight extent. Thus, in pure water or in any aqueous solution the water molecules are in equilibrium with their ions:

$$H_2O \rightleftharpoons H^+ + OH^-$$

This equation introduces useful conceptions of conditions existing in aqueous solutions; for it at once becomes apparent that the addition of an acid to water does not remove all OH^- but instead merely decreases its concentration. In the same manner the addition of a base to water decreases the H^+ concentration. If, therefore, very small concentrations of these ions are important, the ionization of water cannot be neglected.

An illustration of the need for considering this equilibrium was involved in the discussion of the previous chapter when the behavior of H_2S in basic solutions was considered. It was pointed out that the concentration of $S^=$ in any aqueous solution was dependent upon the H^+ concentration, the $S^=$ concentration varying inversely as the square of the H^+ concentration. Now if a base is added to water, the H^+ concentration is thereby reduced; consequently, if such a solution contains H_2S, the $S^=$ concentration will be *increased*. For that reason the comparatively soluble sulfides of the Group III cations can be precipitated by the action of H_2S in alkaline solutions.

Other illustrations of the need for considering the ionization of water will be seen in the discussion of hydrolysis, as well as (in the next two chapters) of amphoteric hydroxides and of colloids. To make these subjects of the greatest use to the chemist, however, it is necessary to know the quantitative relationships

involved in the ionization of water; for only through these can accurate predictions be made.

As with other chemical equilibriums, the law of mass action can be applied to the ionization equation for water, the resulting expression being

$$\frac{[H^+][OH^-]}{[H_2O]} = K \tag{1}$$

In pure water the concentration of H_2O may be obtained by dividing the weight of 1 liter of water by the gram-molecular weight of water. Similarly, the concentration of H_2O in an aqueous solution can be calculated by dividing the weight of water in 1 liter of the solution by the gram-molecular weight of water. When such calculations are made, however, the results lead to the extremely useful conclusion that for either pure water or dilute aqueous solutions the concentration of H_2O is not significantly different from 55.5 moles per liter. This means that for dilute solutions, the value of $[H_2O]$ will not change significantly from one solution to another or from pure water to a solution; consequently, equation (1) may be simplified and rearranged to obtain

$$[H^+][OH^-] = K(55.5) \tag{2}$$

Since both K and 55.5 are constants, their mathematical product may be set equal to another constant, K_w, and equation (2) becomes

$$[H^+][OH^-] = K_w \tag{3}$$

The constant, K_w, has been evaluated for water at several temperatures and at 25°C. has been found to be approximately 1×10^{-14}.

In *pure water* the molar concentration of H^+ is, of necessity, equal to that of OH^-, since the only source of either is the water itself, and since one molecule of water yields one H^+ and one OH^- when it ionizes. Consequently, for pure water $[H^+]$ and $[OH^-]$ may be substituted for each other in equation (3) to obtain

$$[H^+]^2 = [OH^-]^2 = K_w \tag{4}$$

$$\therefore [H^+] = [OH^-] = \sqrt{K_w} \tag{5}$$

In pure water at 25°C., therefore, the concentration of H^+ or of OH^- will be 1×10^{-7} mole per liter.

It was pointed out earlier that in *basic* solutions there is, nevertheless, some H^+ and that in acidic solutions there is still some OH^-. In other words, any aqueous solutions will always contain some H^+ and some OH^-. If an acid such as hydrochloric acid is added to pure water at 25°C., *the concentration of* H^+ *is increased* above $1 \times 10^{-7}M$ and that of OH^- is decreased below that concentration. This leads to the accurate definition of a *neutral* solution as one in which *the molar concentrations of* H^+ *and* OH^- *are equal,* of an acid solution as one in which the H^+ concentration is greater than that of the OH^-, and of a basic solution as one in which the OH^- concentration is greater than that of the H^+.

pH and pOH Values. From equation (3) it can be seen that without even mentioning OH^- a knowledge of its concentration can be conveyed. For example, if the concentration of H^+ is known to be 1×10^{-9} mole per liter at 25°C.,* it will be understood that the OH^- concentration of the solution must be 1×10^{-5} mole per liter; for

$$[H^+][OH^-] = 1 \times 10^{-14}$$

$$(1 \times 10^{-9})[OH^-] = 1 \times 10^{-14}$$

$$\therefore [OH^-] = \frac{1 \times 10^{-14}}{1 \times 10^{-9}} = 1 \times 10^{-5} \text{ mole per liter}$$

On the basis of this relationship, it is now customary to speak of the pH of a solution instead of its H^+ or OH^- concentration. The pH of a solution is *the logarithm of the reciprocal of its* H^+ *concentration; i.e.,*

$$\text{pH} = \log \frac{1}{[H^+]} \tag{6}$$

Since the logarithm of the reciprocal of any number is mathematically equal to the negative logarithm of the number,

$$\text{pH} = \log \frac{1}{[H^+]} = -\log [H^+] \tag{7}$$

If the logarithms of both sides of equations (3) are taken, the following expression results:

$$\log [H^+] + \log [OH^-] = \log (1 \times 10^{-14}) = -14 \tag{8}$$

* In the remaining discussion it will be assumed that the temperature is 25°C. Under these conditions, K_w is 1×10^{-14}.

Multiplying both sides of this equation by -1 gives

$$(-\log [H^+]) + (-\log [OH^-]) = +14$$

In this expression, the term $-\log [H^+]$ is the pH of the solution, while $-\log [OH^-]$ is a term known as the pOH of the solution.

Hydrogen ion concentration (moles per liter)	pH	pOH	Hydroxyl ion concentration (moles per liter)
10^{-14}	14	0	1.0
10^{-13}	13	1	0.1
10^{-12}	12	2	0.01
10^{-11}	11	3	0 001
10^{-10}	10	4	0 0001
10^{-9}	9	5	10^{-5}
10^{-8}	8	6	10^{-6}
10^{-7}	7 Neutral	7	10^{-7}
10^{-6}	6	8	10^{-8}
10^{-5}	5	9	10^{-9}
0 0001	4	10	10^{-10}
0.001	3	11	10^{-11}
0.01	2	12	10^{-12}
0.1	1	13	10^{-13}
1.0	0	14	10^{-14}

FIG. 12.—Ion concentrations, pH values, and pOH values.

Consequently this expression becomes

$$\text{pH} + \text{pOH} = 14 \tag{9}$$

Figure 12 shows the relationship between $[H^+]$, and $[OH^-]$, the pH, and the pOH of any solution. It will be recalled from the earlier discussion that in any neutral aqueous solution at 25°C., $[H^+] = [OH^-] = 1 \times 10^{-7}$ mole per liter. Therefore, for such solutions,

$$\text{pH} = \text{pOH} = 7 \tag{10}$$

For *acid solutions*, therefore, the pH must be *less* than 7, and *the smaller the* pH *the greater is the* H^+ *concentration*. Similarly, in *basic solutions* the pH will be *greater* than seven, and the greater the OH^- the greater will be the pH of the solution.

When it is desired to speak of H_3O^+ instead of H^+ in a solution, the same expressions as those given may be used, H_3O^+ being substituted in place of H^+; *e.g.*,

$$[H_3O^+][OH^-] = K_w = 1 \times 10^{-14} \text{ (at } 25^\circ\text{C.)} \qquad (11)$$

The substitution of H_3O^+ for H^+ in any mathematical expression where the latter appears is permissible because H_3O^+ is so stable that any H^+ existing in an aqueous solution may be considered as hydrated. Numerically, then, the molar concentration of H_3O^+ will be equal to the molar concentration that one would have calculated for H^+ if the hydration of the latter had not occurred.

Neutralization: Hydrolysis. When a solution of an acid is mixed with one of a base, a reaction of the type known as *neutralization* takes place. In beginning courses in chemistry it is usually said that the products of neutralization are a salt and water. That such a conception of neutralization is by no means complete, however, is readily seen if the ionic equations for some typical neutralizations are written. Take, for example, the reaction between sodium hydroxide and hydrochloric acid. Both of these compounds are completely ionized; consequently, the sodium hydroxide solution may be considered a solution of Na^+ and OH^-, and the hydrochloric acid, a solution of H^+ and Cl^-. Reaction between these two will be

$$\begin{array}{lll} H^+ & + & Cl^- \\ + & & + \\ OH^- & + & Na^+ \\ \downarrow\uparrow & & \downarrow \\ H_2O & & \text{(no reaction)} \end{array}$$

In other words, this particular neutralization consists of a reaction between H^+ and OH^- only. The Na^+ and Cl^- do not react with each other while in solution, since sodium chloride is itself a strong electrolyte and remains in the form of Na^+ and Cl^-.

Suppose, however, that a solution of a weak acid is mixed with one of a strong base. The type of reaction occurring can be illustrated with acetic acid and sodium hydroxide solution. Again it will be remembered that sodium hydroxide solution is a

solution of Na^+ and OH^-; the acetic acid, on the other hand, is a weak electrolyte and is only partly ionized. Consequently, the reaction between these substances is best represented as follows:

$$\begin{array}{lll} HC_2H_3O_2 \rightleftharpoons H^+ & + & C_2H_3O_2^- \\ & + & + \\ & OH^- & Na^+ \\ & \downarrow\uparrow & \downarrow \\ & H_2O & \text{(no reaction)} \end{array}$$

Again there is a reaction between H^+ and OH^-; but this time, the reaction will not be so complete as before; for since $HC_2H_3O_2$ is a weak electrolyte, some of the H^+ from the water will react with $C_2H_3O_2^-$ to form $HC_2H_3O_2$ molecules.

The consequences of this reversibility are more easily seen if the problem is approached from a different angle. Suppose that some sodium acetate is dissolved in some water. The sodium acetate, which is a strong electrolyte, may be considered as completely ionized, while the water itself ionizes very slightly. The conditions existing in such a solution, therefore, may be represented as follows:

$$\begin{array}{lll} H_2O \rightleftharpoons H^+ & + & OH^- \\ & + & + \\ & C_2H_3O_2^- & + \ Na^+ \\ & \downarrow\uparrow & \downarrow \\ & HC_2H_3O_2 & \text{(no reaction)} \end{array}$$

or

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$$

From this ionic equation it can be seen that some of the H^+ furnished by the ionization of the water is removed by its reaction with $C_2H_3O_2^-$ to form $HC_2H_3O_2$. More of the water will then ionize to furnish more H^+ and OH^-; and as this happens, more H^+ and $C_2H_3O_2^-$ will combine to form $HC_2H_3O_2$. This whole chain of happenings will continue until *both reversible reactions involved are at equilibrium.* When this point is reached, however, it will be seen that though the H^+ concentration has been reduced, *the* OH^- *concentration has increased.* Therefore, the solution will be *slightly basic!*

Such reactions as this between the ions of a salt and those of water are known as *hydrolysis* reactions and are essentially the

reverse of the neutralization reaction needed to produce the salt.

It will be noticed that sodium acetate, which is a salt formed by the reaction of a weak acid with a strong base, hydrolyzes to give a basic solution, *i.e.*, a solution whose pH is greater than seven. If a solution of the salt of a strong acid and a weak base is used, hydrolysis will result in the solution containing more H^+ than OH^-— in other words, the solution will be acidic. The salt of a weak acid and a weak base hydrolyzes in water solutions, but whether the solution will be acidic or basic depends upon which is the more highly ionized, the acid or the base. If the acid ionizes more than does the base, the solution will be acidic; if the base is more highly ionized, the solution will be basic; but if the acid and the base ionize to the same extent, the solution will be neutral. As can be seen from the equation for the reaction between sodium hydroxide and hydrochloric acid, salts of strong acids and strong bases do not ordinarily hydrolyze.

It is often desirable to calculate the hydrolysis constant, K_h, or the degree of hydrolysis, α, of a salt, as well as the H^+ concentration of the resulting solution. This may be done for solutions in which hydrolysis is not greater than 5 per cent by using the following equations,* in which C is the concentration of salt.

Type of salt	K_h	α	$[H^+]$
Weak acid, strong base	$\frac{K_w}{K_a}$	$\sqrt{\frac{K_w}{K_a C}}$	$\sqrt{\frac{K_w K_a}{C}}$
Strong acid, weak base	$\frac{K_w}{K_b}$	$\sqrt{\frac{K_w}{K_b C}}$	$\sqrt{\frac{K_w C}{K_b}}$
Weak acid, weak base	$\frac{K_w}{K_a K_b}$	$\sqrt{\frac{K_w}{K_a K_b}}$	$\sqrt{\frac{K_w K_a}{K_b}}$

The derivation of such equations can be illustrated by considering a solution of sodium cyanide, NaCN. This is a salt of the strong base NaOH and the very weak acid HCN. The salt is completely ionized in water solution, and part of the CN^- reacts with the water as follows:

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

* Salts of only monobasic acids and monacid bases are considered here.

Applying the law of mass action to this equilibrium and making use of the fact that the concentration of H_2O is essentially constant, one obtains

$$\frac{[HCN][OH^-]}{[CN^-][H_2O]} = K, \quad \text{or} \quad \frac{[HCN][OH^-]}{[CN^-]} = K[H_2O] = K_h \tag{12}$$

in which K_h is known as the hydrolysis constant. The hydrolysis constant can be evaluated in terms of K_w and K_a (the ionization constant of the acid) as follows. If the left-hand side of equation (12) is multiplied by the fraction $\frac{[H^+]}{[H^+]}$ the following is obtained:

$$\frac{[H^+]}{[H^+]} \times \frac{[HCN][OH^-]}{[CN^-]} = K_h \tag{13}$$

This can be rearranged to give

$$[H^+][OH^-] \times \frac{[HCN]}{[H^+][CN^-]} = K_h \tag{14}$$

But as was learned earlier,

$$[H^+][OH^-] = K_w \tag{3}$$

Also, from the ionization equation for HCN it can be found that

$$\frac{[HCN]}{[H^+][CN^-]} = \frac{1}{K_a} \tag{15}$$

By substituting K_w and $\frac{1}{K_a}$ for their equivalents [equations (3) and (15)] in equation (14) it is found that

$$\frac{K_w}{K_a} = K_h \tag{16}$$

By comparing equations (12) and (16), one may obtain the equation

$$\frac{[HCN][OH^-]}{[CN^-]} = \frac{K_w}{K_a} \tag{17}$$

From the original equation for the hydrolysis it will be seen that [HCN] is equal to $[OH^-]$; consequently, by substitution,

equation (17) can be changed to the following:

$$\frac{[OH^-]^2}{[CN^-]} = \frac{K_w}{K_a}$$

$$\therefore [OH^-] = \sqrt{\frac{K_w[CN^-]}{K_a}} \qquad (18)$$

Now $[OH^-]$ is numerically equal to the number of moles of CN^- per liter used by the hydrolysis, and the degree of hydrolysis, α, is *approximately* equal to the ratio of the CN^- which combined with H^+, to the CN^- remaining in the solution.*
Consequently, from these two facts, it follows that

$$\alpha = \frac{[OH^-]}{[CN^-]} \qquad (19)$$

Substituting in this equation the expression for $[OH^-]$ as given in equation (18) gives

$$\alpha = \sqrt{\frac{\frac{K_w[CN^-]}{K_a}}{[CN^-]^2}} = \sqrt{\frac{K_w[CN^-]}{K_a[CN^-]^2}} = \sqrt{\frac{K_w}{K_a[CN^-]}} \qquad (20)$$

The hydrogen ion concentration in such a solution can be calculated by using the relationships in equations (3) and (18) as follows:

$$[OH^-] = \frac{K_w}{[H^+]}, \quad \text{and} \quad [OH^-] = \sqrt{\frac{K_w[CN^-]}{K_a}} \qquad (3, 18)$$

$$\therefore \sqrt{\frac{K_w[CN^-]}{K_a}} = \frac{K_w}{[H^+]}$$

$$\therefore [H^+] = \frac{K_w}{\sqrt{\frac{K_w[CN^-]}{K_a}}} = \sqrt{\frac{K_w^2K_a}{K_w[CN^-]}} = \sqrt{\frac{K_wK_a}{[CN^-]}} \qquad (21)$$

In each of these cases, $[CN^-]$ may be considered as equal to the concentration of the CN^- furnished by the salt, the small amount lost by hydrolysis being disregarded.

A study of the formulas in the table reveals the fact that *for any salt of a weak acid and a weak base,* (1) if K_a and K_b are equal,

* The degree of hydrolysis would be *exactly* equal to the ratio of the CN^- used up by the hydrolysis to that used in making the solution.

the solution will be neutral, (2) within limits* imposed by approximations used in the derivation of the foregoing equations, the degree of hydrolysis and the concentration of H^+ are independent of the concentration of the salt, and (3) the degree of hydrolysis is greater for these salts than for the other salts.

If the mechanism of hydrolysis is as described in this discussion, it is apparent that hydrolysis is due to the ability of one or both ions of the salt to remove H^+ or OH^- from the solution. If this is true, then, it is conceivable that *slightly soluble* bases or basic salts, or slightly soluble acids might remove OH^- or H^+ and cause the salts of these bases or acids to hydrolyze, even though the slightly soluble base or acid is a strong electrolyte. Many compounds hydrolyze owing to such reactions. If aluminum sulfide, Al_2S_3, for example, is placed in water, it hydrolyzes completely owing to the facts that $S^=$ is very effective in removing H^+ and also that $Al(OH)_3$ is quite insoluble. The hydrolysis is forced, therefore, by both the anion and cation, the former removing H^+ and the latter removing OH^-. Similarly, ferric chloride hydrolyzes in water solution owing to the formation of ferric hydroxide complexes;† while in nearly neutral solutions of aluminum or ferric compounds to which a fairly high concentration of sodium acetate has been added, hydrolysis will occur to give a precipitate of basic aluminum or ferric acetate.

Although the ionization constants for most weak electrolytes are affected but slightly by temperature, K_w increases greatly with increases in temperature. For this reason, the degree of hydrolysis is always greater at higher temperatures. The hydrolysis of any compound is repressed, however, by the addition of organic compounds such as ethyl alcohol.

There are a number of important consequences of hydrolysis that deserve discussion. One of these is the frequent reduction in the effectiveness of reagents, which often makes modifications

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* The assumption that the concentration of unreacted ion of the salt is equal to the original concentration of the salt, C, is an approximation that disregards the decrease in this value due to loss of ions through hydrolysis. Those equations in which C appears, therefore, do not hold with sufficient accuracy if hydrolysis is greater than about 5 per cent.

† It is believed that, instead of the normal hydroxide, a ferric hydroxide complex of variable formula is produced. At higher temperatures the reaction goes further and yields a hydrated ferric oxide.

in these reagents necessary. Consider, for example, a 0.1*M* solution of sodium sulfide which is being used as a source of $S^{=}$. The sulfide in a 0.1*M* solution of Na_2S is about 98 per cent hydrolyzed; consequently, the actual $S^{=}$ concentration in such a solution is only 0.002*M*. If it is desired to increase the $S^{=}$ in such a solution, some sodium hydroxide or potassium hydroxide must be added to the mixture. The OH^- furnished by either base will repress the hydrolysis, as would be expected from the equation

$$S^{=} + H_2O \rightleftharpoons HS^- + OH^-$$

and thereby increase the concentration of $S^{=}$. In general, an increase in the concentration of any of the products of a hydrolysis will repress the hydrolysis

Frequently the hydrolysis of reagents causes the formation of products entirely different from those ordinarily expected. If, for example, a solution of sodium carbonate is added to a solution containing Cu^{++}, the reaction that one might expect would be

$$Cu^{++} + CO_3^{=} \rightleftharpoons CuCO_{3\,(solid)}$$

Instead, however, a basic carbonate forms. This is a result of the hydrolysis of the sodium carbonate, such hydrolysis resulting in a lower $CO_3^{=}$ concentration and at the same time making the solution definitely basic. The ions of many other heavy metals behave similarly; consequently, to precipitate the normal carbonate, a solution of sodium bicarbonate is often used as the reagent. The $CO_3^{=}$ concentration in such a solution is much less than it is in a solution of sodium carbonate, but hydrolysis is also much less and the OH^- concentration is not sufficiently great to cause a basic salt to form.

Hydrolysis and Bronsted's Theory. Although in the first part of the preceding section, hydrolysis was pictured as the reaction of H^+ or OH^- from water with the ions of a salt, *e.g.*, for ammonium chloride in aqueous solution,

$$\begin{array}{l} H_2O \rightleftharpoons H^+ + OH^- \\ \qquad\qquad\quad + \\ Cl^- + NH_4^+ \\ \qquad\qquad\quad \downarrow\uparrow \\ \qquad\qquad\quad NH_4OH \end{array}$$

the more modern conception is that of a direct reaction of the ions of the salt with *water molecules*. According to Bronsted's

theory, the hydrolysis of an ammonium salt may be considered a reaction in which NH_3 molecules and H_2O molecules are competing for protons. Since the hydronium ion is extremely stable, it is able to take some part in the reaction and the hydrolysis would therefore be represented by the equation

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ *$$

Now, according to Bronsted's conceptions, an acid is a *proton donor* whereas a base is a *proton acceptor.* According to these definitions, it is possible to classify NH_4^+ and H_3O^+ as acids, *e.g* ,

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$
$$H_3O^+ \rightleftharpoons H_2O + H^+$$

whereas in the reverse reactions NH_3 and H_2O may be classified as bases, *e.g.*,

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$
$$H_2O + H^+ \rightleftharpoons H_3O^+$$

Consequently, the hydrolysis reaction is seen to be essentially a reaction between an acid and a base to form an acid and a base:

$$\underset{\text{Acid}}{NH_4^+} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Base}}{NH_3} + \underset{\text{Acid}}{H_3O^+}$$

If the hydrolysis of a salt of a strong base and a weak acid, such as sodium acetate, is considered, a similar situation is found, the water in this case acting as an acid:

$$\underset{\text{Base}}{C_2H_3O_2^-} + \underset{\text{Acid}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{HC_2H_3O_2} + \underset{\text{Base}}{OH^-}$$

Now, suppose that neutralization reactions are considered in a similar manner. The reaction between NaOH and HCl is

$$Na^+ + OH^- + H_3O^+ + Cl^- \rightleftharpoons Na^+ + Cl^- + 2H_2O$$
$$\therefore \underset{\text{Base}}{OH^-} + \underset{\text{Acid}}{H_3O^+} \rightleftharpoons \underset{\text{Acid or base}}{2H_2O}$$

---

* The formation of NH_3 in this reaction is in line with the idea that NH_4OH molecules do not exist in aqueous solutions but that "ammonium hydroxide" solution consists of the equilibrium mixture

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

whereas that between acetic acid and sodium hydroxide would be

$$\underset{\text{Acid}}{HC_2H_3O_2} + \underset{\text{Base}}{OH^-} \rightleftarrows \underset{\text{Base}}{C_2H_3O_2^-} + \underset{\text{Acid}}{H_3O^+}*$$

By comparing the hydrolysis equations with the neutralization equations, it is easy to see that in each case the reaction is of the following type:

$$\text{Acid}_1 + \text{base}_1 \rightleftharpoons \text{acid}_2 + \text{base}_2$$

In other words, from the modern point of view, there is no real difference between neutralization and hydrolysis. It is therefore becoming increasingly customary to speak of both types of reaction as *acid-base reactions*, and to eliminate the use of the older terms. The chief value in retaining the terms *neutralization* and *hydrolysis* lies in the fact that these terms indicate the *direction* of the reaction that is of the most importance to the purpose at hand.

The hydrolysis of salts of metals whose hydroxides are only slightly soluble or are weak electrolytes presents a similar situation. Since a simple metal ion contains no hydrogen, however, it is obvious that if it is to act as a proton donor, some other factor must enter. It is well known that most cations are hydrated to some extent in aqueous solutions. Although cupric ions are usually written as Cu^{++} for the sake of simplicity, actually these ions are hydrated, having the formula $Cu(H_2O)_4^{++}$. Similarly, zinc compounds in solution give $Zn(H_2O)_4^{++}$. As a rule, it is unnecessary to consider this hydrated condition; and since they are less cumbersome, the simpler formulas are used. In cases in which the acidic nature of the cation must be considered, however, it is necessary to use the hydrated form. The first step in the hydrolysis of the salt of a metal of this type, therefore, may be illustrated by the equation for the hydrolysis of a zinc salt:

$$\underset{\text{Acid}}{Zn(H_2O)_4^{++}} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Base}}{Zn(H_2O)_3(OH)^+} + \underset{\text{Acid}}{H_3O^+}$$

* In writing ionic equations of this type it is customary to write the formulas of weak electrolytes as molecular formulas rather than as the separate ions. Thus, in this equation molecular formulas are written for the $HC_2H_3O_2$ and the water. Such an equation does not necessarily represent the true mechanism of the reaction; it is more a statement of the starting substances and the final products.

Although the $Zn(H_2O)_3(OH)^+$ is represented here as a base, it is also capable of undergoing further hydrolysis, in which case it acts as an acid.

Indicators. It has already been pointed out that a knowledge of the H^+ concentration is extremely important for the proper control of many reactions, both in their analytical and in their industrial applications. Although a number of instruments are available to measure the pH of a solution, use is frequently made of a class of substances known as *indicators*. Indicators are dyes that are able to assume a color that, for a given dye within certain limits of pH, varies with the pH of the solution in which it is contained. Some of these are familiar even to students of elementary chemistry, *e.g.*, litmus, which is usually described as being red in acidic and blue in basic solutions, and phenolphthalein, described as colorless in acid and red or pink in basic solutions. Many others, however, are used only for special purposes and are usually encountered only in more advanced courses.

To understand the behavior of acid-base indicators it is necessary to realize that these substances are themselves either weak acids or weak bases, the unionized molecules of which have one color while the ion, other than H^+ or OH^-, furnished by the indicator has a different color. The conditions existing in a solution of any acid-type indicator may be represented by the equation

$$HInd_{(\text{color A})} \rightleftharpoons H^+ + Ind^-_{(\text{color B})}$$

in which *HInd* represents the molecule of the indicator and Ind^- represents the anion of the indicator. The law of mass action applied to this equilibrium mixture yields the equation

$$\frac{[H^+][Ind^-]}{[HInd]} = K_I \tag{22}$$

in which K_I is known as the *indicator constant*. For *acid-type* indicators, K_I is the same as the ionization constant.*

By algebraic rearrangement, this equation becomes

$$\frac{[H^+]}{K_I} = \frac{[HInd]}{[Ind^-]} \tag{23}$$

* It should be noted that these indicators are typical weak acids. Consequently, the generalizations discussed here are, with the exception of the color changes, the same as would be true for any weak acid, *e g.*, acetic acid.

Now suppose that the undissociated molecule, $HInd$, is red while the ion, Ind^-, is yellow. Under these conditions, if H^+ is adjusted to a value equal to K_I, the concentration of Ind^- will equal that of $HInd$ and the solution will be *orange*. If, now, the concentration of H^+ is increased, the concentration of $HInd$ will also increase and that of Ind^- will decrease. The result will be that with less yellow and more red, the solution will change from orange to a red-orange; and if H^+ is made sufficiently great, the red $HInd$ will become concentrated enough to mask completely the yellow of the small concentration of Ind^- that remains. On the other hand,

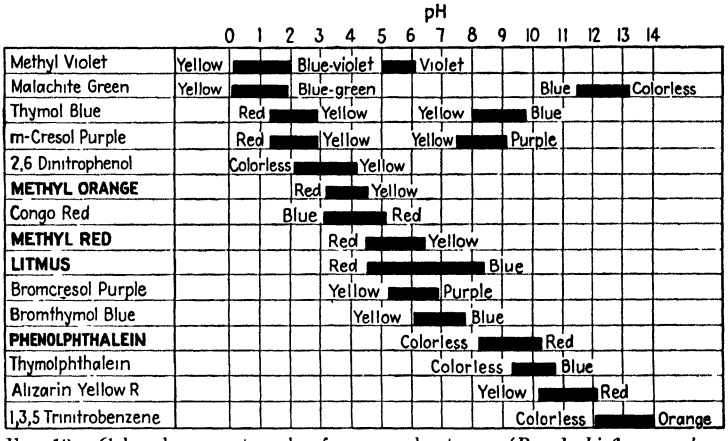


FIG. 13.—Color-change intervals of some indicators. (*Based chiefly on values given by Eastman Kodak Company for its products.*)

suppose a base is added, little by little, to the solution. The *increase in* OH^- means that the H^+ *concentration must decrease;* but as H^+ decreases, the concentration of $HInd$ must also decrease and that of Ind^- must increase. The solution will, therefore, finally reach the point where the $HInd$ is so low in concentration and the Ind^- is so great that the yellow of the latter predominates and little or no red can be seen. This indicator would, then, be classified as one that is red in acidic and yellow in basic solutions. Methyl orange is of this type.

A study of this equation reveals another fact. If, as was shown, the mid-point color of this indicator is obtained only when $[H^+]$ equals K_I, then for the indicator to be used to tell when a solution is really neutral, K_I must have a value of 1×10^{-7}

—for that is the concentration, at room temperature, of H^+ in a neutral solution. Actually, indicators of this type have dissociation constants of quite different values; consequently, many indicators cannot be used to show whether or not the solution is actually neutral.

For most indicators the change in concentration of H^+ between the point at which the color of the Ind^- is the most visible and that at which the color of $HInd$ predominates is about a hundredfold. This means that for the indicator to undergo a complete change in color from its so-called *basic* color to its so-called *acid* color, the pH of the solution must change by about *two* pH *units*. More definitely, since the *mid-point* of this color change is that pH at which $[H^+]$ approximately equals the ionization constant for the indicator, the *color-change interval* (see Fig. 13) for the indicator will be approximately from $pH = [(-\log K_I) - 1]$ to $pH = [(-\log K_I) + 1]$.

To illustrate, suppose that one is considering the color-change interval of an acid-type indicator whose ionization constant is 1×10^{-4}. The color-change interval will be from approximately

$$\begin{aligned} pH &= (-\log K_I) - 1 \\ &= (-\log 10^{-4}) - 1 = +4 - 1 = 3 \end{aligned}$$

to

$$pH = (-\log 10^{-4}) + 1 = +4 + 1 = 5$$

In other words, the acid color will be the only noticeable color in a solution whose pH is 3 or less; whereas when the solution has a pH of 5 or more, the *basic color* of the indicator will predominate. Thus, even though the solution is still definitely acid, if its pH is 5 or greater, the indicator will give the same color as it does when the solution is definitely basic!

It is evident, therefore, that a given indicator can be used for pH determination only if the pH of the solution falls within the color-change interval of the indicator; for solutions of higher pH will all give the same basic color, while those of lower pH will all give the same acid color.

Although the derivations used in this discussion were based on the behavior of acid-type indicators, those indicators which are classified as weak bases follow, in many respects, the same general rules. The color-change intervals usually cover a range of about two pH units, and the color is dependent upon the H^+

concentration of the solution. The mathematical relationships are slightly different, however. If the indicator is represented by *Ind*OH, then

$$Ind\text{OH}_{(\text{color A})} \rightleftharpoons Ind^{+}_{(\text{color B})} + \text{OH}^{-} \tag{24}$$

$$\therefore \frac{[Ind^{+}][\text{OH}^{-}]}{[Ind\text{OH}]} = K$$

$$\therefore [\text{OH}^{-}] = K\frac{[Ind\text{OH}]}{[Ind^{+}]} \tag{25}$$

It will be remembered, however, that in any aqueous solution,

$$[\text{OH}^{-}] = \frac{K_w}{[\text{H}^{+}]}$$

$$\therefore K\frac{[Ind\text{OH}]}{[Ind^{+}]} = \frac{K_w}{[\text{H}^{+}]}$$

$$\therefore \frac{[\text{H}^{+}]}{K_w/K} = \frac{[Ind^{+}]}{[Ind\text{OH}]} \tag{26}$$

The ratio $K_w \div K$ may be set equal to another constant, K_I, which is the *indicator constant* for this type of indicator. The equation thus becomes

$$\frac{[\text{H}^{+}]}{K_I} = \frac{[Ind^{+}]}{[Ind\text{OH}]} \tag{27}$$

Inspection of this equation reveals a striking similarity between it and the corresponding equation for the acid-type indicator. In the first place, as with the acid-type indicators, the mid-point of the color-change interval for base-type indicators is approximately at the pH at which $[\text{H}^{+}]$ equals K_I. Secondly, the color-change interval again will be in the pH range given by the expression

$$(-\log K_I) \pm 1 \tag{28}$$

Finally, if it is remembered that for the acid-type indicator, $[Ind^{-}]$ represents the concentration of the basic form of the indicator and $[HInd]$ represents the concentration of the acid form, then

$$\frac{[\text{H}^{+}]}{K_I} = \frac{[HInd]}{[Ind^{-}]} = \frac{\text{concentration of acid form}}{\text{concentration of basic form}}$$

Similarly, for the base-type indicator, $[Ind^+]$ is the concentration of the acid form, and $[Ind\text{OH}]$ is that of the basic form of the indicator; therefore,

$$\frac{[\text{H}^+]}{K_I} = \frac{[Ind^+]}{[Ind\text{OH}]} = \frac{\text{concentration of acid form}}{\text{concentration of basic form}}$$

Thus the form of the equations for both types is essentially the same.

SUMMARY

In any aqueous solution there are always both hydrogen ions and hydroxyl ions. Their concentrations are related mathematically by the equation $[\text{H}^+][\text{OH}^-] = K_w$, in which K_w at 25°C. is 1×10^{-14}. In neutral solutions at 25°C.,

$$[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ mole per liter}$$

The pH of a solution is the logarithm of the reciprocal of the hydrogen (or hydronium) ion concentration. A neutral solution has a pH of 7; a solution whose pH is less than 7 is acid; and one whose pH is greater than 7 is basic.

The reaction of one or more ions of a salt with those of water is known as *hydrolysis*. Salts that were formed by the reaction of weak acids and strong bases hydrolyze to give basic solutions; those of strong acids and weak bases give acid solutions; those of weak acids and weak bases hydrolyze to give acidic, neutral, or basic solutions according to the relative degrees of ionization of the acid and the base; while salts formed by the reaction of strong acids with strong bases do not hydrolyze. Salts of slightly soluble bases give an effect similar to that obtained with salts of weak bases, etc. The degree of hydrolysis of any salt can be calculated from relationships illustrated in this chapter. It is greater at higher temperatures than at low temperatures but is smaller in solutions to which liquids such as alcohol have been added than it is in pure water.

Hydrolysis frequently causes basic salts to precipitate when normal salts might ordinarily have been expected.

Bronsted's definitions of acids and bases leads to the classification of both neutralization and hydrolysis as acid-base reactions. According to this theory, the hydrolysis of salts of slightly soluble

bases involves the loss of H^+ by the *hydrated* cation—the cation thus acting as an acid.

Indicators are dyes exhibiting colors that, within limits characteristic of the indicator, are characteristic of the pH of the solution. These indicators are weak bases and weak acids. Each indicator undergoes a complete change from its "acid" color to its "basic" color between definite limits of pH. This range of pH is known as the *color-change interval* for the indicator and usually covers two pH units. Many of the indicators used have color-change intervals that do not include a pH of 7 and therefore cannot be used to tell whether or not a solution is really neutral.

Review Questions

1. Define: (*a*) pH, (*b*) pOH, (*c*) hydrolysis, (*d*) indicator, (*e*) color-change interval

2. What is the color-change interval for methyl orange? Phenolphthalein?

3. By means of equations, show which of the following hydrolyze. Also explain why they hydrolyze and what kind of solution will be obtained:

(*a*) $KC_2H_3O_2$. (*b*) KNO_3 (*c*) $ZnCl_2$
(*d*) Na_2CO_3. (*e*) $NH_4C_2H_3O_2$. (*f*) $(NH_4)_2SO_4$.

4. Explain why basic silver carbonate precipitates when sodium carbonate solution is added to silver nitrate solution.

5. Explain by equations why the concentration of NH_4^+ is *not* 0.02*M* and that of $CO_3^=$ is *not* 0.01*M* in a 0.01*M* solution of ammonium carbonate.

6. Explain, using equations, why sodium hydroxide must be added to a solution of Na_2S if a high concentration of $S^=$ is desired in the solution. Do the same for Na_2CO_3 and $CO_3^=$.

7. Which types of salts hydrolyze to give acidic solutions? Basic solutions? Neutral solutions? Which do not hydrolyze?

8. What effect is produced on the hydrolysis of a salt by (*a*) increasing the temperature, (*b*) adding alcohol?

9. Ordinary soap consists of the sodium salts of certain weak organic acids. Would its aqueous solution be acidic or basic? How could you test to see if the soap contained any *excess* alkali?

10. By means of ionic equations explain why $MgCO_3$ can be precipitated from moderately basic solutions by means of $CO_3^=$. Explain why it cannot be precipitated if the basic solution is strongly buffered by ammonium salts.

Problems

1. What is the OH^- concentration in (1) moles per liter and in (2) grams per liter in solutions whose H^+ concentration is:

(*a*) 1×10^{-5} mole per liter? (*b*) 1×10^{-8} mole per liter?
(*c*) 2×10^{-11} mole per liter? (*d*) 2.5×10^{-6} mole per liter?
(*e*) 0.00014 mole per liter? (*f*) 0.000005 mole per liter?

Answers: (*a*) 10^{-9} mole per liter, or 17×10^{-9} g. per liter. (*c*) 5×10^{-4} mole per liter, or 8.5×10^{-3} g. per liter.

2. What is the H^+ concentration in solutions having OH^- concentrations of

(*a*) 1×10^{-3} mole per liter? (*b*) 1×10^{-9} mole per liter?
(*c*) 8×10^{-7} mole per liter? (*d*) 12.5×10^{-8} mole per liter?
(*e*) 0.00004 mole per liter? (*f*) 0.0025 mole per liter?

Answers: (*a*) 1×10^{-11} mole per liter, or 1×10^{-11} g. per liter. (*c*) 1.25×10^{-8} mole per liter, or 1.25×10^{-8} g. per liter.

3. What is the pH of each of the solutions in Problem 1?

Answers: (*a*) 5. (*c*) 10.70.

4. What is the pOH of each solution in Problem 1?

Answers: (*a*) 9. (*c*) 3.30.

5. What is the pOH of solutions of the following pH:

(*a*) 5.031. (*b*) 8.149. (*c*) 4.82.
(*d*) 10.716. (*e*) 7.45. (*f*) 1.30.

Answers: (*a*) 8.969. (*c*) 9.18.

6. Calculate the H^+ concentration of each solution in Problem 5.

Answers: (*a*) 9.31×10^{-6} moles per liter. (*c*) 1.514×10^{-5} moles per liter.

7. Calculate the degree of hydrolysis of $0.1M$ solutions of

(*a*) $NaC_2H_3O_2$. (*b*) NH_4Cl. (*c*) $NH_4C_2H_3O_2$. (*d*) KNO_2.

Answer: (*a*) 7.4×10^{-5}.

8. What are the $[H^+]$ concentrations of the solutions in Problem 7?

Answer: (*a*) $1.3 \times 10^{-9}M$.

9. What concentration of $HC_2H_3O_2$ would be required to make a solution having a pH of 3.8?

10. What concentration of NH_4OH would be necessary in a $0.01M$ solution of NH_4Cl to give the solution a pH of 9?

CHAPTER VIII

COMPLEX IONS; AMPHOTERIC SUBSTANCES

In the earlier portions of this book it has been customary for the sake of simplicity to speak of aqueous solutions as containing simple ions such as Cu^{++}, Ag^{+}, Na^{+}, Cl^{-}, I^{-}, etc. There is evidence, however, that all ions are hydrated, at least to some extent; and sufficient evidence has been accumulated to enable chemists to write definite formulas for some hydrated ions. Thus, in aqueous solutions the ions H^{+}, Cu^{++}, Zn^{++}, and Co^{++} probably really exist as H_3O^{+} $[H(H_2O)^{+}]$, $Cu(H_2O)_4^{++}$, $Zn(H_2O)_4^{++}$, and $Co(H_2O)_6^{++}$. In fact, some of these ions are sufficiently stable for compounds in which the ion is still hydrated to be crystallized from aqueous solution. Others, though too unstable to exist in the solid state, give evidence of their presence in solution.*

Although the existence of chemical entities consisting of simple ions combined with neutral water molecules is itself sufficiently difficult to explain in terms of either electrovalence or covalence, such ions are only a small group in a large class of ions known as *complex ions.*

In general, complex ions may be formed by the reaction of ions either with neutral molecules or with ions of opposite charge. For example, Ag^{+}, Cd^{++}, Cu^{++}, Zn^{++}, Ni^{++}, and Co^{++} react with an excess of ammonium hydroxide, especially in the presence of ammonium salts, to yield complex cations:

$$Ag^{+} + 2NH_3 \rightleftharpoons Ag(NH_3)_2^{+}$$
$$Cd^{++} + 4NH_3 \rightleftharpoons Cd(NH_3)_4^{++}$$
$$Cu^{++} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{++}$$
$$Co^{++} + 6NH_3 \rightleftharpoons Co(NH_3)_6^{++}$$

* The abnormally low conductivities of some dilute solutions have been attributed to the probability that the ions are dragging with them water molecules, the masses of the resultant bodies being much greater than those of the simple ions. Similarly, the fact that some solids dissolve in water with evolution of heat indicates that a chemical reaction is occurring, a phenomenon often ascribed to hydrate formation.

On the other hand, Ag^+, Hg^{++}, and Fe^{++} react with excess CN^- to form complex anions,

$$Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-$$
$$Hg^{++} + 4CN^- \rightleftharpoons Hg(CN)_4^=$$
$$Fe^{++} + 6CN^- \rightleftharpoons Fe(CN)_6^{\equiv}$$

and Ag^+, Pb^{++}, and Cu_2^{++} react with excess I^- or Cl^- to form complex anions of the type

$$Ag^+ + 2I^- \rightleftharpoons AgI_2^-$$
$$Pb^{++} + 3Cl^- \rightleftharpoons PbCl_3^-$$
$$Cu_2^{++} + 4Cl^- \rightleftharpoons Cu_2Cl_4^=$$

As mentioned earlier, the ordinary conceptions of valence cannot account for the formation of complex ions; neither has any other theory been able to explain this phenomenon in every case. Some facts are known, however; and though they do not give a complete picture of the situation, it seems evident that these known factors play at least a part in the formation of these ions.

It was pointed out in Chap. I that some molecules, such as water and NH_3 are quite polar in nature; *i.e.*, they behave as if there were an unequal distribution of positive and negative charges in the molecule. In other words, one might roughly picture the molecule of water as a body, one end of which is slightly negative and the other end slightly positive in charge. With this in mind, it would not be difficult to understand that a positive ion in solution might attract the more negative end of a molecule such as that of water and thus hold it more or less firmly. In fact, it might attract several molecules in this way. Similarly, a negative ion might attract the positive end of the molecule and hold the molecule in a like way. Such aggregates would normally be quite unstable, however, and there would be a continuous exchange of water molecules, some leaving and others taking their places. The number of molecules associated with a given ion would not be fixed; and if attempts were made to crystallize a product containing the hydrated ion, certainly many water molecules would be lost from the aggregate. Yet many hydrates and many complex ions of other types are very stable, compounds of which may be readily obtained in solid form. In fact, many complex ions, such as $Fe(CN)_6^{\equiv}$ and $Co(NH_3)_6^{+++}$, are extremely stable and are decomposed only with difficulty.

Consequently, this conception, though it probably accounts at least partly for many phenomena noted in solution, certainly does not explain all complex ion formation.

In the latter part of the nineteenth century, Alfred Werner, a German chemist, postulated the existence of two types of valence: *primary* valence, which is the ordinary type of valence, and *auxiliary* or *secondary* valence (now more commonly called *coordinate* valence), which he described as a type of bond that an ion can exhibit in addition to its ordinary valence. Experience has shown that the auxiliary valence usually manifests itself as an ability of the ion to attach itself to unused electron pairs in another ion or a molecule. For example, as was mentioned in Chap. I, the electronic configuration of the ammonia molecule might be written

$$\begin{matrix} & \mathrm{H} & \\ & \vdots & \\ :\mathrm{N}: & & \mathrm{H} \\ & \vdots & \\ & \mathrm{H} & \end{matrix} \qquad \text{or} \qquad :\mathrm{NH_3}$$

where the dots represent electrons, the hydrogen atoms being held to the nitrogen through shared electron pairs. The unshared pair of electrons makes this molecule readily capable of forming complex ions in a manner that may be illustrated by the equation for the formation of the diammine silver ion:

$$\mathrm{Ag^+} + 2\left[\begin{matrix} & \mathrm{H} & \\ & \vdots & \\ :\mathrm{N}: & & \mathrm{H} \\ & \vdots & \\ & \mathrm{H} & \end{matrix}\right] \rightleftharpoons \left[\begin{matrix} & \mathrm{H} & & \mathrm{H} & \\ & \vdots & & \vdots & \\ \mathrm{H} & :\mathrm{N}: & \mathrm{Ag} & :\mathrm{N}: & \mathrm{H} \\ & \vdots & & \vdots & \\ & \mathrm{H} & & \mathrm{H} & \end{matrix}\right]^+ \text{ or } [\mathrm{H_3N:Ag:NH_3}]^+$$

In this case the coordinate valence of Ag^+ would seem to be **2.** In practice, it is customary to speak of the *number of ions or neutral molecules with which a given ion can combine* as being the *coordination number of the ion.* This does not mean that the formula will always be that which corresponds to the coordination number of the ion, for by varying conditions it is often possible to obtain different combining ratios. A knowledge of the coordination number, however, enables one to predict, with fair accuracy, the formula of a given complex ion; and a knowledge of the formulas of analogous ions gives even greater weight to such predictions. The coordination numbers for several ions are listed in Table V.

TABLE V.—COORDINATION NUMBERS

Ag^+	2
Cd^{++}	4
Co^{++}	6
Co^{+++}	6
Cu^+	2 and 3
Cu^{++}	4
Fe^{++} or Fe^{+++}	6
Hg^{++}	4
Mn^{++}	6
Ni^{++}	4
O^-	3
Pb^{++}	3
Pb^{++++}	6
Sb^{+++}	6
Sn^{++++}	6
Zn^{++}	4

The reason why Ag^+, for example, has a coordination number of 2 while Cu^{++} has one of 4 has not been adequately explained. Attempts have been made to relate this secondary valence to a tendency on the part of the ion to assume a rare gas electronic configuration by this process of attaching itself to unused electron pairs; similarly, there have been attempts to relate this valence to incomplete inner shells in the electronic arrangement of the simple ion. Theories have also been suggested based upon possible spatial arrangements around the ion. Probably all these theories have some usefulness in explaining the formation of complex ions; however, at present no explanation has been advanced that is satisfactory in every respect.

It will be noticed that the electrovalence of any complex ion is equal to the algebraic sum of the electrovalences of the components of the complex ion. For example, the complex ion $AgCl_2^-$ consists of one Ag^+ and two Cl^-. Adding the valences represented gives $+1 - 2 = -1$, the valence of the complex ion. Similarly, $Cu(NH_3)_4^{++}$ consists of one Cu^{++} and four NH_3 molecules. Adding the valences gives $+2 + 4(0) = +2$, the valence of this complex ion.

Formation and Dissociation of Complex Ions. Although our knowledge of the reasons for complex ion formation is as yet limited, fortunately much more is known of the chemical behavior of such ions, and many practical applications are made of this knowledge.

As has been indicated earlier in many equations, the formation of complex ions is a reversible process. Thus the reaction between Ag^+ and NH_3 results in the formation of $Ag(NH_3)_2^+$:

$$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$$

On the other hand, if a diammine silver salt such as $Ag(NH_3)_2Cl$ is dissolved in water, the $Ag(NH_3)_2^+$ ions in the resulting solution will dissociate somewhat to form simple Ag^+ and NH_3. Any solution of a complex ion will therefore contain not only the complex ion itself but also some of the simple ions and molecules of which the complex ion was composed. Thus any solution containing $Ag(NH_3)_2^+$ will contain an equilibrium mixture of the $Ag(NH_3)_2^+$ with Ag^+ and NH_3.

Since complex ions in solution are in equilibrium with their simple components, it is possible either to form or to decompose complex ions by use of the proper reagents. Consider, for example, the equilibrium mixture illustrated above. Suppose that a solution containing a moderate concentration of Ag^+ is treated with an excess of ammonium hydroxide. At once reaction occurs to form some $Ag(NH_3)_2^+$, and within a very short time equilibrium will be established between the Ag^+, NH_3, and $Ag(NH_3)_2^+$. As a result the concentration of Ag^+ in the solution will be reduced markedly. Now suppose that the source of the Ag^+ in the solution is a slightly soluble salt such as silver chromate, silver chloride, or silver iodide:

$$Ag_2CrO_{4(solid)} \rightleftharpoons 2Ag^+ + CrO_4^=$$

If the slightly soluble salt yields a sufficiently high concentration of Ag^+, the reduction in concentration of the latter due to its reaction with NH_3 to form $Ag(NH_3)_2^+$ will cause some of the salt to dissolve. Silver chromate is such a compound; consequently, it dissolves readily in even dilute ammonium hydroxide. If, on the other hand, the silver salt is too slightly soluble, the concentration of Ag^+ that it yields in solution will be too small to permit the salt to dissolve appreciably in even concentrated solutions of NH_3. Such is the case with silver iodide whose solubility in concentrated ammonium hydroxide is too slight to be of any great significance.

Again consider the equilibrium mixture of $Ag(NH_3)_2^+$ and its components. Suppose that the mixture has been prepared by

dissolving silver chloride in ammonium hydroxide solution and that it is now desired to recover (1) the original silver chloride, (2) the silver in the form of another compound, or (3) the Cl^- in a solution separate from the silver. The equilibrium mixture will contain the following ions

$$Ag(NH_3)_2^+ + Cl^- \rightleftharpoons Ag^+ + 2NH_3 + Cl^-*$$

Now, if any source of H^+ is added, *e.g.*, HNO_3, the NH_3 concentration will be effectively reduced by the reaction

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

The equilibrium will then shift to the right, thus increasing the concentration of Ag^+. If $[Ag^+]$ increases beyond the concentration necessary for the ion product, $[Ag^+][Cl^-]$, to equal the solubility-product constant for silver chloride, precipitation of silver chloride must take place.

Suppose that it is desired to form another compound of silver or to remove the silver from the solution and leave the chloride in solution. The addition of $S^=$ (from hydrogen sulfide or ammonium sulfide) or of I^- will precipitate silver sulfide or silver iodide, for these compounds are so slightly soluble that their saturated solutions contain much less Ag^+ than is yielded either by $Ag(NH_3)_2^+$ or by silver chloride. Consequently, the reactions

$$2Ag^+ + S^= \rightleftharpoons Ag_2S_{(solid)}$$
$$Ag^+ + I^- \rightleftharpoons AgI_{(solid)}$$

will take place. Since either reaction causes a pronounced reduction in the concentration of Ag^+, the equilibrium again will shift in such direction as to decompose the $Ag(NH_3)_2^+$. If sufficient reagent is added, therefore, and the product filtered, the remaining solution will contain the NH_3 and Cl^- with only insignificant quantities of Ag^+. Finally, if $S^=$ has been used, the Ag^+ may be recovered readily by dissolving the precipitate of Ag_2S in dilute nitric acid.

In many cases in which it is possible for complex ions to form, competition between the components of the complex equilibrium and those of some other equilibrium in the same mixture may

* Although both Ag^+ and Cl^- are present in this solution, the concentration of Ag^+ is so low that the ion product $[Ag^+][Cl^-]$ is less than the solubility-product constant for AgCl; consequently, no precipitation will occur.

result in unexpected products. It has already been pointed out that in a competition between $Ag(NH_3)_2^+$ and Ag_2S or AgI for Ag^+, either of the latter two will form at the expense of the first. Now suppose that a very small quantity of ammonium hydroxide is added to a solution of Zn^{++} containing *no ammonium salts*. Part of the Zn^{++} will be at once precipitated as $Zn(OH)_2$. In this case two competing reactions occur, for while $Zn(OH)_2$ is forming

$$Zn^{++} + 2(OH^-) \rightleftharpoons Zn(OH)_{2(solid)}$$

a very small amount of Zn^{++} is reacting with the NH_3 in the ammonium hydroxide:

$$Zn^{++} + 4NH_3 \rightleftharpoons Zn(NH_3)_4^{++}$$

Both equilibriums must be satisfied, since the whole is in one mixture, but experience has shown that with a moderate concentration of OH^- and a low concentration of NH_3, the equilibriums are set strongly in the direction of forming $Zn(OH)_2$. Now suppose that it is desired to force these reactions in such direction as to cause tetrammine zinc ion to form and zinc hydroxide to dissolve. If either the OH^- concentration is reduced or the NH_3 concentration is increased, the desired result will be obtained. The OH^- concentration may be reduced by adding H^+—but if this is done, the H^+ will also react with NH_3, since there will be a competition between the OH^- and the NH_3 for the H^+. The best way to reduce the OH^- concentration is by use of a buffering agent such as any ammonium salt, since this will reduce the concentration of OH^- without reducing that of the NH_3. Consequently, in the presence of ammonium salts, zinc hydroxide will dissolve. On the other hand, if an excess of ammonium hydroxide is added, the concentration of NH_3 is again increased sufficiently to cause $Zn(OH)_2$ to dissolve.

Although the qualitative relationships illustrated may be extremely useful, since each kind of complex ion is capable of establishing an equilibrium between itself and its simple components, the law of mass action may be applied to derive quantitative relationships. Consider, for example, the complex ion $Cu(NH_3)_4^{++}$. From the standpoint of dissociation, the equilibrium may be expressed

$$Cu(NH_3)_4^{++} \rightleftharpoons Cu^{++} + 4NH_3$$

from which may be derived the expression

$$\frac{[Cu^{++}][NH_3]^4}{[Cu(NH_3)_4^{++}]} = K$$

Similarly, from the equation

$$Cu(CN)_3^{=} \rightleftharpoons Cu^{+} + 3CN^{-}$$

can be obtained the expression

$$\frac{[Cu^{+}][CN^{-}]^3}{[Cu(CN)_3^{=}]} = K$$

and from the equation

$$HgI_4^{=} \rightleftharpoons Hg^{++} + 4I^{-}$$

can be obtained the expression

$$\frac{[Hg^{++}][I^{-}]^4}{[HgI_4^{=}]} = K$$

In each case the equilibrium constant is known as the *instability constant* for that particular ion.

Now, from the standpoint of the *formation* of these complex ions, the following equations may be written:

$$Cu^{++} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{++}$$

$$\frac{[Cu(NH_3)_4^{++}]}{[Cu^{++}][NH_3]^4} = K'$$

and

$$Cu^{+} + 3CN^{-} \rightleftharpoons Cu(CN)_3^{=}$$

$$\frac{[Cu(CN)_3^{=}]}{[Cu^{++}][CN^{-}]^3} = K'$$

In such cases, the constant is known as the *stability constant.* The instability constant, K, and the stability constant, K', for a given complex ion are related mathematically by the equation

$$K = \frac{1}{K'}$$

The instability constants for many of the more common complex ions have been evaluated (see Table VI); consequently, these relationships may be used to determine many useful facts.

TABLE VI.—INSTABILITY CONSTANTS

Complex ion	Constant	Complex ion	Constant
$Ag(CN)_2^-$	1×10^{21}	$Cu(CN)_4^-$	5×10^{-28}
$Ag(NH_3)_2^+$	6.8×10^{-8}	$HgCl_4^-$	6×10^{17}
$Cd(CN)_4^-$	1.4×10^{-17}	$Hg(CN)_4^-$	4×10^{42}
$Cd(NH_3)_4^{++}$	1×10^{-7}	HgI_4^-	5×10^{-31}

Problem 1. What would be the Ag^+ concentration in a 0.1 *M* solution of $Ag(NH_3)_2Cl$ containing 0.2 mole of NH_3 per liter of solution?

a. This salt ionizes completely in so far as the ionization

$$Ag(NH_3)_2Cl \rightarrow Ag(NH_3)_2^+ + Cl^-$$

is concerned. Consequently, the only equilibrium involved is that between the complex ion and its components:

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$$

$$\frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = K = 6.8 \times 10^{-8}$$

b. It will be noted that the equation defining the instability constant is of the same form as was used to define the constant for a weak electrolyte. Consequently, the same type of reasoning may be applied here as to the cases of weak electrolytes. Suppose, then, that $[Ag(NH_3)_2^+]$ be evaluated by assuming that the loss of this ion due to dissociation is negligibly small compared to that which was initially present. Its concentration may then be considered 0.1 *M*.

c. Substituting the values found in *b* and the concentration of NH_3 as given in the equation

$$\frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = 6.8 \times 10^{-8}$$

one obtains

$$\frac{[Ag^+](0.2)^2}{(0.1)} = 6.8 \times 10^{-8}$$

$$\therefore [Ag^+] = \frac{6.8 \times 10^{-8} \times 0.1}{4 \times 10^{-2}} = 1.7 \times 10^{-7} M$$

Problem 2. What concentration of NH_3 would be required to cause 0.1 mole of AgCl to dissolve in 1 liter of the NH_3 solution?

a. The reaction may be represented by the equation

$$AgCl + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$$

Two equilibriums are involved and under the conditions of the problem, *both must be satisfied.*

$$[Ag^+][Cl^-] = K_{s.p.} = 1.6 \times 10^{-10}$$
$$\frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = K = 6.8 \times 10^{-8}$$

Now when the 0.1 mole of AgCl has *just dissolved,* the concentration of Cl^- will be $0.1M$. Since the solubility-product equation must be satisfied at this point, then

$$[Ag^+](0.1) = 1.6 \times 10^{-10}$$
$$\therefore [Ag^+] = \frac{1.6 \times 10^{-10}}{0.1} = 1.6 \times 10^{-9}M$$

But the equation for the instability constant must also be satisfied; consequently, $[Ag^+]$ in that expression will also be $1.6 \times 10^{-9}M$

b. Since the complex ion $Ag(NH_3)_2^+$ is fairly stable, practically all the silver from the dissolved AgCl will form $Ag(NH_3)_2^+$ This may also be seen if one considers that of the 0.1 mole of silver from the dissolved AgCl, only 1.6×10^{-9} mole remains as simple Ag^+. Without significant error, therefore, $[Ag(NH_3)_2^+]$ may be considered $0.1M$

Substituting the values found for $[Ag^+]$ and $[Ag(NH_3)_2^+]$ in the equation

$$\frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = 6.8 \times 10^{-8}$$

one obtains

$$\frac{(1.6 \times 10^{-9})[NH_3]^2}{0.1} = 6.8 \times 10^{-8}$$
$$\therefore [NH_3]^2 = \frac{6.8 \times 10^{-8} \times 0.1}{1.6 \times 10^{-9}} = 4.25$$
$$\therefore [NH_3] = \sqrt{4.25} = 2.06M$$

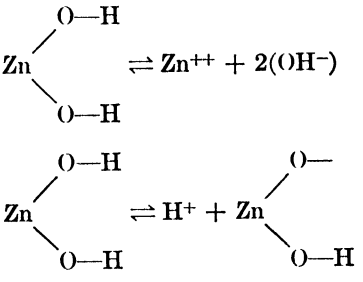
c. It must be remembered, however, that the concentration of NH_3 calculated here is only that which was *left free in the solution* at the end of the reaction In addition, the 0.1 mole of $Ag(NH_4)_2^+$ formed required 0.2 mole more of NH_3 At the beginning, therefore, the concentration of NH_3 needed would be

$$2.06 + 0.2 = 2.26M$$

Amphoteric Hydroxides. It has already been mentioned that a number of metals form hydroxides that, though only slightly soluble in water, are capable of dissolving either in acids *or in active bases.**

* Ammonium hydroxide is too slightly ionized to yield enough OH^- to cause a hydroxide to exhibit its amphoteric characteristics. When a slightly soluble base dissolves in excess ammonium hydroxide, therefore, it is due to the formation of ammonia complex ions.

The fact that these amphoteric hydroxides are soluble in strong bases would seem to indicate that they possess acidic characteristics in addition to the properties normally associated with bases. In other words, the hydroxide might be considered able to ionize, in aqueous solutions, in either of the following two ways:



Such is the classical explanation of amphoterism. It has been customary, therefore, to consider the equilibrium between solid $Zn(OH)_2$ and its ions in solution as follows:

$$H^+ + HZnO_2^- \rightleftharpoons \begin{bmatrix} Zn(OH)_2 \\ H_2ZnO_2 \end{bmatrix} \rightleftharpoons Zn^{++} + 2(OH^-)$$

In any solution in which solid $Zn(OH)_2$ is in equilibrium with its ions in solution, there will be both $HZnO_2^-$ (zincate ion) and Zn^{++}, in addition to the H^+ and OH^- present in all aqueous solutions.

If an acid is added to this mixture, the H^+ from the acid will react with the OH^- to form water; consequently, the OH^- concentration will be reduced and the whole equilibrium represented above will shift to the right. This accounts for the dissolving of $Zn(OH)_2$ in acids. On the other hand, if a strong base such as sodium hydroxide is added to this mixture, the OH^- from the active base will react with the H^+ to form water. The consequent reduction in the concentration of the H^+ will cause the equilibrium to shift to form $HZnO_2^-$ and the solid $Zn(OH)_2$ will again dissolve.

The reactions of $Al(OH)_3$ may be represented in a somewhat similar fashion. In this case, however, the acid form is written as a monobasic hydrated acid, to account for the formation of AlO_2^- when the hydroxide is dissolved in solutions of alkalies.

$$H^+ + AlO_2^- \rightleftharpoons \begin{bmatrix} Al(OH)_3 \\ HAlO_2 \cdot H_2O \end{bmatrix} \rightleftharpoons Al^{+++} + 3(OH^-)$$

The reactions for chromic hydroxide are similar to those of aluminum hydroxide; while those of lead hydroxide and stannous hydroxide are like those of zinc hydroxide.

Antimonous and stannic hydroxides are usually said to be amphoteric also, these hydroxides dissolving in alkalies to form ions which may be written SbO_2^- and $SnO_3^=$, respectively. Actually, these hydroxides dissolve most readily in *halogen* acids such as HCl, and there is much evidence to support the belief that Sn^{++++} ions exist in only very low concentrations in these solutions. It has been fairly well established that stannic chloride solutions contain chiefly $SnCl_6^=$ rather than Sn^{++++}; and owing to its acidic nature, the hydroxide is more often written as $H_2SnO_3 \cdot xH_2O$ (metastannic acid) instead of as $Sn(OH)_4$.

More recently a different theory has been advanced to account for the behavior of amphoteric elements. This theory is based upon the well-known fact that the amphoteric elements are capable of forming complex ions, especially with anions. Thus Pb^{++} is capable of reacting with an excess of I^- to form PbI_3^-:

$$Pb^{++} + 3I^- \rightleftharpoons PbI_3^-$$

In similar manner it is suggested that Pb^{++} may react with excess OH^- to form $Pb(OH)_3^-$, which may then lose one molecule of water to form the ion $HPbO_2^-$:

$$Pb^{++} + 3(OH^-) \rightleftharpoons Pb(OH)_3^-$$
$$Pb(OH)_3^- \rightleftharpoons HPbO_2^- + H_2O$$

It is assumed that three hydroxyl ions are involved in the complex, since the usual coordination number for lead is three in compounds of this type.

Likewise, the reaction between Zn^{++} and strong bases is suggested as being

$$Zn^{++} + 4(OH^-) \rightleftharpoons Zn(OH)_4^=$$

or possibly

$$Zn^{++} + 3(OH^-) \rightleftharpoons Zn(OH)_3^-$$

while that of Al^{+++} might be represented as

$$Al^{+++} + 4(OH^-) \rightarrow Al(OH)_4^-$$

and that of Cr^{+++} as

$$Cr^{+++} + 4(OH^-) \rightleftharpoons Cr(OH)_4^-*$$

The reaction for Sn^{++} would be like that for Pb^{++}, while that of Sn^{++++} would be

$$Sn^{++++} + 6(OH^-) \rightleftharpoons Sn(OH)_6^{=}$$

In these equations, the formulas for the intermediate products have been written for Cr^{+++} and Al^{+++} as if these ions combined with four ions or molecules in forming complex ions. Actually, there is evidence to support the belief that these ions have coordination numbers of six. Although it is possible to justify the foregoing equations on the grounds that the coordination number of six represents a *maximum* number that is not always attained, there is another method of representing these reactions that takes account of this full coordination number. The theory behind this representation makes use of the mechanism suggested by Bronsted's acid-base theory to explain the hydrolysis of salts of cations whose hydroxides are only slightly soluble. According to this mechanism, the precipitation of zinc hydroxide would be represented by the following equations:

$$Zn(H_2O)_4^{++} + 2H_2O \rightleftharpoons Zn(H_2O)_2(OH)_2 + 2H_3O^+$$
$$H_3O^+ + OH^- \rightleftharpoons 2H_2O$$

while with excess OH^- the reaction would be

$$Zn(H_2O)_4^{++} + 3H_2O \rightleftharpoons Zn(H_2O)(OH)_3^-\dagger + 3H_3O^+$$
$$H_3O^+ + OH^- \rightleftharpoons 2H_2O$$

In a similar way, the corresponding reactions for aluminum would be written

$$Al(H_2O)_6^{+++} + 3H_2O \rightleftharpoons Al(H_2O)_3(OH)_3 + 3H_3O^+$$
$$Al(H_2O)_6^{+++} + 4H_2O \rightleftharpoons Al(H_2O)_2(OH)_4^- + 4H_3O^+$$
$$H_3O^+ + OH^- \rightleftharpoons 2H_2O$$

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* The relationship between this conception and that previously suggested can be seen by noting the fact that if the hydroxyl complexes were partly dehydrated, the products would be the simpler ions suggested earlier

† The existence of complex ions in which the coordination number is satisfied by more than one kind of ion, or by ions and molecules together, has been well established, particularly for the complex ions of Co^{+++} and of Cr^{+++}; consequently, the mixed complex ions illustrated here are not suggested without excellent grounds.

It is obvious that since amphoteric hydroxides dissolve in either acids or bases—in other words in solutions of either low or high pH—there must be some pH between these extremes at which a given hydroxide will exhibit a minimum solubility. This pH is called the *isoelectric* point for the amphoteric hydroxide.

Analytical Applications. Of the many applications of complex ions to analysis, one of the earliest met in the laboratory is that in which ammonium hydroxide is used to dissolve AgCl in order to effect the separation of silver from mercurous mercury. The process by which the AgCl dissolves has already been explained in this chapter,* as has also the establishment of the presence of silver by reprecipitating it as AgI or AgCl.

In Cation Group II, complex ion formation is used many times. The tin and copper subgroups are separated by making use of the fact that a moderately high concentration of $S^{=}$ will cause members of the tin group to form thio complexes. Either ammonium or sodium monosulfide may be used as the source of $S^{=}$; and the procedure employed is that of treating the mixed sulfides of Group II with successive portions of the hot solutions of the alkali monosulfide. The reactions that take place are

$$As_2S_3 + 3S^{=} \rightleftharpoons 2AsS_3^{\equiv}$$
$$Sb_2S_3 + 3S^{=} \rightleftharpoons 2SbS_3^{\equiv}$$
$$SnS_2 + S^{=} \rightleftharpoons SnS_3^{=}$$

Stannous sulfide is not soluble in ammonium monosulfide; consequently, any tin present must be oxidized to the stannic state before Group II is precipitated, or else ammonium polysulfide instead of ammonium monosulfide must be used in the subgroup separation. Ammonium polysulfide itself, which is formed by dissolving sulfur in $(NH_4)_2S$ solution, contains complex ions of the type $S_x^{=}$,† in which x may be 2, 3, 4, etc. The extra sulfur

* The NH_3 also reacts with the Hg_2Cl_2 present at that point in the analysis to form a mixture of Hg^0 and $HgNH_2Cl$ (mercuric ammonochloride).

$$Hg_2Cl_2 + 2NH_3 \rightarrow Hg^0 + HgNH_2Cl + NH_4^+ + Cl^-$$

The compound $HgNH_2Cl$ is not an ammonia complex in the usually accepted sense of the term.

† Complex ions that contain only one kind of atom are known as *homatomic* complex ions. Another example of this kind of ion is I_3^-, which is formed when I_2 is dissolved in solutions of iodides. The formation of this and similar ions accounts for the unusually high solubility of iodine in KI solution.

enables these ions to act as oxidizing agents; consequently, polysulfides can dissolve stannous sulfide:

$$SnS + S_x^{=} \rightleftharpoons SnS_3^{=}$$

and they are also capable of oxidizing arsenous sulfide to form soluble thioarsenates:

$$As_2S_3 + S_1^{=} \rightleftharpoons 2AsS_4^{=}$$

Whether it is the monosulfide or the polysulfide that is used to dissolve the sulfides of the tin group, the sulfides of these metals can be reprecipitated by *acidifying* the solution *slightly*. The reaction of H^+ with $S^=$ reduces the concentration of the latter to a point lower than that needed to form appreciable quantities of the complex thio ions; consequently, the equilibrium shifts in such a way as to precipitate the sulfides. Too great excess of H^+ will, however, reduce the concentration of $S^=$ so much as to cause the more soluble sulfides, Sb_2S_3 and SnS_2, to redissolve.

In the identification of lead an interesting application is made of the amphoteric nature of this element. The lead is precipitated as the chromate, but under certain conditions a chromate of bismuth may also form at this point. Since trivalent bismuth is not amphoteric, the presence of lead is confirmed if the precipitate proves to be soluble in sodium hydroxide solution. The reactions involved may be represented as follows:

$$PbCrO_{4(solid)} \rightleftharpoons Pb^{++} + CrO_4^{=}$$
$$Pb^{++} + 3(OH^-) \rightleftharpoons HPbO_2^- + H_2O$$

The formation of ammonia complexes serves a number of purposes in Cation Groups II and III. In the former, an *excess* of ammonium hydroxide is added to the solution when all cations except Bi^{+++}, Cu^{++}, and Cd^{++} have been removed. Since Bi^{+++} does not form ammonia complexes while Cu^{++} and Cd^{++} form $Cu(NH_3)_4^{++}$ and $Cd(NH_3)_4^{++}$, respectively, $Bi(OH)_3$ is precipitated and the other two remain in solution. Similarly, in weakly alkaline solutions containing ammonium hydroxide and ammonium salts, zinc hydroxide cannot precipitate, owing to the formation of $Zn(NH_3)_4^{++}$, but under the same conditions $Al(OH)_3$ precipitates readily. In Group III, therefore, the unknown frequently (see Optional Method I) is carried to the point where it contains only AlO_2^- and $HZnO_2^-$, and then the solution is buffered

with ammonium acetate. The concentration of OH^- is thereby reduced to the point where $Al(OH)_3$ precipitates while at the same time ammonium hydroxide is produced:

$$NH_4^+ + OH^- \rightleftharpoons NH_4OH$$

The ammonia in this ammonium hydroxide reacts with the Zn^{++} to form $Zn(NH_3)_4^{++}$, with the result that the zinc remains in solution.

The separation of the Group III subgroups in Optional Method I depends upon the fact that the hydroxides of aluminum, chromium, and zinc are amphoteric whereas those of the other metals of this group are not. Similarly, the separation of Fe^{+++} from Co^{++} and Ni^{++} depends upon the formation of $Co(NH_3)_6^{++}$ and $Ni(NH_3)_4^{++}$ and the precipitation of $Fe(OH)_3$ when an excess of ammonium hydroxide is added to the solution from which the other cations have been removed.

SUMMARY

Complex ions may be formed by the reaction of ions with neutral molecules (such as water, forming hydrated ions, or ammonia, forming ammonia complexes) or with ions of the opposite kind of charge. The number of molecules or ions with which a given ion can combine to form a complex ion is known as its *coordination number*. The auxiliary (or coordinate) valence exhibited by ions in forming complexes is generally used to attach the ion to unused electron pairs in the molecules or ions with which it is combining.

Complex ions form by means of reversible reactions; consequently, any solution of a complex ion contains some of its simple components. The resulting equilibrium can be shifted in either direction by applying the principles usually used for the shifting of equilibriums, and by this means many slightly soluble compounds can be dissolved and reprecipitated. Also the relative concentrations of the complex ions and their simpler components in any solution are controlled by the relationship for the instability constant for the ion.

Amphoteric hydroxides are slightly soluble hydroxides capable of dissolving in either acids or strong bases. The amphoterism exhibited by the hydroxides of these metals seems to be due either to a partial ionization of the hydroxide to yield H^+ or to an

ability of the ion to form complex ions by combining with more hydroxyl ions than are required to form the normal hydroxide. In terms of the Bronsted acid-base theory, however, the reaction would be explained as involving a loss of protons by the hydrated metal ion to form hydronium ions and leave hydroxyl ions in place of the water of hydration. This reaction would be aided by the subsequent reaction of the hydronium ions with the OH^- from the active base.

For any slightly soluble amphoteric hydroxide there is a certain pH at which the hydroxide has its lowest solubility. This pH is known as the *isoelectric point* for that hydroxide.

Many applications are made of the formation of complex ions and of amphoterism in analytical separations.

Review Questions

1. Define: (*a*) complex ion, (*b*) coordinate valence, (*c*) coordination number, (*d*) amphoteric hydroxide, (*e*) isoelectric point

2. Explain briefly Werner's theory of the formation of complex ions

3. Give the formulas for the ammonia complex ions of (*a*) Cu^{++}, (*b*) Ag^+, (*c*) Zn^{++}, and (*d*) Co^{++}. What is the coordination number of each of these ions?

4. The coordination number of Pt^{++++} is six, and that of Au^{+++} is four. What would be the formulas for the chloro complex ions of these cations?

5. By means of equations show why

(*a*) AgI dissolves in KCN solution.

(*b*) $PbCl_2$ dissolves in an excess of sodium hydroxide solution.

(*c*) HgS dissolves in concentrated hydriodic acid

(*d*) $ZnCO_3$ dissolves in an excess of sodium hydroxide solution.

6. Using aluminum hydroxide, show the three mechanisms used to explain the behavior of an amphoteric hydroxide in the presence of excess alkali Repeat, using first chromic hydroxide, then stannous hydroxide.

7. What would you expect to happen in each case in Question 6 if the solution were to be buffered with ammonium salts?

8. Of the cations covered by the analytical scheme outlined in this book, list all those which form ammonia complex ions. Similarly, list those whose hydroxides are amphoteric.

9. Using equations to aid you, explain why a basic salt is precipitated if a very little ammonium hydroxide is added to a solution of $CuCl_2$ but, if sufficient ammonium salts are present, no precipitate forms.

10. If you were given the slightly soluble hydroxide of a metal of which you knew nothing, how could you determine whether or not the hydroxide is amphoteric? Whether or not the cation forms an ammonia complex ion whose hydroxide is soluble?

11. Making use of complex-forming and amphoteric characteristics, how could you separate Cu^{++}, Bi^{+++}, and Pb^{++}?

12. Answer Question 11 for the case of a mixture of Fe^{+++}, Zn^{++}, and Al^{+++}.

Problems

1. What would be the concentration of Hg^{++} in a solution that was made by dissolving 0.002 mole of HgI_2 in 1 liter of 0.104*M* KI solution?

Answer: 1×10^{-31} mole per liter.

2. What would be the concentration of Ag^{+} in a solution made by dissolving 0.005 mole of AgCl in 1 liter of a solution that is 0.1*M* with CN^{-}?

3. What would be the concentration of Cd^{++} in a solution made by adding 0.02 mole of Cd^{++} to a liter of a solution that is 0.18*M* with CN^{-}?

4. Would it be possible to precipitate CdS from the solution in Problem 3 by making it $1 \times 10^{-9}M$ with S^{-}? Prove that your answer is correct.

5. If the solution in Problem 1 was made 0.3*M* with HCl and the solution was saturated with H_2S, would HgS precipitate? Give mathematical proof of the correctness of your answer.

6. What theoretical concentration of NH_3 would be required to dissolve 0.05 mole of CdS in 1 liter of the solution? Is it possible to obtain such a solution of NH_3?

CHAPTER IX

COLLOIDS; COPRECIPITATION PHENOMENA

Formation of Colloids. It is not uncommon during an analysis to obtain mixtures in which the liquid contains quantities of solid that remain suspended and cannot be removed either by filtering or by centrifuging. Such mixtures are known as *colloidal systems* or *colloidal solutions*, and the colloidal material and the medium in which it is suspended are known as the *dispersed phase* and the *dispersing phase*, respectively.

In analytical work the formation of colloidal solutions may take place when reagents have been added to cause the formation of slightly soluble salts (in other words, the colloid may form by the process known as *condensation*), or it may occur during the washing of a slightly soluble substance owing to the ability of the substance to *peptize*, or break up into smaller particles and thus go into the colloidal state. The presence of such colloidal material means that the separations involved will be incomplete; consequently, it is usually essential that colloidal substances be precipitated—or, more properly, *coagulated*—whenever such systems are encountered in qualitative analytical work.

Colloidal material resists coagulation for two main reasons. One of these is the extremely small size of the individual colloidal particles, or *micelles*. The micelles have so little mass that they do not settle readily and even centrifugalization has little effect upon the smaller ones. Although micelles are much larger than ordinary molecules, they are small enough that the rapidly moving molecules of the dispersing medium hammer the colloidal particles in every direction.* This movement of the micelles obviously retards any settling of the dispersed phase.

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* The resultant random movement of the colloidal particles, which is readily observed under the microscope with some colloids, is known as the *Brownian movement*. It is one of the best direct evidences attesting to the truth of the kinetic molecular theory.

Now if the micelles could gather into larger aggregates, the mass of the resulting bodies would be great enough for the material to precipitate and the dimensions of the particles would be large enough to permit their removal by filtration. This coagulation, however, does not occur readily, owing to the fact that the micelles carry electrical charges. The *numbers* of charges vary from micelle to micelle—in other words, the numbers of charges on the micelles of a given dispersed phase are not fixed as they are in the case of ions. The number of charges on the different micelles may vary from no charge at all to a fairly large number of charges. For a *given dispersed* phase in a *given environment*, however, the *kind* of charge will be the same for all the micelles; consequently the like charges on the micelles cause them to repel one another and make it difficult for the micelles to get close enough together to coagulate.

A number of theories have been evolved to explain the presence of the charges on the colloidal particles of different colloidal systems. Although any extensive discussion of these would require too much space and would be of too little use to be included here, a few special cases are worthy of consideration as illustrating (1) the probable mechanisms of the formation of colloids, (2) the possible ways of predicting the kind of charges on the micelles, and (3) the ways in which the formation of colloids might be minimized.

Suppose that it is desired to precipitate silver chloride from a Cation Group I unknown. When the dilute hydrochloric acid is added to the unknown, the reaction

$$Ag^+ + Cl^- \rightleftharpoons AgCl_{(solid)}$$

takes place. Now if the reagent is added drop by drop, with stirring and centrifuging after each addition, it is usually found that at first some of the silver chloride remains in colloidal form. This condition continues until most of the silver has been converted to silver chloride; then suddenly the colloidal material is observed to have coagulated. If, however, the hydrochloric acid is added in large excess, again much of the solid will be found in the colloidal state. The micelles in the first case will be positively charged; in the latter case they will be negatively charged. The suggested explanation for this phenomenon is illustrated in Fig. 14. It will be noticed that the surface of solid

AgCl consists of a regular arrangement of Ag^+ and Cl^- (Fig. 14*a*). If the solid is formed in a solution in which Ag^+ is in excess, some of the Ag^+ in the solution will be held to the surface of the crystal by the attraction of the surface Cl^- for the Ag^+ (see Fig. 14*b*). The crystal in this manner, *i.e.*, by *adsorption* of Ag^+, acquires a charge equal in number and kind to those of the adsorbed ions—

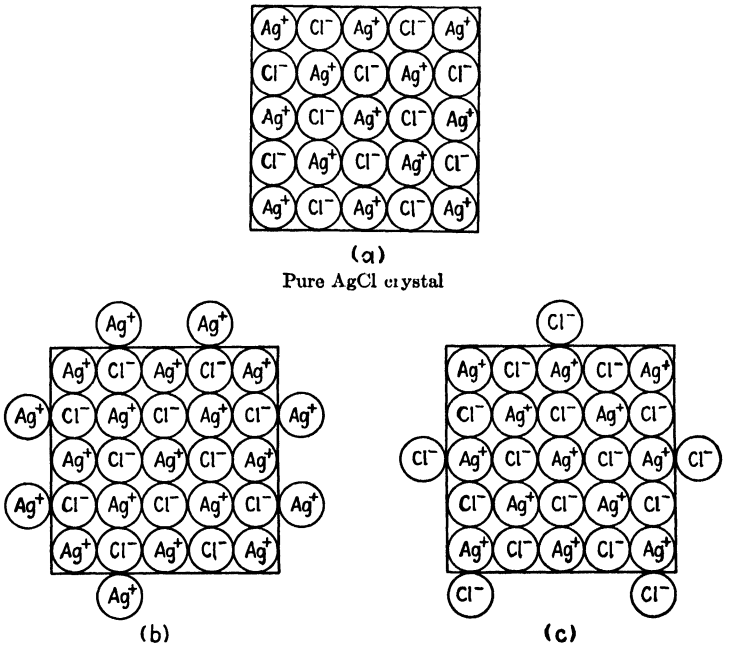


FIG. 14.—Silver chloride crystals in different environments.

in this case an indefinite number of *positive* charges. Now suppose that Cl^- instead of Ag^+ is in excess in the solution. Some of the Ag^+ on the surface of the crystal (Fig. 14*a*) will attract Cl^- from the solution (Fig. 14*c*), and the particle will thus acquire an indefinite number of *negative* charges.

As would be expected, since the forces of attraction are apparently electrostatic, other kinds of ions might also be adsorbed by the solid silver chloride. As will be seen later in this chapter (see Coprecipitation Phenomena), such adsorption actually occurs; however, relatively few kinds of ions are adsorbed so

readily by silver chloride as are the ions of which the main mass of the solid is composed.

The colloid-forming characteristics of many other slightly soluble electrolytes are explained in a similar manner. Thus, it is known that many sulfides are capable of adsorbing excess sulfide ions to form colloidal solutions in which the micelles are negatively charged. In fact some of them—notably the sulfides of cadmium, nickel, and cobalt—form colloids so readily that very small amounts of sulfide ion can cause the precipitated solids to peptize.

The formation of colloids by slightly soluble hydroxides has been explained in a manner similar to that described above, H^+ being presumably held to the surface of the micelles by the attraction of the surface OH^- for the positively charged H^+. More recently, however, an idea based somewhat on the theories of complex ions has been postulated. Consider, for example, the formation of a ferric hydroxide colloid when a solution of a ferric salt is added to hot water. It is known that the ferric ions present in any dilute aqueous solution are hydrated, the formula usually being written $Fe(H_2O)_6^{+++}$. Suppose that one of the water molecules in this ion loses a hydrogen ion.* A particle will be left that contains *two* positive charges instead of the original three and that contains one hydroxyl group:

$$Fe(H_2O)_6^{+++} \rightleftharpoons Fe(H_2O)_5(OH)^{++} + H^+$$

Now although the original water of hydration presumably was held to the Fe^{+++} through an electron pair on the oxygen atom in the water molecule, the hydroxyl ion is held by an electrovalent bond. Consequently, the oxygen atom in the OH^- still has a usable electron pair. A second hydrated ferric ion which has lost one molecule of water may therefore attach itself to an unoccupied pair in the hydroxyl group, giving a particle having almost double the mass of a single hydrated ferric ion:

$$Fe(H_2O)_5(OH)^{++} + Fe(H_2O)_6^{+++} \rightarrow [Fe(H_2O)_5O{:}Fe(H_2O)_5]^{+++++} + H_2O$$

(H)

* It may equally well be supposed that the water molecule is merely replaced by an OH^- furnished by the ionization of the solvent. The actual mechanism by means of which the OH^- gets into the ion is immaterial in so far as this discussion is concerned.

If this second ion also loses a proton, leaving it with a hydroxyl ion, a third ferric ion may attach itself to the oxygen in this new hydroxyl group to form $[Fe(H_2O)_5O{:}Fe(H_2O)_4O{:}Fe(H_2O)_5]^{+7}$. In this way *enormous chains* or *clusters* of partly hydrated basic ions may form. The clusters will be positively charged, owing to the charges on the only partly neutralized ferric ions.

Methods of Coagulating Colloids. From a knowledge of the nature of colloids and of the ways in which they probably form, it is possible to deduce methods of preventing the formation of colloids and of precipitating them whenever they form. Some of these are as follows:

1. Add the reagent *a little at a time,* with stirring, *until sufficient reagent has been used* to precipitate everything that should be precipitated, but *avoid* the use of a *large excess* of reagent. An excess is, of course, unavoidable if completeness of reaction is to be assured. A *small* excess is not harmful, however, owing to the fact that a large concentration of the reagent is usually needed before the tendency to peptize manifests itself to any marked extent.

An illustration of the need for sufficient reagent to prevent the formation of colloids is found in Cation Group III. Quite frequently a very turbid mixture that cannot be filtered is obtained during the precipitation of this group. As a rule if more ammonium hydroxide and more hydrogen sulfide is added, more precipitate forms at once and the colloidal material disappears. When such colloidal solutions form, therefore, it is well to add a little more reagent to see if insufficient reagent is not the cause.

2. *Moderately high concentrations of electrolytes* tend to neutralize the charges on the micelles and thus hasten coagulation. The *anions* of the electrolyte used are effective in precipitating positive colloids, whereas the *cations* perform the same task for negatively charged colloids. For this purpose bivalent ions are more than twice as effective as the same molar concentration of univalent ions, while trivalent ions are much more effective than a chemically equivalent concentration of bivalent ions. Unfortunately, the addition of bivalent or trivalent ions to an unknown is seldom permissible, either because such ions are of a kind for which tests are to be made later or because they will interfere with the separation and identification of the original ions. For

example, if magnesium sulfate is used to coagulate a Cation Group III precipitate when that group is being precipitated from a general unknown, the sulfates of barium, strontium, and some calcium from Group IV will precipitate with Group III. Also, tests performed later for Mg^{++} will have no significance, since that ion is known to have been added. Consequently, unless other electrolytes are already present in sufficient concentration,* ammonium nitrate is frequently used to prevent the formation of colloids during cation analysis; for the ammonium ion test is always made on the original unknown, and neither the ammonium nor the nitrate interferes with the subsequent separations. Illustrations of the use of this substance to prevent peptization are found in the wash solutions used on the Cation Group II and III precipitates (see analytical procedure for these groups).

Frequently substances whose colloids would have opposite kinds of charges are formed simultaneously. In such cases the micelles, if formed at all, neutralize each other and thus readily precipitate.

3. Quite often *merely heating* a colloidal solution for a while will cause coagulation. This is effective in many cases and should always be tried before one resorts to the addition of electrolytes.

Coprecipitation Phenomena. So far precipitations have been treated as if the resulting products were pure, no consideration having been given to the possibility of impurities being dragged down with the precipitates. For a number of reasons, however, it is exceedingly difficult to precipitate substances without contamination. Some of the phenomena responsible for this are discussed in the following section.

Adsorption. It was pointed out in the previous section that the addition of electrolytes caused colloids to precipitate owing to the neutralization of the charges on the micelles by ions of opposite charge. Obviously, the only way in which an ion can neutralize any part of the total charge on a micelle is by attaching

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* Quite often the unknown itself contains enough dissolved electrolytes, in the form of the substances for which tests are being made, to prevent the formation of colloids. In other cases, *e.g.*, at the beginning of the Cation Group III precipitation where ammonium chloride is added as a buffer, the reagents themselves may give a sufficiently great concentration of ions.

itself more or less firmly to the micelle. Consequently, whenever a dispersed phase is coagulated by the action of electrolytes, the coagulating ion precipitates with the solid, even though the ion would normally form no slightly soluble compounds with any substance present. This phenomenon, which is one type of *adsorption*, is obviously a surface process.

Even though no colloid formation has been apparent, adsorption usually accompanies any precipitation. As an illustration, suppose that Cation Group II is being precipitated and that the electrolytes preventing the formation of colloids are compounds of the cations of the later groups. The micelles present in colloidal solutions of metal sulfides are usually negative; consequently, the ions that cause coagulation must be cations. This means that some of the cations of the later groups will be carried down with the Group II precipitate. Thus tests for some of the cations of later groups will be weakened by loss of these cations, and interference in the tests for the members of Cation Group II may be expected. Fortunately, the magnitude of this occurrence is not usually great enough to cause serious interference unless the unknown contains a large amount of any one cation and only a small quantity of the other.

Inclusion. Certain gelatinous precipitates, such as aluminum and ferric hydroxides, consist of extremely tiny crystals intermeshed in such a fashion as to form minute pockets in which are enclosed small portions of the original solution. Washing does not remove these protected portions of solution; and when the precipitate is redissolved, the resulting solution is contaminated with ions that should have remained in the original filtrate. In the analytical procedure used in some texts, ferric, chromic, and aluminum hydroxides of a less gelatinous, more crystalline nature are formed from hydroxyl ions furnished by the hydrolysis of ammonium benzoate. The precipitation with ammonium benzoate has been recommended by Kolthoff as reducing the error due to inclusion. In general, inclusion is lessened by slow precipitation or by digesting (heating the mixture of precipitate and mother liquor) for some time.

Mixed-crystal Formation. Most of the trouble caused by coprecipitation is due to the formation of mixed crystals of isomorphous compounds. *Isomorphous compounds* are those having the *same type of crystalline structure* and *atoms of nearly the*

the same size. Cadmium sulfide and barium sulfide are isomorphous, as are also sodium chloride and potassium chloride. When cadmium sulfide is precipitated in Group II, some barium ions occasionally attach themselves momentarily to the sulfide ions on the surface of the cadmium sulfide. Many of these barium ions escape into the solution again, but some of them fail to escape before more cadmium and sulfide ions attach themselves to the surface of the solid and enclose the barium ions within the crystal. This results not only in contaminating the precipitate with barium ion but also, in extreme cases where cadmium ion concentration is much higher than that of the barium ion, in removing so much barium that the test for the latter in Group IV is missed entirely. In case the cadmium ion concentration is extremely high, therefore, it is often necessary to redissolve the Group II precipitate in as small a volume of acid as possible and reprecipitate with hydrogen sulfide. In this solution, more of the barium ion will escape coprecipitation, and the two filtrates, combined and concentrated by evaporation, may be used for the barium test. Such a procedure is frequently used in quantitative analysis where separations must be quite complete.

Occasionally, however, coprecipitation can be of service to the analyst. For example, the tests for zinc, copper, and cobalt, using ammonium mercuric thiocyanate reagent, depend, for their greatest sensitivity, on the formation of mixed crystals. The test is made for cobalt or copper by adding zinc ion to the solution and then adding the reagent. In the absence of cobalt or copper the following reaction occurs:

$$Zn^{++} + Hg(SCN)_4^{=} \rightarrow ZnHg(SCN)_{4(\text{white ppt})}$$

If cobalt is present, the following additional reaction occurs:

$$Co^{++} + Hg(SCN)_4^{=} \rightarrow CoHg(SCN)_{4(\text{blue ppt})}$$

If both ions are present, mixed crystals of these two compounds form, the precipitate having a blue color the depth of which will be greater the larger the concentration of cobalt ion. This test will detect cobalt in solutions that would give no precipitate whatsoever with the reagent in the absence of zinc.

In the case of the copper and zinc tests the same type of reaction is involved. However, if the copper is present in concentra-

tions greater than the zinc, an apple-green precipitate of copper mercuric thiocyanate will form.

SUMMARY

The components of a colloidal solution are known as the *dispersed* phase and the *dispersing phase*, respectively. The individual particles of the dispersed phase are called *micelles*.

In analytical work, colloidal solutions are usually formed either by *condensation* or by *peptization*. Condensation is the formation of colloids by the reaction of soluble substances to form slightly soluble products; the latter is the more or less spontaneous passing of a precipitate into the colloidal form.

The micelles in a colloidal solution are too small to settle rapidly or to be removed by filtration, and they carry an indefinite number of electrical charges. In some cases the kind of charge can be predetermined by the method whereby the colloid is formed. Thus if the dispersed phase is an electrolyte formed by condensation, the use of an excess of the source of the cation will usually yield a positive colloid owing to adsorption of the cation, while the use of an excess of the anion will yield a negative colloid.

Substances that readily form colloids precipitate best (1) if exactly equivalent quantities of reactants are used to form the precipitate, (2) if considerable amounts of soluble electrolytes other than the reactants are present in the solution, and (3) if the solution is hot

Adsorption occurs when any foreign material clings to the surface of precipitates or dispersed material. The precipitation of colloidal material by the action of electrolytes always results in adsorption of the precipitating ions.

Inclusion occurs when rapid precipitation or the formation of a fluffy precipitate results in the trapping of some of the mother liquor within the precipitate. Inclusion is lessened by either *slow* precipitation or *digestion*.

Mixed-crystals result when a precipitate forms in such a way as to include within its lattice some of the ions of a compound with which it is *isomorphous*, *i.e.*, a compound whose crystal lattice is of the same type and whose ions are of nearly the same size as those of the main precipitate.

Although coprecipitation phenomena result in incomplete separations, they are occasionally put to good use, *e.g.*, in the

ammonium mercuric thiocyanate tests for zinc, cobalt, and copper.

Review Questions

1. Define: (*a*) dispersed phase, (*b*) micelle, (*c*) condensation, (*d*) peptization, (*e*) coagulation, (*f*) adsorption, (*g*) inclusion, (*h*) isomorphous compounds.

2. Give two reasons why colloidal substances do not precipitate readily.

3. How is it possible to prevent the formation of colloidal solutions?

4. Describe the function of each component in the wash solution used on the precipitate in Cation Group III.

5. How is it possible to hasten the coagulation of colloidal material that is dispersed in water?

6. What relationship exists between the valence of an ion and its ability to coagulate colloidal material?

7. If barium sulfate is being precipitated from a dilute solution of barium chloride by the addition of a solution of potassium sulfate, under what conditions would any colloidal barium sulfate be negatively charged? Positively charged? What conditions would be most likely to produce no colloidal material?

8. It has been found that on the addition of a solution of potassium chromate to solid silver iodide the silver iodide tends to peptize. Explain this phenomenon, and tell what kind of charges the resulting micelles are most likely to have.

9. Explain why coprecipitation causes trouble in analytical work.

10. How may coprecipitation be useful in testing for copper? For cobalt? For zinc?

11. How is adsorption used in testing for aluminum? (See notes on aluminum in the analytical procedure.)

CHAPTER X

OXIDATION-REDUCTION REACTIONS

Nature of Oxidation and Reduction. Thus far most of the reactions discussed have been of the type in which simple exchanges of radicals or ions or simple combinations of ions occurred. In many reactions, however, changes occur in the *valences* of some of the elements involved in the reaction. Such reactions are classified as *oxidation-reduction reactions.*

As a simple example, consider the reaction between a solution of bromine in water and a piece of metallic copper. Using the ordinary molecular equation, this reaction would be expressed as follows:

$$Cu + Br_2 \rightarrow CuBr_2 \qquad (1)$$

The product, $CuBr_2$, however, is a salt; consequently, since it is in solution, a more accurate representation of the facts would be

$$Cu^0 + Br_2^0 \rightarrow Cu^{++} + 2Br^- \qquad (2)$$

Now suppose that we examine each of the reactants to see what has happened to it. It will be recalled from studies of atomic structure and of what happens when atoms react that the valence of an unreacted atom is zero; also it will be remembered that a typical metal gets its positive valence by losing electrons, whereas a nonmetal gets its negative valences by taking on electrons. With these facts in mind, it becomes possible to write equations for the reaction undergone by each of the foregoing reactants as follows:

$$Cu^0 - 2 \text{ electrons } (\epsilon) \rightarrow Cu^{++} \qquad (3)$$
$$Br_2^0 + 2 \text{ electrons } (\epsilon) \rightarrow 2\,Br^- \qquad (4)$$

Now by definition the *loss of electrons* is *oxidation*, whereas the *gain of electrons* is *reduction.* The copper, therefore, is oxidized by the bromine, and the bromine is reduced by the copper. Consequently, to express the functions of these reactants, it is

customary to speak of the copper (the *electron donor*) as a *reducing agent*, or *reductant*, and the bromine (the *electron acceptor*) as an *oxidizing agent*, or *oxidant*.

If other combination reactions are examined in a similar way, the general conclusion is reached that the chemical *combination* of any two elements is an *oxidation-reduction reaction*. Likewise, *decompositions*

$$2HI \rightarrow H_2 + I_2$$
$$2H^+ + 2\epsilon \rightarrow H_2^0$$
$$2I^- - 2\epsilon \rightarrow I_2^0$$

and *displacements*

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$
$$Zn^0 - 2\epsilon \rightarrow Zn^{++}$$
$$Cu^{++} + 2\epsilon \rightarrow Cu^0$$

are oxidation-reduction reactions. In addition to these simple types, however, there are many important oxidation-reduction reactions of a more complex nature. Some of these, such as the reaction between potassium permanganate and hydrochloric acid to produce chlorine

$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$
$$MnO_4^- + 8H^+ + 5\epsilon \rightarrow Mn^{++} + 4H_2O$$
$$2Cl^- - 2\epsilon \rightarrow Cl_2$$

should already be familiar because they are reactions studied in general chemistry. Others, such as the reduction of arsenate to arsenite by the action of iodides in acid solution (see the precipitation of Cation Group II)

$$AsO_4^{\equiv} + 2H^+ + 2I^- \rightarrow AsO_3^{\equiv} + H_2O + I_2$$

are used in qualitative analysis; still others, such as the reaction between potassium dichromate and ferrous sulfate

$$K_2Cr_2O_7 + 6FeSO_4 + 8H_2SO_4 \rightarrow 2KHSO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$
$$Cr_2O_7^{=} + 14H^+ + 6\epsilon \rightarrow 2Cr^{+++} + 7H_2O$$
$$Fe^{++} - \epsilon \rightarrow Fe^{+++}$$

find important applications in quantitative analysis.

Balancing Oxidation-reduction Equations. Although many simple oxidation-reduction equations may be balanced easily by

the inspection method, the more complex types are often difficult to balance in that manner. The characteristics discussed in the preceding section, however, suggest a number of methods, any of which systematizes that procedure greatly. These methods are based on the fact that the *number of electrons yielded* by the reducing agent must, in the *balanced* equation, be equal to the *number of electrons accepted* by the oxidizing agent. Two methods will be discussed here.

Ion-electron Method. Suppose that it is desired to balance the equation

$$KMnO_4 + HCl \rightarrow KCl + MnCl_2 + H_2O + Cl_2$$

1. First write the equation as if all the reactants and the products were in solution. In that case, all the *strong* electrolytes would be written as ions:

$$K^+ + MnO_4^- + H^+ + Cl^- \rightarrow K^+ + Cl^- + Mn^{++} + H_2O + Cl_2$$

2. Now from the foregoing equation it can be seen that *some* of the ions *undergo no reaction* whatsoever. Thus K^+ and some of the Cl^-, *i.e.*, that Cl^- which is finally supposed to be associated with the K^+ and the Mn^{++} among the products, remain in the same form at the end of the reaction. Evidently these ions take no active part in the reaction. Consequently, they may be removed from the equation temporarily, and the reaction may be written*

$$MnO_4^- + H^+ + Cl^- \rightarrow Mn^{++} + H_2O + Cl_2$$

3. It can be seen that the two atoms undergoing valence changes are the manganese in the MnO_4^- and the chlorine. The reactions undergone by the ions in which these atoms occur should therefore be written

$$MnO_4^- + H^+ \rightarrow Mn^{++} + H_2O$$
$$Cl^- \rightarrow Cl_2^0$$

Balancing each of these equations by inspection gives the equations

* The Cl^- is retained on the left side of the equation, but it must be remembered that this *represents only that which is oxidized to* Cl_2.

$$MnO_4^- + 8H^+ \rightarrow Mn^{++} + 4H_2O$$
$$2Cl^- \rightarrow Cl_2$$

4. Next considering the equations separately, add *algebraically* all the charges on the left side of the equation, do the same for the right side, and then subtract the charges on the right from those on the left. The answer represents the number of electrons that must be *added* (algebraically) to the left side of the equation. Thus for the MnO_4^-,

$$[-1 + (+8)] - [+2 + 4(0)] = +5$$

while for the chloride ions,

$$-2 - 0 = -2$$

Consequently, the equations become

$$MnO_4^- + 8H^+ + 5\epsilon \rightarrow Mn^{++} + 4H_2O$$
$$2Cl^- - 2\epsilon \rightarrow Cl_2$$

5. To balance these equations with respect to each other, however, it is necessary to have *equal numbers of electrons* in them. This will be the case if the first equation is multiplied by two and the second equation is multiplied by five:

$$2(MnO_4^- + 8H^+ + 5\epsilon \rightarrow Mn^{++} + 4H_2O)$$
$$5(2Cl^- - 2\epsilon \rightarrow Cl_2)$$

By multiplying through and then *adding* the resulting equations one obtains

$$2MnO_4^- + 16H^+ + 10\epsilon \rightarrow 2Mn^{++} + 8H_2O$$
$$10Cl^- \qquad\qquad - 10\epsilon \rightarrow 5Cl_2$$
$$\overline{2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{++} + 8H_2O + 5Cl_2}$$

6. Actually the foregoing equation is balanced and represents the true reaction. The molecular equation is of importance in many cases, however; consequently the data included in the ionic equation should be used to balance the original molecular equation. To do so, remember that in this method of balancing the equation, *no hydrogen, oxygen,* or *manganese,* but all the potassium ions and some of the chloride ions were left out. Evidently, therefore, the preceding equation *fixes* the number of MnO_4^- and

of H^+, as well as the number of Mn^{++}, H_2O, and Cl_2. The number of these, therefore, are fixed in the original equation:

$$2KMnO_4 + 16HCl \rightarrow KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

When this is done, only the KCl remains unbalanced; and since the number of $KMnO_4$ is fixed at two (owing to the fact that the number of MnO_4^- was fixed) there must be 2KCl to take care of the potassium. The balanced equation, therefore, is

$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

Valence-electron Method. To illustrate this method consider the same equation as before so as to make a comparison of the two methods easy:

$$KMnO_4 + HCl \rightarrow KCl + MnCl_2 + H_2O + Cl_2$$

1. Pick out those *elements* which undergo changes in valence, and write these changes, in terms of the gain or loss of electrons, as unbalanced equations. In the preceding equation, Mn^{+7} changes to Mn^{+2}, and some of the Cl^- changes to Cl_2:

$$Mn^{+7} + \epsilon \rightarrow Mn^{+2}$$
$$Cl^- - \epsilon \rightarrow Cl_2$$

2. Balance these equations with respect to both *atoms* and *electrons*,

$$Mn^{+7} + 5\epsilon \rightarrow Mn^{+2}$$
$$2Cl^- - 2\epsilon \rightarrow Cl_2$$

then multiply these equations by the smallest numbers that will give equal numbers of electrons in the two equations:

$$2(Mn^{+7} + 5\epsilon \rightarrow Mn^{+2})$$
$$5(2Cl^- - 2\epsilon \rightarrow Cl_2)$$

3. After multiplying through, add the equations together to form a composite equation (the electrons will disappear by cancellation):

$$2Mn^{+7} + 10\epsilon \rightarrow 2Mn^{+2}$$
$$10Cl^- - 10\epsilon \rightarrow 5Cl_2$$
$$\overline{2Mn^{+7} + 10Cl^- \rightarrow 2Mn^{+2} + 5Cl_2}$$

4. Using the fact that the numbers obtained here for manganese and Cl_2 are *fixed,* balance the original molecular equation as far as possible. Note, however, that the number of the Cl^- is *not* fixed by the results given above. Therefore the equation becomes

$$2KMnO_4 + HCl \rightarrow KCl + 2MnCl_2 + H_2O + 5Cl_2$$

5. Finally, starting with the left side and balancing each element in turn, complete the process by inspection. Thus $2KMnO_4$ means that two potassium atoms must be used. These form 2KCl. The manganese is already balanced. $2KMnO_4$ means eight oxygen atoms; therefore, since none of the products but water contains oxygen, $8H_2O$ must appear among the products. Hydrogen, which is next in the equation, also forms no product but water. To furnish the 16 hydrogens required by the eight water molecules, 16HCl is necessary. Finally, a check of the chlorine shows that the equation is balanced.

$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

Although the detailed steps used in balancing equations will not be repeated, a number of balanced equations together with their half-cell reactions will appear in the following sections. The technique of balancing such equations can best be learned by applying each of these two methods to the equations and checking results against the balanced equations illustrated.

Oxidizing Potentials. It is a well-known fact that both oxidizing agents and reducing agents vary widely in ability to oxidize or reduce. For example, one would never use iodine to oxidize a bromide to form bromine, for the iodine is not a sufficiently strong oxidizing agent to do so. On the other hand, iodine is capable of oxidizing sulfite to sulfate, while chlorine, which is a much stronger oxidizing agent than is iodine, can oxidize either bromide or sulfite with ease.

A number of reagents, of course, can be tried out whenever it is desired to oxidize or reduce a given substance, and in that way a suitable reagent for the purpose can be found. Such a procedure is inconvenient and time-consuming, however; consequently, a much better method has been devised.

At the beginning of this chapter the reaction between metallic copper and a solution of bromine was used to illustrate oxidation

and reduction. In that illustration it was assumed that the reactants were actually in contact with each other, in which case the exchange of electrons indicated in equations (3) and (4) took place directly between the copper and the bromine. Now suppose that the copper and bromine are not allowed to come into contact with each other but instead that the copper is immersed in cupric sulfate solution in one container (see Fig. 15), while the bromine, in potassium bromide solution, is placed in another con-

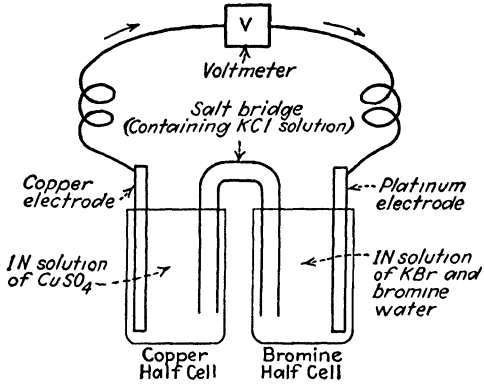


FIG. 15.—Arrangement of a copper bromine cell.

tainer with an inert electrode such as platinum. The two *half-cells** are connected by an inverted U tube filled with a solution of an electrolyte such as potassium chloride. Now if the electrodes are connected by a metallic conductor, a current will flow between the electrodes. The reaction

$$Cu - 2\epsilon \rightarrow Cu^{++} \qquad (3)$$

takes place at the copper electrode, the electrons from this reaction accumulating on the metallic copper. From this electrode

* A *half-cell* is a metal in contact with a solution containing its ions or an inert electrode in contact with a solution containing both the oxidized and reduced forms of a substance that is capable of losing or gaining electrons. Thus a copper half-cell consists of metallic copper in contact with a solution containing Cu^{++}. A bromine half-cell consists of an electrode of platinum, gold, or other very inactive metal in contact with a solution that contains free bromine and bromide ions (the reduced form of bromine).

A combination of any two half-cells is known as a *cell.*

the electrons pass through the outer circuit to the platinum electrode at whose surface they are picked up by the bromine to give the reaction

$$Br_2 + 2\epsilon \rightarrow 2Br^- \qquad (4)$$

With this arrangement, therefore, the reaction

$$Cu + Br_2 \rightarrow Cu^{++} + 2Br^-$$

can take place even though the copper and the bromine are not in contact with each other.

When different half-cells are assembled in the manner described above, the *voltages* of the different cells are found to be different. For example, the voltage of a zinc-bromine cell is *larger* than that of a copper-bromine cell. The explanation for this difference is easily understood if one remembers that zinc loses electrons more readily than copper does. Evidently this difference is a measure, therefore, of the relative ease with which zinc and copper give up electrons—or viewed differently, it is a measure of the relative activities of zinc and copper as reducing agents. On the other hand, if a zinc half-cell is combined with a chlorine half-cell, the voltage will be greater than was obtained with the zinc-bromine combination. It is obvious, therefore, that the voltage measured for any cell depends upon the nature of *both half-cells* and that it is a measure of the tendency for the full reaction represented by the combination to occur.

To measure every combination on which such information might be desirable would be an almost endless task; but if the component of the voltage contributed by each half-cell (sometimes called the *electrode potential*) could be determined, then the voltage of any combination could be easily calculated. Although it is not feasible to do this, usable values have been obtained by measuring each against the *same standard half-cell.* The standard used is the *normal hydrogen electrode.* This is a half-cell in which pure hydrogen gas at 1 atm. pressure is bubbled slowly over an especially prepared platinum electrode dipping into a solution that is $1M$ with H^+. Since the platinum electrode is inert in the presence of the more active reducing agent, hydrogen, the half-cell reaction really involves the change from H_2 to H^+ and the reverse. The normal hydrogen electrode is *arbitrarily* assumed to have a zero potential; consequently, the voltage of

any combination in which the standard is used is arbitrarily assumed to be due to the half-cell other than the standard.

A list of the potentials for various half-cell reactions is given in Tables VII and VIII in the Appendix. In Table VII the reactions are arranged according to electrode potentials; in Table VIII the same reactions are organized under the key element involved, *i.e.*, the element undergoing the valence change.

A study of Table VII reveals a number of interesting and useful facts. In the first place, all the reactions listed are *reversible;* consequently, the oxidized form of any substance in the list *theoretically is capable of acting as an oxidizing agent,* while the *reduced form theoretically* is capable of *acting as a reducing agent.*

Thus one oxidized form of bromine is elementary bromine; in that form it may oxidize strong reducing agents such as $SO_3^{=}$:

$$SO_3^{=} + H_2O + Br_2 \rightarrow SO_4^{=} + 2H^+ + 2Br^-$$

On the other hand, the reduced form of bromine is Br^-; in that form this element is capable of reducing strong oxidizing agents such as Cl_2:

$$2Br^- + Cl_2 \rightarrow Br_2 + 2Cl^-$$

The second point to note is the fact that if each substance is considered *in its reduced form,* those at the *top* of the list in Table VII (*i.e.*, with the most *negative* potential) have the greatest tendency to *lose* electrons. Conversely, *in the oxidized form,* those at the *bottom* (*i.e.*, with the most *positive* or *least negative* potential) have the greatest tendency to *accept* electrons, *i.e.,* to act as oxidizing agents. Consequently, the reduced form of any substance is *theoretically* capable of reducing the oxidized form of any substance *below* it in the table, while the oxidized form of any substance should be able to oxidize the reduced form of any substance *above* it.

The third point is the fact that for any pair of substances whose relative positions indicate the possibility of their reacting, the greater the difference between their potentials the more nearly complete the reaction will be at equilibrium.

These generalizations must be qualified, for it must be remembered that they say nothing about the *rate* of reaction. For example, the reaction between hydrogen and oxygen to form water consists of the two half-reactions

$$2H_2 - 4\epsilon \rightarrow 4H^+$$
$$O_2 + 4H^+ + 4\epsilon \rightarrow 2H_2O$$

The large difference (1.23 volts) between the potentials for these two reactions indicates that the reaction should be very complete. On the other hand, these potentials are measured at 25°C., and it is well known that mixtures of these two gases can stand at 25°C. for years without any appreciable reaction occurring. Consequently, although with equilibrium established the reaction should be very complete, it is quite impractical under the conditions given here.

One must consider not only if the reaction will be rapid enough to be useful but also whether or not another possible reaction might occur instead of the one desired. To illustrate, consider the reduction of Sn^{++++} to Sn^{++}, in the test for tin in Cation Group II. The reduction takes place in a strongly acid solution, and the reducing agents used are metals. Three of the metals that have been used in different suggested procedures are zinc, aluminum, and lead. Now it will be noted that the half-reactions of all three metals are above the reaction

$$Sn^{++++} + 2\epsilon \rightarrow Sn^{++}$$

Also, however, the half-reactions for all three metals are above the reaction

$$2H^+ + 2\epsilon \rightarrow H_2$$

and the H^+ concentration in the solution is large. On still closer examination, the half-reactions for two of these metals, aluminum and zinc, are found to be well above the reaction

$$Sn^{++} + 2\epsilon \rightarrow Sn^\circ$$

Obviously any of these three metals should be able to reduce Sn^{++++} to Sn^{++}, and in practice it is found that they are capable of so doing. The reduction with lead, however, is quite slow; consequently, the more active metals are frequently used. When aluminum or zinc is used, however, there will be a marked competition between the reaction of Sn^{++++} and that of H^+ with the metal. This competition is so serious that it is possible, in solutions whose H^+ concentration is large and whose Sn^{++++} concentration is low, for a surprising amount of either aluminum or

zinc to react to produce hydrogen, with only insignificant quantities of Sn^{++++} being reduced to Sn^{++}. On the other hand, if the H^+ concentration is low, the Sn^{++++} is reduced—but the Sn^{++} formed is reduced further to form metallic tin. It is obvious, therefore, that the rapid reduction of Sn^{++++} to Sn^{++} is by no means simple. As a matter of fact, frequently it is easier to perform the reduction with zinc or aluminum in a solution of low H^+ concentration and then dissolve any precipitated tin and excess metal by adding more hydrochloric acid.

Equilibrium Constants. Although for combinations of half-reactions whose electrode potentials differ greatly the probability of reaction occurring can be determined at a glance, frequently the differences in potentials are so small as to make such information less apparent. As has been illustrated in previous chapters, however, if the equilibrium constant for the reaction could be determined, the probable completeness of reaction could be calculated.

From the potentials listed in Tables VII and VIII equilibrium constants can be calculated for the reaction represented by any pair of these electrode reactions. Although it is unnecessary to show how the equation is developed, the difference between the potentials for two half-reactions, ΔE, is related to the equilibrium constant, K, by the equation

$$\Delta E = \frac{0.059}{n} \log K$$

in which n is the *number of electrons* indicated in the balancing of the complete equation as *having been transferred.* To illustrate how these terms are obtained and how K may be evaluated, consider the reaction

$$Zn + 2Ag^+ \rightarrow Zn^{++} + 2Ag$$

The half-reactions and the corresponding potentials as obtained from Table VIII and adjusted so the numbers of electrons are equal, are

$$Zn - 2\epsilon \rightarrow Zn^{++} \qquad E = -0.762 \text{ volt}$$
$$2Ag^+ + 2\epsilon \rightarrow 2Ag \qquad E = 0.797 \text{ volt}^*$$

* Note that though the equation for the reduction of Ag^+ is doubled throughout so that the number of electrons used will be the same as the number furnished by the zinc, the *potential* is *not* doubled.

Although the reaction written here for the reduction of Ag^+ is in exactly the same form as it appears in the table, that for the oxidation of the zinc is just the reverse of the one in the table. Consequently, although the equation must be left as it is so that the addition of the half-reactions can be used as a check, *change the sign of the electrode potential* for the zinc (the electron donor), then add the two potentials *algebraically.** Similarly add the two equations, canceling the electrons.

$$\begin{array}{rl} Zn \rightarrow 2\epsilon + Zn^{++} & +0.762 \\ 2Ag^+ + 2\epsilon \rightarrow 2Ag & +0.797 \\ \hline Zn + 2Ag^+ \rightarrow Zn^{++} + 2Ag & \Delta E = +1.559 \text{ volts} \end{array}$$

By comparing the chemical equation here with that at the beginning, it is possible to be sure that the proper steps have been taken. Now the potential difference, ΔE, is 1.559 volts, while the number of electrons, n, exchanged during the reaction is *two*. Consequently the equation

$$\Delta E = \frac{0.059}{n} \log K$$

becomes

$$1.559 = \frac{0.059}{2} \log K$$

$$\therefore \log K = 52.84$$

$$\therefore K = 10^{52.84} = 9.2 \times 10^{52}$$

Now by applying the law of mass action to the equilibrium

$$Zn + 2Ag^+ \rightleftharpoons Zn^{++} + 2Ag$$

the following expression is obtained:

$$\frac{[Zn^{++}][Ag]^2}{[Zn][Ag^+]^2} = K$$

For reasons that are beyond the scope of this book the "concentration" of any solid reactant may be considered unity.

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* Actually this change of signs followed by algebraic addition amounts to the same thing as if one followed the rule of *subtracting algebraically the* potential of the *reductant* or *electron donor* in the reaction from that of the *oxidant* or *electron acceptor*, *i.e.*, in this case, the potential of the zinc from that of the silver.

Then [Zn] and [Ag] are each equal to *one* and thus disappear from the equation, which becomes

$$\frac{[Zn^{++}]}{[Ag^{+}]^2} = K = 9.2 \times 10^{52}$$

The reaction, therefore, should proceed until no significant quantity of silver ions remains.

To illustrate further, suppose that it is desired to determine the probable feasibility of

$$Ag^0 + Cu^{++} \rightarrow Ag^{+} + Cu^0$$

The half-reactions and potentials would be

$$2Ag^0 - 2\epsilon \rightarrow 2Ag^{+} \qquad E = +0.797 \text{ volt}$$
$$Cu^{++} + 2\epsilon \rightarrow Cu^0 \qquad E = +0.344 \text{ volt}$$

In this case, the equation for the *silver* is the one that does not correspond in form to that given in the table. Consequently, the voltage, +0.797, must be changed to −0.797. Adding the whole, one obtains

$$\begin{array}{rr} 2Ag - 2\epsilon \rightarrow 2Ag^{+} & -0.797 \\ Cu^{++} + 2\epsilon \rightarrow Cu & +0.344 \\ \hline 2Ag + Cu^{++} \rightarrow 2Ag^{+} + Cu & \Delta E = -0.453 \end{array}$$

From this, therefore, it can be calculated that

$$\log K = -15.35$$
$$\therefore K = 10^{-15.35} = 4.5 \times 10^{-16}$$

From the expression for the equilibrium constant,

$$\frac{[Ag^{+}]^2}{[Cu^{++}]} = K = 4.5 \times 10^{-16}$$

then, it is easily seen that silver will not displace copper to any significant extent.

By considering these two examples it is clear that if the potential difference, ΔE, is *negative*, the reaction will not proceed far spontaneously, the reaction being less complete the *smaller* the value.*

Some Common Oxidizing Agents (Electron Acceptors). As can be seen from any good table of oxidizing-reducing potentials,

* It must be remembered that, for example, −4 is smaller than −2.

many substances are capable, under the proper conditions, of acting as oxidizing agents. The nonmetals, *e.g.*, chlorine, bromine, iodine, oxygen, and sulfur, are among the more usable *elements* having oxidizing properties. The oxidizing actions of these elements sometimes involve their reaction with H^+, as illustrated by the half-reaction for oxygen:

$$O_2 + 4H^+ + 4\epsilon \rightarrow 2H_2O$$

With the halogens, however, the reaction is a simple one in which the element takes on electrons:

$$Cl_2 + 2\epsilon \rightarrow 2Cl^-$$

The oxidizing agents most commonly used in qualitative and quantitative analysis are the compounds potassium permanganate, $KMnO_4$; potassium chromate, K_2CrO_4; nitric acid; sodium or hydrogen peroxide, and ammonium persulfate, $(NH_4)_2S_2O_8$. In each of these compounds, with the possible exception of the peroxides, the *anion* is the real oxidizing agent. Owing to the importance of these reagents, a few useful facts concerning each should prove helpful.

Permanganates undergo different reactions in acid solutions from those in neutral or alkaline solution. Thus in solutions of relatively high acidity the reaction for the reduction of permanganate ion is

$$MnO_4^- + 8H^+ + 5\epsilon \rightarrow Mn^{++} + 2H_2O$$

while in neutral or alkaline solutions the reaction is

$$MnO_4^- + 4H^+ + 3\epsilon \rightarrow MnO_2 + 2H_2O$$

From these equations it would seem that both reactions should be favored by a high concentration of H^+. As a matter of fact, such is the case with the first reaction; the second reaction, however, is not apparent if the H^+ concentration is too great, for in highly acid solutions, MnO_2 is readily reduced further:

$$MnO_2 + 4H^+ + 2\epsilon \rightarrow Mn^{++} + 2H_2O$$

Chromates or dichromates are somewhat weaker oxidizing agents than are permanganates—in fact, MnO_4^- in acid solution is

capable of oxidizing Cr^{+++} to $Cr_2O_7^{=}$. The half-reaction for $Cr_2O_7^{=}$ is

$$Cr_2O_7^{=} + 14H^+ + 6\epsilon \rightarrow 2Cr^{+++} + 7H_2O$$

Thus when $BaCrO_4$ is dissolved in hydrochloric acid (see Cation Group IV), the $CrO_4^{=}$ in the acid medium becomes $Cr_2O_7^{=}$

$$2CrO_4^{=} + 2H^+ \rightarrow Cr_2O_7^{=} + H_2O^*$$

and the $Cr_2O_7^{=}$ reacts with the hydrochloric acid as follows:

$$\begin{array}{rl} Cr_2O_7^{=} + 14H^+ + 6\epsilon & \rightarrow 2Cr^{+++} + 7H_2O \\ 6Cl^- - 6\epsilon & \rightarrow 3Cl_2 \\ \hline Cr_2O_7^{=} + 14H^+ + 6Cl^- & \rightarrow 2Cr^{+++} + 7H_2O + 3Cl_2 \end{array}$$

The reactions of *nitric acid* vary greatly with the nature of both reactants. In general (1) with *concentrated* nitric acid and *mild* reducing agents, the NO_3^- furnished by the nitric acid is reduced to NO_2:

$$NO_3^- + 2H^+ + \epsilon \rightarrow NO_2 + H_2O$$

(2) with *mild* reducing agents and *less* concentrated (1:1) nitric acid, a mixture of NO_2 and NO is produced; (3) with *dilute* nitric acid and *moderately active* reducing agents (or stronger reducing agents in very low concentration), the reduction product of NO_3^- is chiefly NO:

$$NO_3^- + 4H^+ + 3\epsilon \rightarrow NO + 2H_2O$$

With quite active metals (such as zinc, aluminum, or magnesium) *nitrate ion* may be reduced to NH_3. This is particularly true of the action of active amphoteric elements such as aluminum or zinc if the reaction is performed in an alkaline medium.

When *sodium peroxide* is used, the reactions involved may be considered as those of *hydrogen peroxide*, the latter having been formed from the sodium peroxide by hydrolysis:

$$Na_2O_2 + 2H_2O \rightarrow 2Na^+ + 2OH^- + H_2O_2$$

Many of the reactions for which hydrogen peroxide is used as an oxidizing agent are performed in an alkaline solution. This may seem surprising in view of the fact that H^+ appears as one of the

* No oxidation or reduction is involved in this reaction. Its nature was explained on p. 87 (which see).

reactants in the half-cell reaction for the reduction of hydrogen peroxide,

$$H_2O_2 + 2H^+ + 2\epsilon \rightarrow 2H_2O$$

It must be remembered, however, that the *reducing* agent may function best in an *alkaline* solution; and if such is the case, it will be a question as to which is influenced more by changes in the H^+ concentration. Thus the reaction

$$Pb^{++} + 2H_2O - 2\epsilon \rightarrow PbO_2 + 4H^+$$

is favored strongly by a *low* concentration of H^+. If the two half-reactions are added to get the complete reaction between Pb^{++} and H_2O_2

$$\begin{array}{r} Pb^{++} + 2H_2O - 2\epsilon \rightarrow PbO_2 + 4H^+ \\ H_2O_2 + 2H^+ + 2\epsilon \rightarrow 2H_2O \\ \hline Pb^{++} + 2H_2O + H_2O_2 + 2H^+ \rightarrow PbO_2 + 4H^+ + 2H_2O \end{array}$$

the simplified equation, which is found to be

$$Pb^{++} + H_2O_2 \rightarrow PbO_2 + 2H^+$$

shows that the net effect of an increase in H^+ is to *reverse* the desired reaction. It is obvious, therefore, that *both half-reactions* must be considered before any definite conclusions can be reached as to the H^+ concentration most favorable to a given reaction.

Among the strongest oxidizing agents used in the laboratory are the *persulfates*. These are used in the form of the solid potassium or ammonium salts, in the presence of Ag^+ as a catalyst. An example of the use of persulfates is the oxidation of Mn^{++} to MnO_4^- by ammonium persulfate, $(NH_4)_2S_2O_8$, as a test for manganese. The reaction is carried out by adding solid ammonium persulfate to a nitric acid solution containing Ag^+ and any Mn^{++} present. Written in molecular form, the equation is

$$5(NH_4)_2S_2O_8 + 2Mn(NO_3)_2 + 8H_2O \rightarrow 10NH_4HSO_4 + 2HMnO_4 + 4HNO_3$$

while ionic equations are

$$\begin{array}{r} 5S_2O_8^= + 10\epsilon \rightarrow 10SO_4^= \\ 2Mn^{++} + 8H_2O + 10\epsilon \rightarrow 2MnO_4^- + 16H^+ \\ \hline 5S_2O_8^= + 2Mn^{++} + 8H_2O \rightarrow 10SO_4^= + 2MnO_4^- + 16H^+ \end{array}$$

It is apparent from its half-reaction equation that the oxidizing potential of $S_2O_8^=$ is independent of the H^+ concentration, though this particular composite reaction should be repressed by high H^+ concentration.

Some Common Reducing Agents (Electron Donors). An inspection of the tables of oxidation-reduction potentials reveals the fact that the metals are reducing agents, or electron donors, the most powerful chemical reducing agents being the *active metals.* Thus sodium readily loses an electron to any receptive substance by the reaction

$$Na - \epsilon \rightarrow Na^+$$

while zinc loses two electrons

$$Zn - 2\epsilon \rightarrow Zn^{++}$$

and iron may lose two electrons or, less readily, three electrons:

$$Fe - 2\epsilon \rightarrow Fe^{++}$$
$$Fe - 3\epsilon \rightarrow Fe^{+++}*$$

In aqueous solutions, the very *active* metals are seldom used to reduce anything other than H^+ owing to the rapid rate at which they displace hydrogen from the water. In other words, the reduction of H^+ is so rapid that other dissolved substances are seldom reduced effectively. To some extent the same thing is true of any metal that is above hydrogen, *e.g.*, zinc, if the H^+ concentration of the solution is great (*cf.* page 174). Nevertheless, much use is made of metals as reducing agents, their use

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* It will be noticed that the reactions for the reducing agents are written here in a form different from that used in Tables VII and VIII. Thus in the tables the half-cell reaction for sodium is written

$$Na^+ + \epsilon \rightarrow Na$$

showing sodium *ion* (*i.e.*, the *oxidized* form of sodium) *acting as an oxidizing agent.* In this section, however, the emphasis is placed upon the *reducing action* of the *reduced* form—in this case metallic sodium. This corresponds to the form in which the equation is written when it is used to balance oxidation-reduction equations by the ion-electron method. These half-reaction equations can be changed to the form found in the tables by a simple rearrangement of terms (as in algebra):

$$Na - \epsilon \rightarrow Na^+$$
$$\therefore Na^+ + \epsilon \rightarrow Na$$

merely requiring a careful choice of metals and equally careful control of conditions under which the reduction is to be performed.

A number of substances other than metals, however, are capable of reacting as reducing agents. Of these, stannous chloride and the iodides, sulfites, and sulfides are especially important to analytical work.

Stannous chloride is one of the more powerful reducing agents, owing to the readiness with which Sn^{++} is oxidized to Sn^{++++}. Even oxygen at room temperature is capable of accomplishing this oxidation, as is also Fe^{+++}, Hg^{++}, and a number of other very mild oxidizing agents. Thus in testing for mercury and for tin, use is made of the reduction of mercuric chloride to mercurous chloride or metallic mercury, by $SnCl_2$.

Iodides in acid solutions are also excellent reducing agents. Even nitrites are reduced by iodides, as are also arsenates in *acid* solutions. The reaction with nitrite is frequently used in testing for iodides, iodine being produced and the free iodine being detected by means of starch or CCl_4. The equations concerned in the reaction between I^- and NO_2^- are

$$\begin{array}{r} 2I^- - 2\epsilon \rightarrow I_2 \\ 2NO_2^- + 4H^+ + 2\epsilon \rightarrow 2NO + 2H_2O \\ \hline 2I^- + 2NO_2^- + 4H^+ \rightarrow I_2 + 2NO + 2H_2O \end{array}$$

The reduction of $AsO_4^{\equiv}$ is used in Cation Group II and in Anion Group III to obtain $AsO_3^{\equiv}$ from which the arsenic may be more readily precipitated by hydrogen sulfide. The reactions involved in the reduction are

$$\begin{array}{r} 2I^- - 2\epsilon \rightarrow I_2 \\ AsO_4^{\equiv} + 2H^+ + 2\epsilon \rightarrow AsO_3^{\equiv} + H_2O \\ \hline 2I^- + AsO_4^{\equiv} + 2H^+ \rightarrow I_2 + AsO_3^{\equiv} + H_2O \end{array}$$

Sulfites are also moderately good reducing agents, the $SO_3^=$ being oxidized to $SO_4^=$. The use of sulfites as reducing agents in qualitative analysis is illustrated by the reduction of ClO_3^- to Cl^- in testing for chlorates in Anion Group IV. The equations for the reactions involved in the reduction are

$$\begin{array}{r} 3SO_3^= + 3H_2O - 6\epsilon \rightarrow 3SO_4^= + 6H^+ \\ ClO_3^- + 6H^+ + 6\epsilon \rightarrow Cl^- + 3H_2O \\ \hline 3SO_3^= + 3H_2O + ClO_3^- + 6H^+ \rightarrow 3SO_4^= + 6H^+ \\ + Cl^- + 3H_2O \end{array}$$

or, canceling H^+ and H_2O,

$$3SO_3^{=} + ClO_3^{-} \rightarrow 3SO_4^{=} + Cl^-$$

The reducing action of hydrogen sulfide and of $S^=$ has been mentioned repeatedly in the past, but the importance of the sulfides warrants a review of some of their characteristic reactions. It will be recalled that with mild oxidizing agents, such as air, hydrogen sulfide is oxidized to form water and free sulfur. As a reducing agent H_2S is so powerful as to be able to reduce acid solutions of $SO_3^=$ which itself is a moderately good reducing agent:*

$$\begin{array}{r} 2H_2S - 4\epsilon \rightarrow 2S + 4H^+ \\ SO_3^{=} + 6H^+ + 4\epsilon \rightarrow S + 3H_2O \\ \hline 2H_2S + SO_3^{=} + 6H^+ \rightarrow 3S + 4H^+ + 3H_2O \end{array}$$

or canceling H^+ as far as possible,

$$2H_2S + SO_3^{=} + 2H^+ \rightarrow 3S + 3H_2O$$

In a similar way it is capable of reducing free iodine to form I^-;

$$\begin{array}{r} H_2S - 2\epsilon \rightarrow S + 2H^+ \\ I_2 + 2\epsilon \rightarrow 2I^- \\ \hline H_2S + I_2 \rightarrow S + 2H^+ + 2I^- \end{array}$$

SUMMARY

Oxidation-reduction reactions are reactions in which valence changes are involved. The loss of electrons is *oxidation*, whereas any gain in electrons is *reduction*. Oxidizing agents or electron acceptors are often called *oxidans;* reducing agents or electron donors are called *reductants.*

In addition to more complex types, oxidation-reduction reactions include *combination*, *decomposition*, and *displacement* reactions. Any oxidation-reduction reaction may be written as the combination of two half-reactions, one representing the reduction and the other the oxidation. By putting these half-reaction

* The ability of $SO_3^=$ to act both as a reducing agent and as an oxidizing agent is due to the fact that the sulfur in the $SO_3^=$ is capable of existing in both higher and lower valence states. Any ion involving an atom that may have both higher and lower valences potentially is capable of undergoing either oxidation or reduction.

mixtures in separate containers, inserting electrodes, and connecting the resulting half-cells properly, cells are formed from which electricity may be obtained from oxidation-reduction reactions.

The *ion-electron* and *valence-electron* methods of balancing oxidation-reduction equations are based upon the fact that the electrons used in the reaction must all come from the reducing agent and must all be used by the oxidizing agent.

When cells are assembled in which different half-cells are combined with a normal hydrogen electrode, different voltages are obtained. Molar oxidation-reduction potentials may be obtained in this way for various half-reactions. Tables of these potentials may be used to predict the probability of occurrence of a given reaction. The reactions for which these potentials are known are reversible; consequently, the oxidized form of any substance is theoretically capable of acting as an oxidizing agent, while the reduced form may act as a reducing agent. In the table of oxidation-reduction potentials, the most powerful reducing agents are at the top; but the reducing abilities decrease the farther down in the table the substance is found. The oxidizing agents, on the other hand, vary in exactly the opposite way.

If the relative positions of two substances show that they should be able to react with each other, the greater the difference between their potentials the more complete would be the reaction between them. This fact is expressed mathematically by the equation

$$\Delta E = \frac{0.059}{n} \log K$$

in which ΔE is the difference in potential found by subtracting *algebraically* the potential of the reducing agent in the reaction from that of the oxidizing agent, n is the number of electrons transferred in the reaction, and K is the equilibrium constant for the reaction. If $\log K$ is large *numerically* but is *negative* in sign, the reaction will not occur to a significant extent.

A positive value for $\log K$ indicates that a reaction *may* occur. In practice, however, the reaction may prove unfeasible owing to (1) a too small reaction rate or (2) other possible reactions having much greater reaction rates.

A number of oxidizing agents are available for use by the chemist. Among these the active nonmetals and the perman-

ganates, chromates or dichromates, peroxides, nitrates, and persulfates are especially important.

Among the reducing agents are found many metals that are usable as reagents. Other reducing agents of importance are stannous chloride and the iodides, sulfites, and sulfides.

Review Questions

1. Define: (*a*) oxidation, (*b*) reduction, (*c*) oxidizing agent, (*d*) reductant, (*e*) half-cell, (*f*) cell, (*g*) molar potential, (*h*) hydrogen electrode

2. What distinguishes oxidation-reduction reactions from other reactions?

3. List and illustrate with equations four *types* of oxidation-reduction reactions.

4. What information may be obtained from a table of oxidation-reduction potentials? Why cannot certain parts of this information always be trusted when it is desired to apply it to a particular reaction?

5. Discuss the use of the following as oxidizing agents, giving equations and describing the conditions which should be most favorable for reaction:

(*a*) Chromates. (*b*) Permanganates.
(*c*) Chlorine. (*d*) Nitric acid.

6. The equation for the electrode reaction of hydrogen peroxide shows that its oxidizing action should be favored by a high H^+ concentration. Discuss and illustrate by equations why this is not true in the reaction of H_2O_2 with CrO_2^- to form $CrO_4^=$.

7. Discuss the use of the following reducing agents, illustrating the use of each by means of equations:

(*a*) Iodides. (*b*) Sulfites. (*c*) Zinc.
(*d*) Sulfides. (*e*) Stannous chloride.

8. Write the equations for the half-reactions involved in each of the following reactions From the relative positions of these half-reactions in the table of oxidation-reduction potentials state, with reasons, whether or not these reactions should take place appreciably.

(*a*) $H_2SO_3 + 4H^+ + 4I^- \rightarrow S + 3H_2O + 2I_2$
(*b*) $NO_2^- + H_2O_2 \rightarrow NO_3^- + H_2O$
(*c*) $3S_2O_8^= + 2Cr^{+++} + 7H_2O \rightarrow 6SO_4^= + Cr_2O_7^= + 14H^+$
(*d*) $5Br_2 + 2Mn^{++} + 8H_2O \rightarrow 10Br^- + 16H^+ + 2MnO_4^-$

9. Balance each of the following equations, using the ion-electron method:

(*a*) $KMnO_4 + H_2SO_3 \rightarrow KHSO_4 + MnSO_4 + H_2SO_4 + H_2O$
(*b*) $K_2Cr_2O_7 + H_2S + H_2SO_4 \rightarrow KHSO_4 + Cr_2(SO_4)_3 + S + H_2O$
(*c*) $(NH_4)_2S_2O_8 + H_2O \rightarrow NH_4HSO_4 + H_2O_2$
(*d*) $H_2O_2 + KMnO_4 + H_2SO_4 \rightarrow KHSO_4 + MnSO_4 + H_2O + O_2$
(*e*) $ClO_3^- + I^- + H^+ \rightarrow Cl^- + I_2 + H_2O$
(*f*) $IO_3^- + H_2SO_3 \rightarrow SO_4^= + I^- + H_2O$
(*g*) $IO_3^- + I^- + H^+ \rightarrow H_2O + I_2$

Problems

1. From the values listed in Table VIII, calculate the voltages of cells made of molar half-cells representing the reactions

(*a*) $Zn + Cu^{++} \rightarrow Zn^{++} + Cu$

(*b*) $I^- + Cl_2 \rightarrow I_2 + Cl^-$

(*c*) $I^- + O_2 + H^+ \rightarrow I_2 + H_2O$

(*d*) $Ni + Sn^{++++} \rightarrow Ni^{++} + Sn^{++}$

(*e*) $Fe^{+++} + Br^- \rightarrow Fe^{++} + Br_2$

2. Calculate the equilibrium constants for the reactions in Problem 1. From these constants state whether or not the reaction will take place appreciably.

3. Answer Problem 2 for the equilibriums in Question 8.

PART II

Analytical Procedure

SEMIMICRO TECHNIQUE

As a result of attempts to solve the many problems of science, a number of highly important branches of analytical chemistry have slowly developed. Although the chemical principles involved are much the same for all these branches, the apparatus and techniques used are often highly specialized.

In qualitative analysis there are now three main techniques, *i.e.*, the *macro*, the *semimicro*, and the *microscopic*. These methods differ from one another both in the quantities of materials used, including sample size, and in the apparatus and techniques employed. In macro analysis the unknown may consist of 0.5 to 1.0 g. of solid or 50 to 100 ml. of solution, and the apparatus and techniques are similar in most respects to those used in ordinary general chemistry. In microscopic analysis, a single drop of solution, a tiny fiber, or a bit of solid the size of a pinhead is often sufficient. In this case, however, many of the operations are performed under microscopes equipped with many special attachments, the use of which often makes this analysis even more precise than when performed on a macro scale.

The semimicro technique employs samples consisting of about 1 ml. of solution, or from 10 to 100 mg. of solid. No definite lines can be drawn among the sample sizes belonging to each classification, but in most cases the semimicro sample more nearly approaches the microscopic than it does the macro.

Some of the techniques employed in semimicro analysis will be described in the following paragraphs; others will be discussed at appropriate times during the description of the laboratory work that is to be done. In every case, however, the student will find that frequent reference to these discussions will be of great assistance in improving technique.

Filtrations. In semimicro work the usual filter-paper-funnel method of filtration is seldom used. Many precipitates, especially the hydroxides of the heavy metals, clog the pores of the filter paper and make the process of filtration slow and tedious. Often, too, the precipitate must be separated from highly alkaline or strongly acid solutions, which attack and weaken the filter paper. For these reasons, a number of other techniques are used instead.

Centrifugation is the most rapid and convenient method of separating solids from liquids. The mixture is placed in a small test tube or a centrifuge tube, and the tube is placed in one of the cups of a centrifuge. Another tube the size of the first, containing a volume of water equal to the volume of liquid and solid in the first tube, is placed in the centrifuge cup across the head from the first tube. With the two tubes so placed, the head will be balanced and vibration in the centrifuge will be reduced to a minimum. The operation of the centrifuge will depend upon the type used. If the centrifuge is electrical, it is usually sufficient to turn the switch, allow the centrifuge to attain full speed, let it operate for 10 to 30 sec., and then turn it off. Hand centrifuges are operated by means of a handle that must be turned *smoothly* and rapidly until the precipitate is packed firmly in the bottom of the test tube or centrifuge tube. A little practice enables one to judge the speed and duration of the process. Above all, however, it is important to avoid sudden strains or vibrations as these are highly damaging to the apparatus and often result in stirring up the mixture that is supposedly being separated.

When the precipitate is firmly packed in the bottom of the tube, the liquid (often called the *centrifugate**) may be withdrawn by means of a medicine dropper. Care must be used during this operation, however, to avoid stirring up the precipitate. In difficult cases, it is often advisable to insert a tight twist of cotton into the tip of the dropper, using scissors to cut the protruding tuft of cotton about 3 mm. below the glass tip (see Fig. 16).

For most purposes, 75- or 100-mm. test tubes may be used in the centrifuge. When only minute quantities of solid are present, however, the precipitate is much more clearly visible and the separation is easier if a centrifuge tube is used (Fig. 17).

* In the laboratory instructions it will be the practice to call this liquid the *filtrate*, regardless of the method used for the separation.

Mixtures obtained by performing drop reactions on slides or watch glasses may be filtered by either of two microscopic tech-

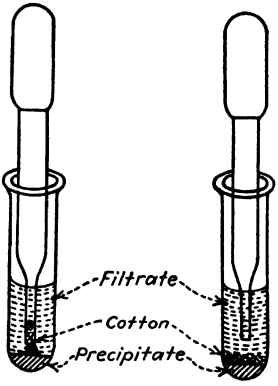


FIG 16.—Separating filtrate and precipitate after centrifuging.

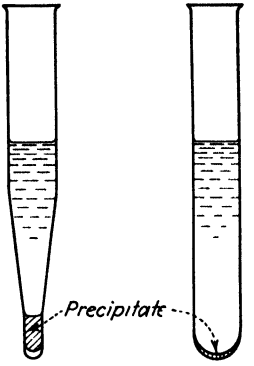


FIG 17.—The visibility of precipitates in centrifuge tubes and test tubes.

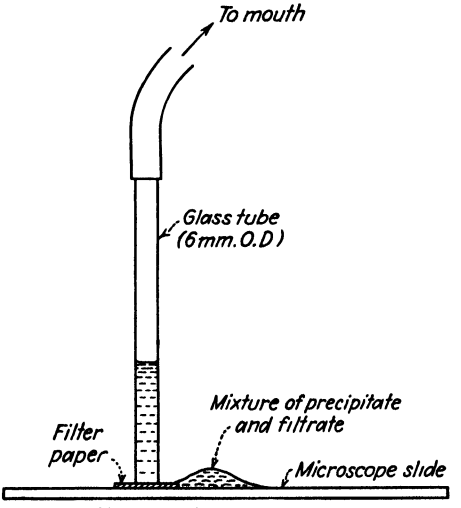


FIG. 18.—A micro filtration

niques of filtration. The first of these consists simply of touching the edge of the liquid portion with the edge of a piece of filter paper and allowing the liquid to soak into the paper. The second

is similar to the first except that a much smaller piece of filter paper is used (about 8 or 10 mm. square), the paper being laid flat on the slide and pushed so that its edge is in contact with the liquid. A bit of glass tubing with one end ground flat and with its other end connected to a 30-cm. piece of rubber tubing is pressed with its ground end flat against the filter paper (see Fig. 18). By applying suction with the mouth it is possible to draw the liquid through the filter paper and into the glass tube. This enables the operator to save the filtrate for other tests.

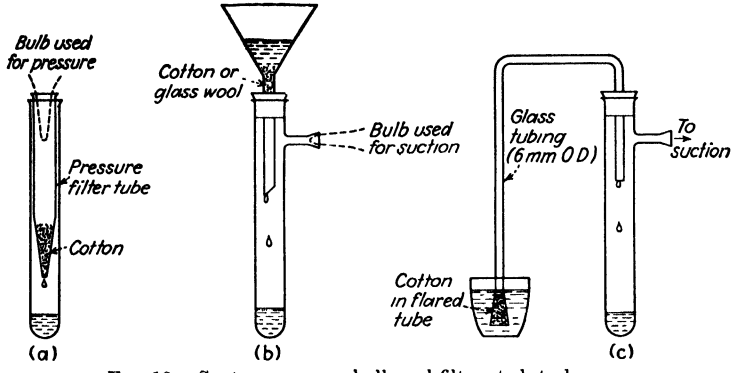


FIG. 19.—Suction-pressure-bulb and filter-stick techniques.

For mixtures of 0.5- to 1-ml. volume the centrifuge is usually to be preferred in separating solids and liquids. For special cases or when centrifuges are not available, however, the suction-pressure-bulb method suggested by H. H. Barber* is very convenient. Essentially the technique is based upon the use of a 2-oz. rubber ear syringe to create either pressure (Fig. 19*a*) or suction (Fig. 19*b*). The filter tube or funnel is packed tightly

* A complete description of this apparatus is given in the article "New Apparatus for Qualitative Semimicroanalysis," by H. H. Barber, *Ind. Eng. Chem., Anal. Ed.*, **12** (1), 58 (1940).

The sidearm test tube and bulb can be purchased from the Wilkens-Anderson Company, Chicago, Ill. Also these pieces, as well as the pressure-filter tube, can be purchased from the Geo. T. Walker Co., Minneapolis, Minn.

Similar filtration methods have been described by Cornog and Krause, in the article "Apparatus for Semimicro Filtration," *J. Chem. Educ.*, **19** (5) 217 (1942).

with either cotton or fine glass wool (Corning, No. 008 has been especially recommended) as filter medium. These techniques are especially to be recommended where it is necessary to separate precipitates of low density that are not readily removed by centrifuging.

In Fig. 19*c* another method of filtration is illustrated. This is an adaptation of the micro filter-stick technique. Cotton or glass-wool packing is used as the filtering medium in this apparatus. Suction may be applied either by a rubber bulb or by a water suction pump.

Transferring Precipitates. Quite often all or part of a precipitate must be transferred from one vessel to another. In some cases it may be done with a spatula. Where this proves difficult, however, a liquid (the wash liquid or the next reagent to be used) may be added, the mixture stirred vigorously, and then a medicine dropper used to transfer the resulting suspension. In general, it is best to use the wash liquid for this purpose. After the transfer is made, the liquid can be removed by filtering, use being made of one of the methods described earlier.

Washing Precipitates. During an analysis it is essential that each precipitate be washed clean of filtrate; otherwise, some of the material in the filtrate that wets the precipitate may cause trouble in the analysis. For example, suppose that one is testing a general unknown for lead in Cation Group I. The test for lead in this group is trustworthy only if the cations of the later groups are absent from the Group I precipitate. If the precipitate is not washed, however, *a little of every metal present in the unknown is going to be in the solution wetting the precipitate;* consequently, the results of the analysis will be undependable.

It is best to wash the precipitate at least *twice* and to *combine the first portion* of wash liquid with the filtrate. This procedure not only will reduce the danger of contamination but will also reduce the loss of material during the analysis.

The best procedure for washing precipitates is to add 5 or 10 drops of the prescribed wash liquid, *stir thoroughly,* then filter.

Evaporations. Quite often it is necessary to evaporate a solution either to dryness or until only a small volume of liquid is left. Such evaporations should always be done in a crucible unless otherwise specified. Test tubes or flasks restrict the escape of vapor, and the boiling of liquids in test tubes quite often results

in loss of liquid due to a bubble of vapor lifting the liquid and throwing it out of the narrow tube.

The best way to evaporate any liquid is to put it in a crucible and heat it with a *micro* flame, either directly (slowly and with

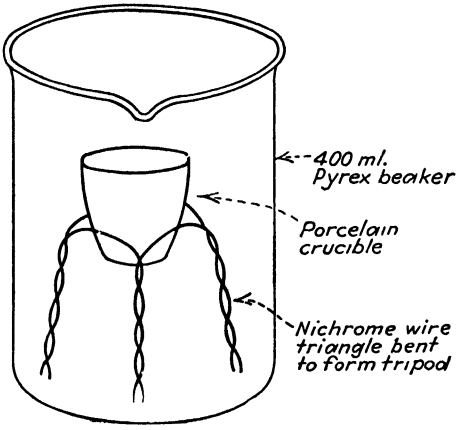


FIG. 20.—Air bath.

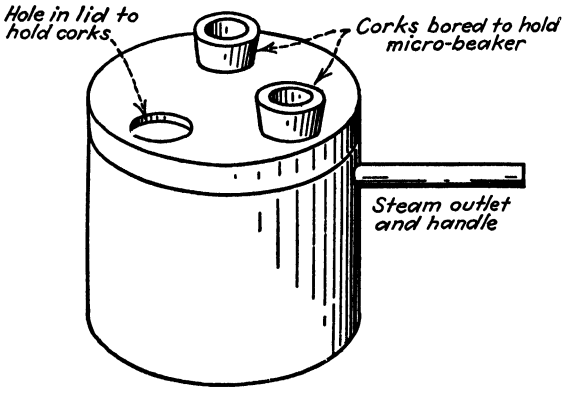


FIG. 21.—Steam bath.

great care) or in an air bath (see Fig. 20) until most of the liquid is gone. Finally, when only a few drops of liquid remain, place the crucible on a steam bath (see Fig. 21) to evaporate the remaining liquid. This treatment has the advantage of avoiding the baking

of the residue and preventing the loss of any compound that might otherwise be lost due to its being unusually volatile (*e.g.*, mercury and arsenic in Cation Group II).

Drop and Spot Tests. Although most of the separations in semimicro analysis involve the use of 0.5 ml. or more of liquid, most of the final identification tests are performed on single drops of solution, the expected results being changes in color or the formation of precipitates of various colors. Quite often these reactions are performed on microscope slides, spot plates, or watch glasses. It should be obvious that if one is looking for a white or other light-colored precipitate, it would be more easily seen if one used a black background, whereas a dark precipitate would be more easily seen against a white background. Careful choice of background should be made, therefore, for each test to be performed. If the results to be expected are not known, a transparent glass container should be used for the reaction mixture and the products viewed against first one then the other color of background.

Many reactions that result in colored precipitates are performed on so-called *drop-reaction* or *spot-test* paper. This is a very soft grade of pure, highly porous paper (soft, highly pure grades of filter paper may be used). The precipitates cannot penetrate into the paper or spread very far, owing to the filtering action of the pores of the paper; consequently, this technique is often used in highly sensitive identification tests, the white paper serving excellently as a background for dark or deeply colored precipitates.

Handling of Reagents. In the handling of reagents, especially from containers that are used by other members of the class, *each student bears the serious responsibility of keeping those reagents pure.* A trace of impurity in a reagent or test-solution bottle may mean any number of errors in the reports of unknowns. For example, a little iron accidentally introduced into the hydrochloric acid bottle means that every person using that bottle while running a Cation Group III unknown may get at least a weak test for iron! The person who introduced the contamination may be among those who suffer; for contaminations are seldom recognized as such; and even when they are recognized, it is frequently difficult to find out which reagent is causing the trouble.

A few simple rules, if strictly followed, will reduce chances of reagent contamination to a minimum.

1. In obtaining reagents from bottles equipped with droppers, never touch the dropper tip to anything outside the reagent bottle. Never rest it against the inside of the container into which the reagent is being dropped; always hold the dropper just *above* the mouth of the vessel and allow the reagent to *fall* into the vessel. If by accident the dropper is touched to anything, take it and the reagent bottle to the instructor *at once* so that he can tell you how to clean the dropper properly.

2. Do not trust the cleanness of your own apparatus so far as reagents are concerned. Never dip your own medicine dropper into a reagent bottle; and if you pour some reagent into one of your containers, never return the reagent to the bottle. It is much better to waste a little material than to take chances of contaminating the rest of the supply.

3. Certain liquids, especially concentrated acids, are kept in ordinary bottles without dropper tops. To obtain such reagents, pour a little of the reagent into one of your own test tubes, then withdraw the reagent, as needed, from the test tube. Again remember *never to dip your medicine dropper into the reagent bottle*, and *never return any reagent to the bottle.*

4. Solid reagents should be poured from the reagent bottle on to a dry watch glass and added to the reaction mixture by means of a dry, clean spatula. Again no reagent should be returned to the bottle. Try to estimate your needs and then pour out only the amount needed. Never dip your own spatula into the reagent vial.

As a rule, solid reagents should not be placed on paper. In some cases, no harm would result; however, certain reagents (*e.g.*, Na_2O_2) can act on the paper, and the use of a watch glass is, in general, much better technique.

Precipitation with Hydrogen Sulfide. One of the most important reagents used in qualitative analysis is hydrogen sulfide, H_2S. The source of this gas differs in different laboratories; sometimes it is supplied from a central generator or tank of the gas, sometimes from conveniently located Kipp generators using ferrous sulfide and dilute sulfuric acid, or perhaps from individual generators of low capacity.

The techniques employed in saturating solutions with hydrogen sulfide vary according to the method used to supply the gas. In those laboratories where the hydrogen sulfide is supplied under a very low pressure—such as from a Kipp-type generator or from a gasometer—precipitations are best done with the solution to be saturated in a 25-ml. flask. To do this, equip the flask with a one-hole rubber stopper through which is inserted a glass delivery tube reaching almost to the bottom of the flask (see Fig. 22). Connect the outer end of the delivery tube to a 50-cm. length of rubber tubing, the other end of which is connected to the low-pressure source of hydrogen sulfide. With the solution in

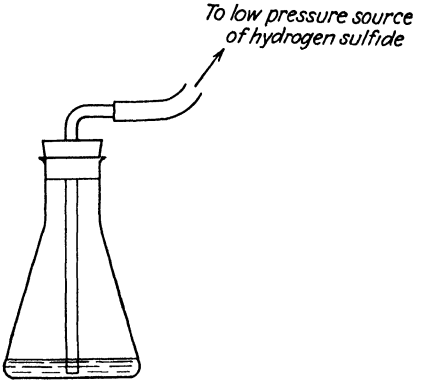


FIG 22.—Low-pressure saturation with hydrogen sulfide.

the flask and with the rubber stopper loosened, turn on a slow stream of the hydrogen sulfide for a few seconds, letting the gas sweep most of the air from the flask; then force the stopper firmly into place, and adjust the glass tube so it dips below the surface of the liquid. Shake the flask frequently to bring about intimate contact between the liquid and gas. When no more hydrogen sulfide bubbles issue from the end of the glass tube, saturation may be considered complete. The method described has the advantage that (1) little or no hydrogen sulfide gets out into the room and (2) the absorption of hydrogen sulfide under pressure is more rapid than is usually obtained by bubbling a stream of the gas through a solution.

At Oklahoma Agricultural and Mechanical College, use is made of individual generators employing a commercial mixture known

as "Aitchtuess." This mixture, which consists essentially of an intimate mixture of a solid hydrocarbon, sulfur, and asbestos,* yields hydrogen sulfide on being heated. The formation of the gas ceases when heating of the mixture is discontinued. The generator (see Fig. 23) consists of a 150-mm. thin-wall Pyrex test tube fitted with a one-hole rubber stopper and a delivery tube. In the delivery tube is a bulb filled loosely with cotton and also

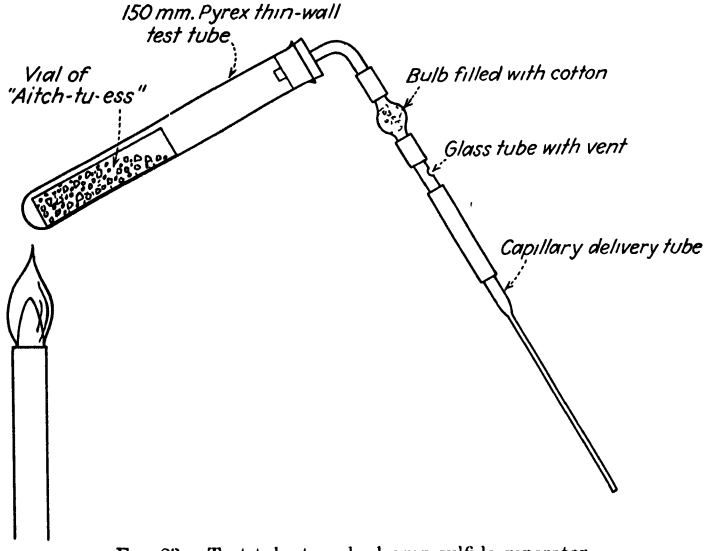


FIG. 23.—Test-tube-type hydrogen sulfide generator.

a short bit of glass tubing in the side of which a small hole is blown. Capillary delivery tubes with tips of about 1-mm. bore are used with this generator, the gas being merely bubbled through the solution in a test tube. To operate the generator, a vial of "Aitchtuess" is placed in the test-tube generator and the apparatus is assembled. Gentle heat is applied to the generator, the rate of gas evolution being controlled by the temperature at which the mixture is maintained. With the glass delivery tube

* A mixture of 1 part of paraffin and 3 parts of sulfur by weight with enough medium-grade asbestos to make the mass porous may be used instead of the commercial mixture. It is not so good, however, for the gas from the crude mixture carries over much sulfur.

dipping into the liquid and with the finger tip pressed firmly over the side hole of the delivery tube, a stream of fine bubbles will pass into and through the solution. When heating of the generator is discontinued, the finger tip must be removed from the side vent; otherwise as the apparatus cools, the liquid will be forced by atmospheric pressure into the generator.

The capillary delivery tubes may be made as illustrated in Fig. 24. The advantage of these delivery tubes over those of larger diameter lies in the fact that the tiny bubbles from the capillary tip dissolve rapidly, this action not only saving time

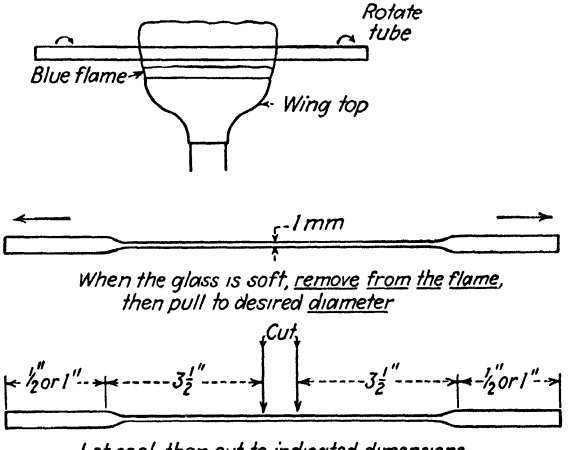


FIG. 24.—Steps in making capillary delivery tubes

but also diminishing the amount of hydrogen sulfide likely to escape into the room. The capillaries should not be much smaller than 1 mm. in diameter, however, as smaller ones clog too readily.

Capillary delivery tubes are best cleaned by immersing the capillary portion of the tube in an appropriate solvent in a test tube. For example, if the delivery tube was used in precipitating PbS, immerse it in dilute HNO_3; if used for HgS, immerse it in fresh aqua regia; etc.

Some Helpful Suggestions. While the experiments outlined in the laboratory section are being performed, a number of things *must* be kept in mind at all times. Serious consideration of these

points definitely will make the difference between good and poor work. As it is impractical to learn everything at once, this section should be reread at intervals until the habit of using these suggestions has been thoroughly fixed.

1. When you are performing the different experiments, do so thoughtfully, and intelligently. Never dismiss the experiment with the thought that it is to be done merely because "the teacher assigned it to be done." Every experiment and every part of an experiment has a reason behind it. Sometimes the purpose is to enable you to understand the fundamental reactions used in separating and identifying the different ions; sometimes it is to illustrate certain difficulties that may arise during the analysis; and in some cases, the purpose is to broaden your knowledge of the properties of the ions studied and of the laws governing reactions in solution. No experiments are given without good reason; and the thoughts that should be uppermost at all times are why does this happen? and of what importance to me is this particular experiment, *i.e.*, how will I be able to use it? If any other attitude is prevalent, most of the point of the course is lost!

2. The instructions given for performing the different experiments are, in most cases, *only suggestive*. When the suggestion is made to use 10 drops of aqua regia to dissolve the Cation Group III precipitate, look at the quantity of precipitate you have to dissolve. Maybe you need only 5 drops of the reagent—or maybe you need 20 drops! No set rule can be given, for unknowns vary widely in the relative amount of different ions present. For example, an alloy may be 85 per cent copper, 10 per cent zinc, and 5 per cent tin. This would mean that no precipitate would be obtained for Cation Groups I, IV, or V, that the amount of precipitate for Cation Group II would be very large, and that the amount of the precipitate for Cation Group III would be much smaller than that for Cation Group II. Obviously, *more* than the suggested quantity of each reagent would be required in separations within Cation Group II, and much less would be needed in Cation Group III. The one rule that must be kept in mind is the fact that if you understand the function of each reagent, you will be able to modify the instructions intelligently to fit your own particular problems.

3. Be sure to use an *adequate amount* of reagent to accomplish the desired result. In dissolving a precipitate, for example, the

instructions may suggest 10 drops of a certain reagent. If this procedure is followed, it is often found that a large part of the precipitate dissolves but some remains. In such cases, filter, saving the filtrate; then add more of the same reagent to the precipitate to see if it will not dissolve more.* This should be repeated until no significant additional results are obtained.

In precipitating substances from solutions, a similar rule should be followed. All precipitations must be complete—in other words, care must be taken to add enough reagent to react with all the ions that are to be precipitated at that point. Failure to do this means that the analysis of subsequent groups will be ruined owing to the presence of the ions that have not been precipitated because of insufficient reagent. On the other hand, a large excess of reagent must be avoided, too, as in many cases such an excess will either redissolve or peptize (see Chap. IX) all or part of the precipitate, with the result that the cations that should have been precipitated appear in the next group. To avoid adding either excess or insufficient reagent, it is desirable to use the following procedure:

Add a couple of drops of reagent, and stir the mixture thoroughly. If a precipitate forms, centrifuge; and then to the clear supernatant liquid add one more drop of reagent, and stir once more. Centrifuge, and repeat the foregoing procedure until on addition of a drop of reagent, no more precipitate forms in the clear layer of liquid. This marks the point when exactly enough reagent has been added.

If on addition of the first two drops of reagent no precipitate forms at once, it is well to rub the inside of the container with a stirring rod for about 1 min. and let the solution stand for a few minutes, as it may be supersaturated.

4. Clean all apparatus thoroughly before using it. The best procedure is to rinse all possible material from the apparatus,

* Suppose that you had 1 g of ordinary table salt, sodium chloride, and the instructions said to treat this with 1 ml. of water to dissolve it. In spite of the fact that we consider sodium chloride as being fairly soluble in water, only about one-third of the solid would dissolve in this quantity of water. If sodium chloride were a less familiar substance, we would be led to the conclusion that not all of it would dissolve in water. If however, we repeated the treatment with water two more times, the whole would dissolve. By combining the liquid portions used, then, we would have all the sodium chloride in one solution.

using tap water for the purpose; then with a test-tube brush and a solution of Dreft or Vel, thoroughly wash the apparatus. Finally rinse each piece carefully with a stream of distilled water from a wash bottle (see Fig. 25).* In a few cases, especially with small apparatus, a pipe cleaner will be found a useful substitute for a test-tube brush. Occasionally acids may be needed to dissolve out precipitates that are not easily dislodged. In such cases, use a solvent that your experience has taught you will attack the particular type of precipitate involved; in case of doubt, consult your instructor and remember what he tells you so that you can use that knowledge later.

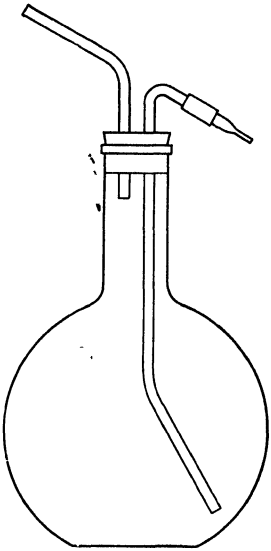


FIG. 25.—Wash bottle.

5. Avoid contaminations from crucible tongs and other metallic objects; always grip objects in such a way as to keep the tongs *outside* the container. A little copper from a brass instrument may give just as good a test for this metal as would be obtained if that metal were issued in the unknown. Also, never lay medicine droppers, stirring rods, or similar apparatus on your desk top. The desk may *look* clean, but it rarely is!

6. Keep detailed notes of everything that you do, with an explanation of each result obtained. This should be done both with the preliminary experiments and with the analysis of any unknowns. Not only does the keeping of notes force you to think of the important things as you proceed, but the notes themselves are excellent for later review. Quite often, too, if a mistake is made in the analysis of an unknown, your instructor will be able to point out in your notes a bit of information that tells you why you went astray and how you might have been forewarned.

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* Tap water must not be used for the final rinse water, since many of the reagents used in qualitative analysis are capable of detecting the impurities present in even the small quantity of tap water left wetting the apparatus.

CATION ANALYSIS

CATION GROUP SEPARATIONS

The analysis of a mixture containing *all known cations* is an exceedingly involved and tedious process; fortunately, however, only a few of the possible cations appear with sufficient frequency to warrant their consideration for most ordinary purposes. For this reason, the cations covered in this course will be restricted to those of silver, lead, mercury, copper, bismuth, cadmium, arsenic, tin, antimony, iron, manganese, cobalt, nickel, zinc, aluminum, chromium, barium, calcium, strontium, magnesium, sodium, potassium, and ammonium.

For analytical purposes, the cations are divided into five groups.

Group I consists of those cations whose chlorides may be precipitated from water solutions by the addition of soluble chlorides such as dilute HCl or NH_4Cl. Lead, silver, and mercurous mercury are the common members of this group.

Group II consists of those cations whose chlorides are soluble but whose sulfides can be precipitated from a 0.3*N* HCl solution by saturating the solution with H_2S. The cations falling in this group are mercuric mercury, lead,* bismuth, cupric copper, cadmium, arsenic, antimony, and tin.

Group III is comprised of those cations whose chlorides are soluble in water and whose sulfides are soluble in 0.3*N* HCl but whose sulfides or hydroxides will precipitate when ammonium sulfide (or H_2S and NH_4OH) is added to a highly buffered solution† containing these cations. The metals in this group are iron, manganese, cobalt, nickel, aluminum, zinc, and chromium. Of these, the aluminum and chromium precipitate as the hydroxides, while the others form sulfides.

Group IV consists of those cations whose chlorides and sulfides are soluble, but whose carbonates are readily precipitated from

*Lead appears in Group II as well as Group I owing to the fact that $PbCl_2$ is appreciably soluble in water (about 1 g. in 100 g. of water at room temperature) and some always escapes the precipitation with Group I.

† In practice, the solution is buffered with NH_4Cl or NH_4NO_3 to prevent any considerable increase of OH^- concentration. If this were not done, Mg^{++} would precipitate in this group as $Mg(OH)_2$ and even some $Ca(OH)_2$ might form.

a *buffered* basic solution by the addition of ammonium carbonate. Barium, strontium, and calcium are in this group.

Group V consists of those cations not precipitated under any of the above conditions. The cations in this group are magnesium, sodium, potassium, and ammonium.

The methods of precipitating these metals into their respective groups and of further separating and identifying them will be outlined in succeeding pages. The procedures will be given in outline form for clarity; and for economy of space, abbreviated sentences will be used throughout.

The outline will describe the method of precipitating and analyzing each group. To analyze a general unknown, it is necessary only that the solution left from the Group I precipitation be used as the unknown for the Group II analysis, the solution from the Group II precipitation for the Group III unknown, etc.

For the usual analysis, *no more* than 1 ml. of unknown should be taken. More will make the analysis difficult.

Preliminary Treatment of Solids. As will be noted from the foregoing discussion, before any systematic analysis for cations can be undertaken the unknown must be in solution. As a rule, the first unknowns issued in an analytical course are already in solution; later, however, as well as in many practical analyses, the unknowns are obtained as solids. The dissolution of such solids is often simple; sometimes, however, highly specialized procedures must be used. The following procedure suffices for most purposes.

1. To a volume of solid the size of a large match head add about 10 drops of distilled water.* Heat on the steam bath for 2 or 3 min., stirring throughout the whole time. Filter, saving the filtrate. If any significant decrease in the volume of the solid has occurred, repeat the treatment with a fresh portion of water, filtering and combining the filtrates.

2. If any residue is left from the water treatment, add to it about 10 drops of dilute HNO_3, and warm. If any reaction seems to occur, continue warming (do not boil) until reaction ceases. Filter, and combine the filtrate with that obtained by the water treatment. As before, if the dilute HNO_3 seems to have dissolved any significant amount of the solid, repeat the treatment with

* If the unknown is an alloy, the water treatment is usually useless, as only those alloys containing significant quantities of very active metals (*e.g.*, sodium amalgam) would be affected by water. With alloys, therefore, start with the acid treatment at once.

fresh acid.* Allow plenty of time for the reaction. The fewer solvents, the easier will be the analysis.

3. If any residue is left from the dilute HNO_3 treatment, treat it with concentrated HNO_3, using the same procedure as before.†

4. To any residue left from (3) add some *fresh* aqua regia (3 drops of concentrated HNO_3 and 9 drops of concentrated HCl). Heat as before; then filter.‡ *Do not combine this filtrate with the others, however.* Save it and any following filtrates until the first three filtrates have been tested for Group I cations;§ combine all, just before beginning the Group II analysis.

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* Never add the new acid to the spent acid in contact with the solid. If the HNO_3 has been used up, the spent acid will merely dilute the fresh to a concentration that may be too low for greatest efficiency.

† If tin or antimony is present, a white precipitate is often formed during this treatment, the precipitate being an oxide of antimony, Sb_2O_4, or a hydrated form of stannic oxide known as *metastannic* acid, H_2SnO_3.

‡ Sb_2O_4 is soluble in either concentrated HCl or aqua regia, but H_2SnO_3 is insoluble in all common reagents. Consequently, a white precipitate that forms during the HNO_3 treatment and remains after the aqua regia treatment is usually metastannic acid. In such cases the precipitate may be dissolved by either of two methods

Method 1. Treat the precipitate with concentrated HCl, and heat for 4 to 5 min. This will not dissolve the metastannic acid; but if the acid is now removed and the precipitate is treated with hot water, the solid will dissolve and the solution may be combined with the filtrates obtained from the aqua regia treatment.

Method 2 Wash the white solid with water to remove any acid; then mix the solid with its own volume of powdered sulfur and three times its volume of solid Na_2CO_3. Place the mixture in a crucible, and heat it to a dull red heat for about 3 min Finally cool the mixture; extract it with water; and filter, discarding any precipitate. Acidify the filtrate with dilute acetic acid and heat on the steam bath 3 or 4 min Filter, discarding the filtrate. Dissolve the precipitate in concentrated HCl; boil for 2 or 3 min. to drive out any H_2S formed; and combine the solution with the filtrates obtained from the aqua regia treatment.

§ The Group I cations should all be in the combined filtrates from the first three treatments, as lead, silver, and mercury nitrates are soluble. The addition of a high concentration of Cl^- (such as is usually present in the aqua regia solution) would tend to precipitate the chlorides of silver and lead and then redissolve them to form the complex ions $AgCl_2^-$ and $PbCl_3^-$. The mercury and lead, if missed in Group I, would be found in Group II; but the silver, if present only in small quantities, might be missed. It is therefore best to analyze the combined filtrates from the first three treatments for Group I, then to take the filtrate from Group I and combine it with those from later treatments of the solid unknown before starting the Group II analysis.

5. If any residue remains after the foregoing treatments [including the treatment for metastannic acid as outlined in the footnote under (4)] an alkaline fusion may be necessary. To perform the fusion, wash the residue with water and then dry it thoroughly on the steam bath. Cool, and mix the residue with an equal volume of Na_2O_2 and three times its volume of solid Na_2CO_3. Transfer to a porcelain crucible,* and heat the mixture as strongly as possible over a Bunsen flame for 10 or 15 min. Cool; add about 10 drops of water; and *carefully acidify* with dilute HCl. Evaporate just to dryness; then add 10 drops of concentrated HCl; and evaporate again. Finally, add about 10 drops of dilute HCl; stir; warm; and filter. Discard the precipitate,† and combine the filtrate with that from the aqua regia treatment.

The procedure outlined here will not suffice for all substances but will for most of those commonly used in elementary qualitative analysis.

GROUP I METALS

Chemical Characteristics

Silver. Silver in the elementary form is fairly inactive chemically, undergoing no reaction with dilute nonoxidizing acids or with alkalis It reacts with aqua regia, forming a mass of difficultly soluble AgCl, and is readily attacked by hot, concentrated H_2SO_4 and by dilute or concentrated HNO_3. Because of the high solubility of $AgNO_3$, HNO_3 is the best solvent for this metal.

Compounds of Silver. Silver forms a large variety of complex ions and only slightly soluble compounds. Solutions containing Ag^+ give the following products when treated with the indicated reagents:

Dilute sodium, potassium, or ammonium hydroxide gives a brown or black precipitate of AgOH, a compound that is unstable and dehydrates readily to produce a mixture of the AgOH with Ag_2O. Ag_2O is an excellent oxidiz-

* If an analysis is to be made for aluminum and sodium, it is necessary to use a crucible made of some material other than porcelain, as part of the crucible itself reacts with the fusion mixture and the crucible contains these elements. Iron or, even better, nickel crucibles can be used in such cases. If a complete analysis is desired, it is best to conduct two fusions, using one kind of crucible for the first and another for the second. Those elements found in *both cases* may be assumed to be present in the unknown sample.

† During the fusion, some of the material from the crucible itself is converted into soluble compounds, among which is Na_2SiO_3. The acidification and evaporation changes the Na_2SiO_3 to silicic acid and finally dehydrates the latter to form SiO_2. This prevents the formation of gelatinous silicic acid at inconvenient points during the analysis.

ing agent, being itself reduced to metallic silver. Both the hydroxide and the oxide are readily soluble in excess NH_4OH to form $Ag(NH_3)_2^+$.

Hydrogen sulfide precipitates black Ag_2S, the least soluble of the ordinary silver compounds, insoluble in HCl or NH_4OH, but soluble in dilute HNO_3, soluble also in NaCN or KCN solution, forming $Ag(CN)_2^-$.

Soluble chlorides (such as HCl, NaCl, etc.) give AgCl, white, insoluble in water or HNO_3, soluble in NH_4OH [forming $Ag(NH_3)_2^+$], in concentrated HCl, NaCl, or KCl solution (forming $AgCl_2^-$), and in NaCN or KCN [forming $Ag(CN)_2^-$].

Soluble iodides and bromides give precipitates of yellow AgI and pale yellow AgBr, respectively. Although AgBr is slightly soluble in NH_4OH, the AgI is insoluble in that reagent. Both are insoluble in water or HNO_3. These compounds are soluble in concentrated solutions of the corresponding alkali halide to form AgI_2^- and $AgBr_2^-$ and in solutions of alkali cyanides to form $Ag(CN)_2^-$. All the halides of silver are soluble in solutions of sodium thiosulfate, $Na_2S_2O_3$. The *fluoride* of silver is very soluble in water.

Sodium carbonate precipitates Ag_2CO_3, white, soluble in either NH_4OH or HNO_3.

Sodium chromate or potassium chromate produces a reddish-brown precipitate of Ag_2CrO_4, soluble in even very dilute HNO_3 or NH_4OH.

Lead. Metallic lead is attacked by all the common acids, however, owing to the fact that most lead compounds are of very low solubility, the metal is best dissolved in dilute HNO_3. The nitrate and acetate are its most soluble compounds

Compounds of Lead. The following reagents added to solutions containing Pb^{++} give compounds that are insoluble in water.

Sodium, potassium, or ammonium hydroxide precipitates $Pb(OH)_2$, white; insoluble in water or NH_4OH; soluble in HNO_3, acetic acid, or excess alkali (forming $HPbO_2^-$); forming insoluble, brown PbO_2 on addition of H_2O_2, hypochlorites, or other oxidizing agents.

Hydrogen sulfide gives PbS, black, insoluble in water, NH_4OH, dilute HCl, $(NH_4)_2S$, and Na_2S_x; soluble in $2N$ or stronger HNO_3 and in concentrated HCl

Soluble chlorides give $PbCl_2$, white, only slightly soluble in cold water, soluble in hot water, and in strong HCl to form $PbCl_3^-$.

Iodides give PbI_2, yellow and less soluble than $PbCl_2$; soluble in concentrated alkali iodides, forming PbI_3^-.

Soluble chromates such as K_2CrO_4 precipitate $PbCrO_4$, yellow, insoluble in water or acetic acid, soluble in HNO_3 and in alkalies (forming $HPbO_2^-$).

Dilute sulfuric acid or soluble sulfates precipitate $PbSO_4$, white; insoluble in water; soluble in concentrated H_2SO_4 [forming soluble $Pb(HSO_4)_2$], in strong ammonium or sodium acetate solution [forming the very slightly ionized $Pb(C_2H_3O_2)_2$], and in strong alkalis (forming $HPbO_2^-$).

Mercury. Metallic mercury is only slightly more active than silver; consequently, mercury is readily displaced from its compounds by even so inactive a metal as copper. As it is below hydrogen, it does not react with dilute H_2SO_4 or HCl. It dissolves readily, however, in hot HNO_3 to form

$Hg(NO_3)_2$, or in cold HNO_3 to form $Hg_2(NO_3)_2$. Mercury also dissolves readily in concentrated HI owing to the formation of very slightly dissociated HgI_4^-, the other product being hydrogen. Hot, concentrated H_2SO_4 dissolves mercury, forming the sulfate and SO_2. The metal is also soluble in aqua regia to form $HgCl_2$ or $HgCl_4^-$.

Compounds of Mercury. Mercury forms compounds of two types—mercurous (Hg_2^{++}) and mercuric (Hg^{++}). The nitrates of both are soluble, but their reactions are so different as to make it necessary to consider them separately. The chloride of either is readily reduced by $SnCl_2$ to dark, finely divided metallic mercury, $HgCl_2$ being first reduced to Hg_2Cl_2.

Mercurous Compounds. *With NH_4OH,* $Hg_2(NO_3)_2$ gives a mixture of white $Hg_2O(NH_2)(NO_3)$ and metallic mercury. Hg_2Cl_2 does not dissolve in NH_4OH, but reacts with it to form a black mixture of finely divided metallic mercury (black)* and $Hg(NH_2)Cl$ (white).

Hydrogen sulfide precipitates a mixture of HgS and Hg, the mixture being soluble in Na_2S_x, but insoluble in $(NH_4)_2S$.

Soluble chlorides precipitate Hg_2Cl_2, white; insoluble in water or dilute acids; soluble in hot, concentrated HNO_3 or H_2SO_4 owing to the fact that the Hg_2^{++} is oxidized to Hg^{++}; insoluble in NH_4OH but reacting with the latter to form a black mixture of $HgNH_2Cl$ and metallic mercury.

Potassium iodide precipitates green Hg_2I_2, which reacts with excess I^- to form HgI_4^- and metallic mercury.

Alkali carbonates give a yellow precipitate of Hg_2CO_3, decomposed on boiling or standing, into a gray mixture of Hg and HgO.

Mercuric Compounds. *Alkalies and alkali carbonates* precipitate, from hot solutions, HgO, red or yellow, insoluble in water, but soluble in acids. The oxide is unstable above 300°C., decomposing to give metallic mercury and oxygen.

Hydrogen sulfide precipitates HgS, black; insoluble in water, dilute acids, concentrated HCl, or $(NH_4)_2S$; soluble in hot, concentrated HNO_3 (with long boiling), in aqua regia, in yellow $(NH_4)_2S_x$, and in Na_2S (forming HgS_2^- from which it is reprecipitated by acidification). When HgS is being precipitated from solutions of Hg^{++} by the addition of H_2S, the first substance to form is a white, insoluble, double salt of the type $(HgS)_2HgCl_2$. This is slowly converted by more H_2S into black HgS. When HgS is dissolved in HNO_3, $(HgS)_2{\cdot}Hg(NO_3)_2$ is produced as an intermediate product, this slowly dissolving to form the normal nitrate.

Soluble chlorides form no precipitate, as $HgCl_2$ is fairly soluble. $Hg(NH_2)Cl$, white, insoluble in water, is formed by treating Hg_2Cl_2 or $HgCl_2$ with NH_4OH. It is soluble in hot NH_4Cl, forming $Hg(NH_3)_2Cl_2$, and in acids.

Soluble iodides precipitate HgI_2, red, insoluble in water, soluble in excess alkali iodide to form HgI_4^-. $HgBr_2$ is more soluble in water than is HgI_2.

Soluble chromates form, in neutral or buffered acid solutions, $HgCrO_4$, orange, insoluble in water, soluble in acids.

* Very finely divided metals are frequently black in color regardless of their color in the massive form.

Alkali thiocyanates precipitate $Hg(SCN)_2$, white; insoluble in water; soluble in excess thiocyanate, forming $Hg(SCN)_4^{--}$.

Preliminary Experiments*

1. Silver Ion, Ag^+. *a.* To 2 or 3 drops of a solution containing Ag^+ (Question 1)† add 1 drop of 1*N* HCl. Filter, and try dissolving a small portion of the precipitate in hot water.

b. Try to dissolve some of the AgCl prepared in *a* in 4 or 5 drops of 6*N* NH_4OH. If any solid refuses to dissolve, filter. Place 1 drop of the clear filtrate on a small watch glass and; with the latter resting on a black surface (Question 2), add 2 drops of 4*N* HNO_3. Examine closely for evidences of a precipitate.

To a second drop of the filtrate, add 1 drop of 0.1*N* KI solution.

c. To 1 drop of Ag^+ solution, add 1 drop of 1*N* K_2CrO_4 solution and note results. Now add 1 drop of 1*N* NH_4Cl solution; stir; and note any change that occurs (Question 3).‡

To a mixture of 1 drop of 1*N* K_2CrO_4 and 1 drop of 1*N* NH_4Cl, add 1 drop of 5 per cent $AgNO_3$ solution. Stir; note any change; then add a second drop of the $AgNO_3$ solution. Repeat until no further precipitation occurs, noting the color of the final precipitate (Question 4).

2. Lead Ion, Pb^{++}. *a.* Precipitate some $PbCl_2$ in the same manner as was used to precipitate AgCl, using a solution of Pb^{++} and some 1*N* HCl. Note the slowness with which the $PbCl_2$ precipitates.

Filter; then to a small portion of the precipitate add 1 or 2 drops of concentrated HCl, noting any results.

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* In these experiments it is necessary to keep careful notes, to identify the products of each reaction, and to watch carefully for *similarities* and *differences* in the behavior of the different metals with the same reagents. Upon these factors are based the separation and identification of the metals. The greater the understanding the student has of these reactions the more accurate will be the results of the analyses performed later. Under Chemical Characteristics and in the equations on p. 212 will be found the necessary information on these reactions.

† At the end of the section on each cation group will be found questions designed as study aids. Attention is drawn to some of these questions by reference to them in the body of the experiment at that point where pertinent information on the particular question should have been obtained. It is advisable to look at each question when such indications are noted, as this experiment is supposed to teach that point.

‡ It should be remembered in this experiment that a white precipitate in a colored solution *appears* to be the color of the solution.

b. To the second portion of $PbCl_2$ from (*a*) add 5 or 6 drops of water, heat almost to boiling, and stir. Note whether or not any of the solid appears to dissolve; then place the mixture on the steam bath to keep it hot, and save for the following experiments (Question 5).

c. On a microscope slide place 1 drop of the hot solution from (*b*), and to it add 1 drop of $1N$ H_2SO_4. Observe results against a black background.

d. Repeat (*c*), using $1N$ K_2CrO_4 solution instead of the H_2SO_4. Try dissolving the precipitate by adding 2 or 3 drops of $6N$ NaOH and stirring.

e. To 2 drops of Pb^{++} solution add 5 drops of water and 1 drop of $0.1N$ KI solution. Heat the mixture just to boiling, noting all occurrences; then cool, again noting occurrences. Finally try dissolving the precipitate by adding an excess of $1N$ KI solution.

f. In a test tube put 2 drops of Pb^{++} solution and 1 drop of dilute NH_4OH. Observe any results against a black background. To this mixture add 2 or 3 drops of H_2O_2 and warm gently, noting occurrences.*

3. Mercurous Ion, Hg_2^{++}. *a.* Precipitate some Hg_2Cl_2, and test its solubility in hot water as was done for AgCl.

b. To some Hg_2Cl_2 add 2 drops of dilute NH_4OH, and note what occurs. Filter; wash the precipitate in cold water, and save the precipitate for *c*.

c. To the precipitate from (*b*), add 3 drops of concentrated HNO_3 and 9 drops of concentrated HCl.†

Warm on the steam bath for at least 3 min. to allow the reaction to be completed, then evaporate *barely to dryness*.‡

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* The reactions that occur when Pb^{++} and H_2O_2 are mixed in alkaline solution are given by the equations

$$Pb^{++} + 2(OH^-) \rightarrow Pb(OH)_2$$
$$Pb(OH)_2 + H_2O_2 \rightarrow PbO_2 + 2H_2O$$

The PbO_2 is a powerful oxidizing agent when in acid solution.

† This will give a mixture of HNO_3 and HCl in the ratio of 1 to 3 by volume. Such a mixture, known as *aqua regia*, is a powerful oxidizing agent. The action of aqua regia on compounds of mercury is described on p. 113.

The products of the reaction of any metallic compound or metal with aqua regia are chlorides.

‡ The product, *mercuric* chloride, sublimes readily; consequently, it is

To the residue add 4 or 5 drops of water and stir. To 1 drop of this solution add 1 drop of 0.1*N* KI solution and note results.

To a second drop of the solution add 1 drop of stannous chloride, $SnCl_2$, solution.*

To the remainder of the solution add a *freshly polished* bit of copper. Let stand 10 to 15 min.; then wash the copper, and examine it closely. Rub your thumbnail over the surface of the copper to see if any silvery droplets of mercury can be obtained.

d. To 1 drop of Hg_2^{++} solution add 1 drop of 0.1*N* KI solution, noting occurrences; then try to dissolve the precipitate by adding an excess of 1*N* KI solution.

Analytical Aspects

A study of the chemical characteristics of the metals shows that the chlorides of the three ions—Ag^+, Hg_2^{++}, and Pb^{++}—are insoluble whereas those of other cations are soluble. It is possible, therefore, to separate these three metals from the others in a general unknown by adding Cl^- to the solution to precipitate the chlorides of lead, silver, and mercurous mercury. This leaves the other metallic ions in solution. A solution of HCl is used, as it furnishes the necessary Cl^- without adding anything undesirable to the solution. Too great excess, however, may result in part of the precipitate redissolving, forming $PbCl_3^-$ and $AgCl_2^-$.

The further separation and identification of these three metals depends upon (1) the high solubility of lead chloride in hot water, (2) the reaction of silver chloride with NH_4OH to form a silver ammonia complex, and (3) the reaction of mercurous chloride with NH_4OH to produce a black mixture of metallic mercury and insoluble mercuric ammonochloride.

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essential not to overheat this at the end of the evaporation or the mercury may be lost.

* Stannous chloride, which is a strong reducing agent, reduces the mercuric chloride (from the aqua regia treatment) in two steps. The first step is the formation of mercurous chloride, a white insoluble substance, and stannic chloride:

$$2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$$

More stannous chloride reduces the mercurous chloride to black metallic mercury:

$$Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg^0 + SnCl_4$$

Group I Analysis

To 1 ml. of the unknown solution (see Note 1) add 2 drops of 1*N* HCl solution, stir thoroughly, and centrifuge Test for completeness of precipitation and add more reagent if necessary (see Note 2 and Preliminary Experiment 2*a*). Stir again, then filter. Wash the precipitate with *cold* water, combining the *first* wash water with the filtrate (see Notes 3 and 4).

Filtrate. Save for Groups II, III, IV, and V.

Precipitate (see Note 5). Consists of $PbCl_2$, AgCl, and Hg_2Cl_2. Add 6 or 7 drops of boiling water and heat, with stirring, for 2 or 3 min. on the steam bath (see Note 6). Centrifuge *quickly* and immediately remove the filtrate while keeping the mixture hot on the steam bath. Wash repeatedly with hot water until the washings give no precipitate upon addition of K_2CrO_4 solution. Keep the first filtrate hot in a test tube on the steam bath.

Filtrate. Contains $PbCl_2$. To 1 drop of the hot filtrate add 1 drop of K_2CrO_4 soln. and observe against a black background

YELLOW PRECIPITATE indicates Pb^{++} present.

To another drop of the filtrate add 1 drop of dil. H_2SO_4

WHITE PPT. confirms Pb^{++}.

Precipitate. Consists of AgCl and Hg_2Cl_2. Add 4 or 5 drops of dil NH_4OH, stir, and filter. Repeat the treatment with NH_4OH if any significant amount of precipitate remains, and combine the filtrates (see Notes 7 and 8).

Filtrate. Contains $Ag(NH_3)_2^+$ and Cl^-. To 1 drop of filtrate, on a watch glass over a black background, add 2 drops of dil HNO_3.

WHITE CLOUDY PPT indicates Ag^+ present.

To 1 drop of filtrate add 1 drop of 0.1*N* KI soln

PALE YELLOW PPT. confirms Ag^+.

Precipitate. Contains Hg and $HgNH_2Cl$ (see Note 8).

BLACK PPT. shows Hg_2^{++} present.

To the precipitate add 3 drops of conc. HNO_3 and 9 drops of conc. HCl. Heat on the steam bath 3 to 5 min, then evaporate *almost to dryness*. Add about 5 drops of water and stir.

To 2 drops of the solution add 1 drop of $SnCl_2$ soln.

WHITE or GRAY PPT. confirms Hg_2^{++}.

* A number of extra identification tests, some of which make use of organic reagents, are described for many cations in the section Auxiliary Tests, beginning on p. 269

NOTES

1. If the unknown is a general, it is essential that the test for ammonium ions be performed first of all; for not only are ammonium compounds easily obtained as contamination from the air of the laboratory, but also they are added to the unknown in Group III. The necessary procedure is described in Group V.

2. After precipitation seems complete, vigorously rub the inside of the test tube with a stirring rod and let stand 3 to 5 min. $PbCl_2$ is very slow to precipitate and may be overlooked in this group if plenty of time is not allowed to insure its precipitation.

3 Some of the original liquid always wets the precipitate after filtration; consequently, the first wash water always contains an appreciable quantity of the cations that should have remained in the filtrate By always combining the first wash water with the filtrate, loss of these cations is minimized Later wash liquids should be discarded, however, as the volume of liquid would otherwise become too great. These procedures should follow every filtration.

4. If the wash water is not sufficiently cold, or if the quantity of lead is small, any lead chloride present may dissolve during the washing process. Any lead missed in Group I, however, will appear in Group II in which provision is made for its analysis.

5. The absence of a precipitate at this point means that the metals of Group I, with the possible exception of lead (which may be found in Group II), are absent.

6 Lead chloride is quite soluble in hot water but reprecipitates at once if the solution is allowed to cool. The small volume of liquid used here cools very rapidly, and the test for lead is often lost through failure to keep the solution hot during the whole procedure If a medicine dropper is used for filtration or for transferring the solution, it should be preheated by placing its tip in a microbeaker full of hot water on the steam bath during the running of the tests for lead.

7. When a mixture of AgCl and Hg_2Cl_2 is treated with NH_4OH (which in this case acts as a source of NH_3 molecules), the reactions occurring are

$$AgCl + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$$
$$Hg_2Cl_2 + 2NH_3 \rightarrow HgNH_2Cl\downarrow + Hg^0\downarrow + NH_4^+ + Cl^-$$

If the quantity of NH_4OH used is not sufficient for both reactions, the reaction with the Hg_2Cl_2 takes place and the AgCl remains precipitated instead of dissolving as it normally should. For this reason, if moderately large quantities of Hg_2^{++} were present (evidenced by a fairly large black or dark gray precipitate left after the first treatment with NH_4OH), silver may be overlooked unless the second portion of NH_4OH is used.

8. If the ammoniacal solution is left in contact with the precipitate of Hg and $HgNH_2Cl$, a displacement reaction occurs between any $Ag(NH_3)_2^+$ and the Hg:

$$2Hg^0 + 2Ag(NH_3)_2^+ \rightarrow Hg_2^{++} + 2Ag^0 + 4NH_3$$

The metallic silver thus remains in the *precipitate;* and if only small quantities of silver were present, the usual test for silver may prove negative. In

the aqua regia treatment of the precipitate, however, the silver will be converted to AgCl; consequently, after the water is added to the residue from the aqua regia treatment, the AgCl may be filtered, washed, and tested with NH_4OH and HNO_3 to show the presence of Ag^+ in the unknown.

Questions

1. Why is it unnecessary to specify which compound to use to furnish the Ag^+? Write the equation for the reaction occurring when Cl^- is added to Ag^+ solution.

2. Why is a black surface preferred instead of a white one when a light-colored precipitate is to be observed?

3. Explain why the color of the precipitate of Ag_2CrO_4 changes when the chloride is added.

4. Explain the results obtained here, drawing conclusions as to the order of precipitation of two compounds having an ion in common but having different solubilities. (Hint: AgCl is less soluble than is Ag_2CrO_4.)

5. How could you use the differences in the action of hot water on AgCl and $PbCl_2$ to separate silver from lead?

6. How could you use the differences in the action of NH_4OH on AgCl and Hg_2Cl_2 to separate silver from mercury?

7. Compare the solubilities of the following pairs of compounds, stating what evidence you obtained during the preliminary experiments to support your conclusions: (*a*) silver chloride and silver chromate, (*b*) silver chloride and silver iodide, (*c*) lead chloride and lead sulfate, (*d*) lead chloride and lead chromate.

8. What is the chemical basis for the separation of the members of Group I from the cations of the other groups? What reagent is used for this separation?

9. Outline briefly the separation of the Group I cations from each other.

10. Write equations for the reactions of

(*a*) Lead and mercurous nitrates with HCl

(*b*) Silver and mercurous chlorides with NH_4OH.

(*c*) Diammine silver chloride with HNO_3 and with KI (see page 142).

(*d*) Hg and $HgNH_2Cl$ with aqua regia

(*e*) $HgCl_2$ with $SnCl_2$ (in two steps).

11. Which of the reactions in Question 10 are oxidation-reduction reactions? Indicate in each case which is the reducing agent and which is the oxidizing agent.

12. Make a chart giving the name, formula, color, and usual solvent for each of the compounds produced in the preliminary experiments.

Equations for Group I Analysis*

Lead

$$Pb^{++} + Cl^- \rightarrow PbCl_2$$

$$PbCl_2 + SO_4^{=} \rightarrow PbSO_4 + Cl^-$$

$$PbCl_2 + CrO_4^{=} \rightarrow PbCrO_4 + Cl^-$$

* The student should balance each of these equations for practice, indicating precipitates by (↓) and gases by (↑). Also the *colors* of any precipitates should be indicated.

SILVER

$$Ag^+ + Cl^- \rightarrow AgCl$$
$$AgCl + NH_4OH \rightarrow Ag(NH_3)_2^+ + Cl^- + H_2O$$
$$Ag(NH_3)_2^+ + H^+ + Cl^- \rightarrow AgCl + NH_4^+$$
$$Ag(NH_3)_2^+ + I^- \rightarrow AgI + NH_3$$

MERCURY

$$Hg_2^{++} + Cl^- \rightarrow Hg_2Cl_2$$
$$Hg_2Cl_2 + NH_4OH \rightarrow Hg^0 + HgNH_2Cl + NH_4^+ + Cl^- + H_2O$$
$$Hg^0 + (Cl)_{\text{(from aqua regia)}} \rightarrow HgCl_2$$
$$HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$$
$$Hg_2Cl_2 + SnCl_2 \rightarrow Hg^0 + SnCl_4$$

GROUP II METALS

CHEMICAL CHARACTERISTICS

Copper. Metallic copper is much like mercury in its reactions. It is insoluble in dilute, nonoxidizing acids in absence of air but dissolves slowly in strong HCl, if air is present, to form the complex cuprochloride ion, $Cu_2Cl_4^-$. The metal dissolves readily in HNO_3 or in hot concentrated H_2SO_4. Copper displaces mercury and silver from their compounds and is itself readily displaced from compounds by metallic iron, aluminum, or zinc. Two types of copper compounds are formed.

Cuprous Compounds. These are similar to the corresponding silver and mercurous compounds in many respects. The chloride, Cu_2Cl_2, is white; insoluble in water; soluble in HCl, forming $Cu_2Cl_4^-$, and in excess NH_4OH, forming $Cu_2(NH_3)_4^{++}$.

With sodium hydroxide, solutions containing Cu_2^{++} give a yellow precipitate of $Cu_2(OH)_2$, decomposed on boiling to form red Cu_2O.

With hydrogen sulfide, black Cu_2S is precipitated, insoluble in dilute nonoxidizing acids but readily soluble in warm HNO_3 to form $Cu(NO_3)_2$.

Cupric Compounds. *With potassium, sodium, or ammonium hydroxide*, solutions of Cu^{++} give green $Cu(OH)_2$, insoluble in water or excess alkali but soluble in excess NH_4OH [giving deep blue $Cu(NH_3)_4^{++}$], in KCN, and in acids.

Hydrogen sulfide precipitates black CuS, insoluble in dilute, nonoxidizing acids and only slightly soluble in $(NH_4)_2S$, readily soluble in warm HNO_3 or in excess KCN [forming $Cu(CN)_3^-$].

Potassium or sodium iodide first forms CuI_2 which is very unstable and at once decomposes to form free iodine and a precipitate of pinkish-white Cu_2I_2. The cuprous iodide is insoluble in water but is soluble in excess alkali iodide or in $Na_2S_2O_3$ solution.

With alkali carbonates, a *basic carbonate* is precipitated, soluble in acids and in NH_4OH.

Cupric nitrate, sulfate, and chloride are very soluble in water.

With potassium ferrocyanide, a precipitate of brownish-red $Cu_2Fe(CN)_6$ is obtained, insoluble in water and weak or dilute acids but soluble in NH_4OH.

Bismuth. Bismuth is a rather inactive metal, insoluble in HCl or cold H_2SO_4 but soluble in HNO_3 or hot H_2SO_4 The element exhibits two principal valences, +3 and +5. The trivalent form is the most stable.

Compounds of Bismuth. The compounds of trivalent bismuth hydrolyze readily in dilute solutions, giving precipitates of the type (BiO)Cl or $(BiO)(NO_3)$. Characteristic reactions of solutions containing bismuth are as follows:

Sodium hydroxide gives white $Bi(OH)_3$, insoluble in water or in excess NH_4OH or NaOH, readily soluble in acids. Ammonium hydroxide precipitates salts of variable composition.

Hydrogen sulfide precipitates Bi_2S_3, brown; insoluble in dilute, non-oxidizing acids or in $(NH_4)_2S$, soluble in hot concentrated HCl or in dilute HNO_3.

Soluble iodides precipitate black BiI_3, soluble in excess to form yellow BiI_4^-.

Alkali carbonates precipitate *basic carbonates* of the type $Bi(OH)CO_3$.

Potassium chromate gives yellow $(BiO)_2CrO_4$, soluble in strong acids but insoluble in alkalies This last is one essential difference between lead and bismuth chromates.

Metallic zinc, or stannite ion ($HSnO_2^-$) reduces Bi^{+++}, BiO^+, or $Bi(OH)_3$ to metallic bismuth, usually as a black powder.

Strong oxidizing agents such as Cl_2, ClO^-, or H_2O_2, added to alkaline suspensions of $Bi(OH)_3$, give a brown precipitate of *metabismuthic acid*, $HBiO_3$, insoluble in water, but an oxidizing agent that is sufficiently powerful to oxidize Mn^{++} in cold HNO_3 solutions to MnO_4^-.

Cadmium. Cadmium is a moderately active metal, being but slightly less active than iron. It is an easily volatilized element (B P , 767°C.). On heating, it combines with oxygen to form brown CdO. It dissolves slowly in HCl or H_2SO_4 but rapidly in HNO_3

Compounds of Cadmium. With solutions containing Cd^{++}:

Sodium hydroxide precipitates white $Cd(OH)_2$, insoluble in excess alkali, soluble in acids or in NH_4OH [forming $Cd(NH_3)_4^{++}$].

Hydrogen sulfide precipitates, from solutions 0 3*N* or less with HCl, yellow or orange CdS; insoluble in $(NH_4)_2S$, Na_2S_x, or KCN, soluble in 3*N* HCl, in dilute HNO_3, and in hot, dilute H_2SO_4.

Sodium or ammonium carbonate forms white $CdCO_3$, insoluble in water; soluble in acids, in KCN, and in solutions of ammonium salts

Potassium ferrocyanide precipitates white $Cd_2Fe(CN)_6$

The nitrate, chloride, and sulfate of cadmium are soluble in water

Arsenic. Elementary arsenic is a gray, very brittle substance, subliming readily at 615°C., giving a vapor of a characteristic garlic-like odor. Its vapors and compounds are extremely poisonous The element is amphoteric, its oxides dissolving in acids or in alkalies. Arsenic does not dissolve in HCl but dissolves slowly in strong alkalies and more rapidly in NaOCl, aqua regia, or concentrated HNO_3. At high temperatures it combines readily with sulfur, oxygen, or chlorine and reacts with metals to form arsenides such as Zn_3As_2.

Compounds of Arsenic. Arsenic exists in both the trivalent and the pentavalent state. If in alkaline solution, the arsenic is present in the form of arsenite or arsenate ions; if in strongly acid solution, as arsenous or arsenic ion. Both types give arsine, AsH_3, a very poisonous gas, on reduction with acid and zinc or aluminum or on reduction with alkalies and aluminum. The trivalent arsenic compounds are the most easily reduced, however.

Arsenious Compounds and Arsenites. *Arsenous oxide*, As_2O_3, is white and is slightly soluble in water, the compound is very soluble in HCl, forming As^{+++}, and in alkalies, forming arsenite, $AsO_3^{\equiv}$, ion.

Hydrogen sulfide causes no precipitation from neutral or alkaline solutions of arsenites, owing to the formation of soluble thioarsenites. From slightly acid solutions of arsenites H_2S readily precipitates As_2S_3, yellow, insoluble in dilute, nonoxidizing acids but soluble (with long boiling) in concentrated HCl and readily soluble in concentrated HNO_3, aqua regia, or ammoniacal H_2O_2 (forming $AsO_4^{\equiv}$), in ammonium carbonate (forming a mixture of thioarsenite, AsS_3^-, and arsenite, AsO_3^-), in alkali sulfides (forming $AsS_3^{\equiv}$), and in Na_2S_x (forming thioarsenate, $AsS_4^{\equiv}$).

Silver nitrate, with neutral or faintly acid solutions of arsenites, gives Ag_3AsO_3, yellow, insoluble in water, but readily soluble in NH_4OH or HNO_3.

Ammonium molybdate, and magnesia mixture give no precipitate with arsenites. This is an important analytical difference between arsenites and arsenates.

Zinc or aluminum with acidic or strongly alkaline solutions of arsenites gives arsine.

Arsine decomposes on heating, giving As and H_2. This is the basis of the Marsh test for arsenic.

Oxidizing agents readily oxidize arsenites to arsenates, the reaction being most easily accomplished in alkaline or neutral solutions. In hot, alkaline solutions, arsenites reduce $Cu(OH)_2$ to yellow or red Cu_2O.

Arsenic Compounds and Arsenates. *Arsenic oxide*, As_2O_5, dissolves readily in water to form arsenic acid, H_3AsO_4, and in alkalies to form arsenates.

Hydrogen sulfide does not form any precipitate with neutral solutions of arsenates. With weakly acid solutions, it will form As_2S_5 only after a long period of time. However, if the solution of arsenate is first made strongly acid with HCl, yellow As_2S_5 precipitates at once.* As_2S_5 is insoluble in

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* The failure of H_2S to precipitate the sulfides from neutral or weakly acid solutions of arsenates is due partly to the formation of soluble complex thioarsenate ions (such as $AsS_4^{\equiv}$, $AsO_3S^{\equiv}$, etc.) and partly to the fact that H_3AsO_4 is quite stable and gives a very low concentration of As^{+++++} ions. A high concentration of H^+ ions, however, favors the formation of As^{+++++} ions, in accordance with the equation

$$H_3AsO_4 + 5H^+ \rightleftharpoons As^{+++++} + 4H_2O$$

Therefore, since As_2S_5 is insoluble in quite concentrated HCl, As_2S_5 precipitates readily from solutions of strong HCl.

water or nonoxidizing acids. It is soluble, however, in the same solvents as those listed for As_2S_3. With $(NH_4)_2CO_3$, As_2S_5 forms a mixture of $AsO_4^{\equiv}$ and $AsS_4^{\equiv}$; with $(NH_4)_2S$, it forms $AsS_4^{\equiv}$.

Soluble iodides reduce *acid* solutions of arsenates to *arsenites*, the reaction being

$$AsO_4^{\equiv} + 2H^+ + 2I^- \rightarrow AsO_3^{\equiv} + H_2O + I_2$$

Silver nitrate gives, with neutral solutions of arsenates, Ag_3AsO_4, chocolate-colored, insoluble in water, but soluble in NH_4OH and in acids.

Ammonium molybdate gives, in dilute HNO_3 solutions of arsenates, $(NH_4)_3AsO_4\ 12MoO_3$, yellow, insoluble in water or dilute HNO_3, but readily soluble in NH_4OH or alkalies. Excess reagent is needed for the precipitation.

Magnesia mixture (a mixture of $MgCl_2$, NH_4OH, and NH_4Cl) precipitates white, crystalline $MgNH_4AsO_4$, insoluble in water or dilute NH_4OH, but soluble in even weak acids. Arsenites give no precipitate with this reagent.

Antimony. Metallic antimony is a brittle, silvery metal, with a melting point of 630°C., a boiling point of 1380°C., and a density of 6.7. At high temperatures, antimony combines readily with oxygen to form Sb_2O_3 and Sb_2O_4, with sulfur to form Sb_2S_3, and with chlorine to form $SbCl_3$ and $SbCl_5$. It does not dissolve in nonoxidizing acids but dissolves readily in aqua regia. HNO_3 attacks it but forms an oxide that is soluble, with great difficulty, in concentrated HNO_3, more readily in HCl or aqua regia.

Compounds of Antimony. Though antimony exists in both the tri- and pentavalent states, the trivalent compounds are the most stable. Both oxides are amphoteric, but Sb_2O_3 is more basic and Sb_2O_5 is more acidic in nature. Antimonic compounds are oxidizing agents.

All antimony salts hydrolyze in dilute solution, $SbCl_3$ giving SbOCl and $Sb(OH)_3$, both of them white, insoluble in water, but soluble in acids or in alkalies. Tartrates repress the precipitation, forming soluble $(SbO)C_4H_4O_6^-$ ions.

Sodium hydroxide, ammonium hydroxide, or alkali carbonates precipitate antimony hydroxide, $Sb(OH)_3$, white, soluble in acids or strong alkalies.

Hydrogen sulfide precipitates Sb_2S_3, orange, insoluble in dilute nonoxidizing acids; soluble in strong HCl, in $(NH_4)_2S$ (forming $SbS_3^{\equiv}$), and in alkalies (forming mixtures of thio- and oxythioantimonite ions).

Zinc or *aluminum* with *nonoxidizing acids* reduces antimony compounds mostly to finely divided, black elementary *antimony*, but partly to stibine, SbH_3, a gas giving reactions very similar to those of arsine, AsH_3. Stibine, unlike arsine, is not formed by alkaline reduction, this difference often being used as a method of identifying arsenic in the presence of antimony. The Marsh test gives a mirror of metallic Sb, which is distinguished from the As mirror by the fact that Sb is not soluble in NaOCl solution.

Tin. Metallic tin is a soft, malleable metal, having a melting point of 232°C., a boiling point of 2270°C., and a density of 7.3. Being just above hydrogen in the displacement series, it slowly dissolves in dilute nonoxidizing acids or more readily in hot concentrated HCl. The metal reacts with HNO_3,

to form metastannic acid, H_2SnO_3, a white substance, insoluble in alkalies or acids In neutral or only slightly acid solutions, zinc displaces tin from its compounds, forming the metal.

Compounds of Tin. Tin forms compounds in which it has a valence of 2 and of 4. The latter are the most stable, as air readily oxidizes the former to the tetravalent state. Both forms are amphoteric, and the compounds of both hydrolyze readily in dilute aqueous solutions. When in aqueous solutions, the tin is in the form of complex ions of the type $SnCl_6^=$ rather than as simple ions

Stannous Compounds. $SnCl_2$ (the most common stannous compound) hydrolyzes in water, giving $Sn(OH)Cl$ or, in more dilute solutions, $Sn(OH)_2$. Solutions of $SnCl_2$ are kept stable by adding HCl, to prevent hydrolysis, and metallic tin, to reduce any stannic ions formed by air oxidation. The tin is actually present as a complex ion such as $SnCl_4^=$.

With NH_4OH, carbonates or alkalies, white $Sn(OH)_2$ is precipitated, only slightly soluble in excess NH_4OH but readily soluble in excess alkali (forming stannite, $HSnO_2^-$, ion) and in mineral acids Stannites decompose slowly on standing (or more rapidly if heated), giving a brown mixture of SnO_2 and metallic tin. The stannites are powerful reducing agents, being capable of reducing the hydroxides of many metals to form the free metal. An example is the use of $HSnO_2^-$ to reduce $Bi(OH)_3$ to Bi in testing for bismuth

Hydrogen sulfide precipitates SnS, brown, insoluble in water or $(NH_4)_2S$, but soluble in moderately strong HCl, in mixtures of oxalic acid and ammonium salts, also in alkali or ammonium polysulfide, forming thiostannate, $SnS_3^=$, ion The latter decomposes on acidification, giving SnS_2.

All stannous compounds are good reducing agents. They reduce $HgCl_2$ to Hg_2Cl_2, then to free Hg Bismuth compounds are reduced by alkaline stannite solutions to black metallic Bi Alkaline solutions of lead are reduced, in a similar manner, to metallic Pb, the reaction being much slower than with bismuth compounds Stannous compounds will also reduce ferric ions to the ferrous state and gold chloride to finely divided gold, Au.

Stannic Compounds. The simple stannic ion seldom exists in solution, as it has strong tendencies to form complex negative ions. In neutral aqueous solutions, stannic compounds hydrolyze, forming $Sn(OH)_4$. To prevent this the solution must be strongly acid, the tin being in ions of the type $SnCl_6^=$.

Alkalies, NH_4OH, or soluble carbonates precipitate $Sn(OH)_4$ from solutions of stannic compounds. The $Sn(OH)_4$ thus formed is white, insoluble in NH_4OH or Na_2CO_3, but soluble in alkalies or K_2CO_3 [forming $Sn(OH)_6^=$], and in mineral acids. If the stannic hydroxide is allowed to stand or is heated for a while, it is converted to metastannic acid, H_2SnO_3, which is insoluble in either acids or alkalies.*

* A very effective method of putting metastannic acid into solution is to fuse it with Na_2CO_3 and sulfur, treating the pulverized residue with water. The reaction is

$$2H_2SnO_3 + 2Na_2CO_3 + 9S \rightarrow 2Na_2SnS_3 + 3SO_2 + 2CO_2 + 2H_2O$$

When this is weakly acidified, SnS_2 precipitates.

Hydrogen sulfide reacts with solutions of stannic compounds, precipitating SnS_2, yellow, insoluble in water or ammonium carbonate, soluble in $(NH_4)_2S$ or alkali polysulfides (forming $SnS_3^=$) and in acids Considerable amounts of oxalic acid prevent this precipitation

Antimony, lead, or iron reduce acid solutions of stannic compounds to the stannous state but not to the metal *Zinc or aluminum* reduces stannic solutions to metallic tin; but if the solution is strongly acid, the tin redissolves, forming stannous ion In analytical work these metals are used to reduce stannic ion to stannous, and the final test for tin depends upon testing the resulting solution for the reducing properties characteristic of Sn^{++}.

Stannic compounds are not reducing agents

Preliminary Experiments*

1. Comparison Tests. *a. Hydroxides.* In each of seven test tubes, place 3 drops of water. To one add 1 drop of Hg^{++} solution; to another, Pb^{++}; to another, Bi^{+++}; to another, Cu^{++}; to another Cd^{++}; to another Sb^{+++}; and to another Sn^{++}. Note results, and record them in a chart, together with the formulas of any products obtained (Question 1). Now to each add 1*N* NaOH, drop by drop, recording results. Finally, add to each an excess (2 or 3 drops) of 6*N* NaOH and stir, noting which precipitates dissolve completely (Question 2).†

Heat any of the mixtures containing undissolved precipitate, and note any changes in the color and form of the precipitate, recording these results in your chart. In every case write the formula of the chief product in the space in which the appearance of the product is recorded (Question 3).

Again precipitate the hydroxides of these metals with 1*N* NaOH, but this time try to redissolve them in concentrated NH_4OH‡ (Question 4).

* *Note to Instructor:* It is suggested that some of these preliminary experiments be omitted. The large number described are included to give a large choice.

† When a water-insoluble hydroxide of a metal dissolves in NaOH or KOH, the phenomenon indicates that the hydroxide is *amphoteric.* A number of metals have this characteristic An explanation of this behavior will be found in the theory portion on p. 146.

‡ When the hydroxides or water-insoluble salts of a metal dissolve in NH_4OH, the dissolution is usually due to the formation of ammonia complexes (see Chap. VIII) with the cation, as NH_4OH is too slightly ionized to furnish the high concentration of OH^- needed to make an amphoteric hydroxide demonstrate its amphoteric nature. In these cases the NH_4OH is furnishing NH_3 molecules, as illustrated in the equation

$$NH_4OH \rightleftharpoons NH_3 + H_2O$$

b. Iodides. On microscope slides place, in separate spots, single drops of Hg^{++}, Pb^{++}, Cu^{++}, Bi^{+++}, Cd^{++}, and Sn^{++}. To each add 1 drop of 0.1*N* KI solution, and note results.* To any that produce precipitates, add an excess (2 or 3 drops) of 1*N* KI solution and stir (Question 5).

2. Mercuric Ion, Hg^{++}. *a.* Pass H_2S through 3 drops of Hg^{++} test solution for about 30 sec., noting any color changes that occur. Complete the precipitation; then filter and wash the precipitate. Divide the precipitate into three parts, and use in the tests that follow:

b. Test one portion of the HgS to see if it is soluble in ammonium monosulfide, $(NH_4)_2S$ (see Note 9).

c. To the second portion of the HgS, add about 5 drops of 4*N* HNO_3 and heat on the steam bath for about 3 min. (Question 6).

d. To the third portion of the HgS, add 6 drops of freshly prepared aqua regia† (Question 7) and heat on the steam bath 2 to 3 min. Finally evaporate to dryness, completing the evaporation on the steam bath. Cool; add 3 drops of water; stir; then filter, and use the solution for *e*.

e. To 1 drop of the filtrate on a watch glass add 1 drop of $SnCl_2$ solution. To a second drop add 1 drop of 0.1*N* KI solution.‡

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* The precipitate produced by the Cu^{++} and KI is white, but the solution is colored by free iodine. The reaction is

$$Cu^{++} + I^- \rightarrow Cu_2I_2 + I_2$$

† When nitric and hydrochloric acids are mixed, as in aqua regia, the following reaction occurs:

$$HNO_3 + 3HCl \rightarrow 2H_2O + NOCl + Cl_2$$

Consequently, if the mixture is used *at once* on mixing, before the reaction is complete and before the chlorine is lost from the solution, it will dissolve substances that would resist the reaction of either acid alone.

In dissolving substances such as HgS, therefore, the nitrate ions, the chlorine, and the nitrosyl chloride (NOCl, which readily breaks down to form nascent chlorine and NO) all act as oxidizing agents, oxidizing the $S^=$ to free sulfur and to sulfate ion. In addition, the ability of Hg^{++} to react with chloride ions to form $HgCl_4^=$ aids markedly in driving the reaction to completion.

It will be noted that the reaction of aqua regia on metals or compounds of metals produces chlorides of the metals.

‡ The nature of these reactions was discussed in connection with the study of Hg_2^{++} in Group I.

f. To 1 drop of Hg^{++} test solution add a clean pellet of copper. Note the change in the appearance of the pellet. Wash it carefully; then rub its surface with the thumbnail, and notice the formation of tiny silvery droplets of mercury.

g. To 1 drop of Hg^{++} solution, add 1 drop of 1*N* HCl, and contrast results with those obtained by adding HCl to Hg_2^{++} in Group I. Finally, add 1 drop of *dilute* NH_4OH to the mixture, and note results (Question 8).

3. Cupric Ion, Cu^{++}. *a.* Precipitate CuS by saturating 2 or 3 drops of Cu^{++} test solution with H_2S. Filter and wash the precipitate; then divide the precipitate into two equal parts.

Try dissolving 1 part of the precipitate in hot 4*N* HNO_3. To the second portion of the CuS precipitate add 5 drops of $(NH_4)_2S$ solution, and warm on the steam bath (see Question 9).

b. To 2 drops of Cu^{++} test solution add 2 drops of 6*N* NH_4OH. Then add, drop by drop until the deep blue color just disappears, a 3 per cent solution of KCN. (*Caution:* KCN is an extremely dangerous poison. If added to acid solutions it gives off very poisonous fumes of HCN. For this reason it is important that every detail in the procedure be checked before KCN is used.) Now bubble H_2S through the solution for a minute.*

c. To 1 drop of Cu^{++} in a test tube, add 1 drop of dilute HCl, 3 drops of water, and a small pinch of iron filings or a bit of iron wire. Heat on a steam bath for 10 or 15 min.; then note the appearance of the solid in the bottom of the test tube and the change in color of the solution.

d. To 2 drops of Cu^{++} solution add 1 drop of $K_4Fe(CN)_6$ solution.

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* When cyanide ion is added to a solution containing cupric ion, two successive reactions occur. First, the ions combine to form cupric cyanide, which is unstable and immediately decomposes to form insoluble cuprous cyanide and a *very poisonous gas*, cyanogen, C_2N_2. The cuprous cyanide then reacts with more cyanide to form the highly soluble, extremely stable cuprocyanide ion. The reactions are

$$Cu^{++} + 2CN^- \rightarrow Cu(CN)_2$$
$$2Cu(CN)_2 \rightarrow Cu_2(CN)_2 + C_2N_2$$
$$Cu_2(CN)_2 + 4CN^- \rightarrow 2Cu(CN)_3^-$$

As cuprocyanide ions are very stable, their solutions contain few copper ions. Consequently, hydrogen sulfide will not precipitate the sulfides of copper from solutions of cuprocyanide ions in the presence of excess cyanide ions.

4. Bismuth Ion, Bi^{+++}. Bismuth forms a sulfide under the same conditions as does copper. Like CuS, Bi_2S_3 is black in color and is soluble in $4N$ HNO_3. To save time, only a few of the other characteristic reactions of its ions will be tried experimentally.

a. To 1 drop of Bi^{+++} test solution add 10 drops of water. Add $6N$ NH_4OH, drop by drop, until the solution is basic. Can you see any precipitate in the solution? Try to dissolve it by adding more NH_4OH (see Note 12).

b. To 1 drop of Bi^{+++} test solution on a filter paper add 1 drop of $1N$ NaOH solution and 1 drop of freshly prepared sodium stannite solution.*

c. To compare the action of K_2CrO_4 on Bi^{+++} with its action on Pb^{++}, to 1 drop of Bi^{+++} add 1 drop of $6N$ sodium acetate and 1 drop of $1N$ K_2CrO_4 solution. Similarly, precipitate some $PbCrO_4$; then to both precipitates add 2 drops of $6N$ NaOH, and stir. Note whether or not it would be possible to distinguish between the two cations by these reactions.

5. Cadmium Ion, Cd^{++}. *a.* Into 3 drops of Cd^{++} test solution pass H_2S until precipitation is complete. Filter and wash the precipitate; then add a mixture of 3 drops of $6N$ H_2SO_4 and 3 drops of water. Warm on the steam bath for 8 to 10 min.; then filter. Dilute the filtrate with twice its volume of water; then pass in H_2S again.

b. To 1 drop of Cd^{++} test solution add 1 drop of Cu^{++} test solution and 4 drops of water. To this add 2 drops of concentrated NH_4OH; then add 3 per cent KCN solution, drop by drop, until the blue color of the copper is discharged. Bubble H_2S through this solution for a few seconds.

c. To a mixture of 1 drop of Cu^{++}, 1 drop of Cd^{++}, 1 drop of dilute HCl, and 3 drops of water, add a tiny pinch of iron filings or a bit of iron wire, and warm on the steam bath for 15 min. Filter; then add 2 drops of $1N$ HCl, and pass H_2S into the solution (Question 11).

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* To make sodium stannite, $NaHSnO_2$, solution, add $6N$ NaOH drop by drop to 2 drops of stannous chloride, $SnCl_2$, solution until the gelatinous precipitate of $Sn(OH)_2$ that first forms just dissolves.

Stannites are powerful reducing agents, and the stannite ion reduces the $Bi(OH)_3$, forming finely divided bismuth and stannate ion

$$Bi(OH)_3 + HSnO_2^- \rightarrow Bi^0 + H_2O + SnO_3^=$$

6. Arsenous, As^{+++}, and Arsenic, As^{+++++}, Ions. *a.* Pass H_2S through a mixture of 2 drops of As^{+++++} test solution and 2 drops of 1*N* HCl until a precipitate forms. Note the length of time that it takes.

To a mixture of 2 drops of As^{+++++} test solution and 2 drops of 1*N* HCl add a small crystal of NH_4I; heat to boiling, and pass H_2S through the solution. Note the length of time required before a precipitate forms this time (see Note 5). Complete the precipitation; then filter and wash the precipitate.* Divide the precipitate into two portions.

To one portion of the precipitate add 5 drops of $(NH_4)_2S$ solution (see Note 9) and warm. When solution is complete, add 6*N* $HC_2H_3O_2$, drop by drop until the solution is faintly acid, then warm on the steam bath 1 or 2 min. (see Note 16).

To another portion of the precipitate add 3 to 5 drops of concentrated HCl, and heat on the steam bath. Does the precipitate dissolve?

b. Precipitate some As_2S_3 by adding H_2S to a mixture of 2 drops of As^{+++} and 1 drop of dilute HCl. Filter; wash the precipitate; then dissolve it, with stirring, in 5 drops of dilute NH_4OH and 5 drops of H_2O_2. Warm on the steam bath for 2 or 3 min. to complete the conversion to $AsO_4^{\equiv}$; filter if necessary, and divide the filtrate into two parts.

To one part add 2 drops of *freshly filtered* magnesia mixture. Rub the inside of the container with a stirring rod to overcome supersaturation, and let stand 10 or 15 min. Observe results against a black background. The fine, white, crystalline pre-

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* These reactions, which are used in the Group II precipitation to bring down any pentavalent arsenic quickly, are as follows: When NH_4I is added to an acid solution containing As^{+++++} (or $AsO_4^{\equiv}$), the following reduction of the arsenic takes place

$$AsO_4^{\equiv} + 2H^+ + 2I^- \rightarrow AsO_3^{=} + H_2O + I_2$$

When H_2S is passed into the solution, the I^- is reformed by the reaction

$$I_2 + H_2S \rightarrow 2H^+ + 2I^- + S^0$$

and the I^- formed goes through the process again. Consequently, only a very small quantity of NH_4I is required for the reduction, even though the quantity of As^{+++++} in the unknown is great.

cipitate is $MgNH_4AsO_4$.* Make the second portion strongly acid with HNO_3 by adding 2 drops of concentrated HNO_3; then add 6 or 7 drops of ammonium molybdate, and stir. Heat for 15 min. on the steam bath, and note results.†

7. Antimony Ion, Sb^{+++}. *a.* Pass H_2S into 2 drops of Sb^{+++} test solution until precipitation is complete. Filter and wash the precipitate; then divide it into two parts.

To one portion of the precipitate add 5 drops of $(NH_4)_2S$ solution, and warm on the steam bath. To the solution so obtained add 6*N* $HC_2H_3O_2$, drop by drop, until the solution is acid. Warm on the steam bath, and note occurrences.

To the second portion of precipitate add 5 drops of concentrated HCl, and heat until the precipitate dissolves. Now add 5 drops of cold water, and pass H_2S into the mixture for 1 min.

b. To 1 drop of Sb^{+++} test solution add 5 drops of water. Now try to redissolve the resulting precipitate by adding concentrated HCl.

c. To 1 drop of Sb^{+++} add 1 drop of water and a single small granule of aluminum. Keep hot on the steam bath until all visible reaction ceases. Try to dissolve any residue left in 1 or 2 drops of HCl, and see if any of the residue fails to do so. The residue is finely divided antimony.

8. Stannous, Sn^{++}, and Stannic, Sn^{++++}, Ions. *a.* Pass H_2S into 2 drops of Sn^{++} test solution until precipitation is complete.

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* Sometimes a flocculent or gelatinous white precipitate is obtained instead of the fine crystalline precipitate This is $Mg(OH)_2$, which forms when the concentration of NH_4OH is too great or that of NH_4Cl in the magnesia mixture is too low. If the precipitate is not definitely fine and crystalline, acidify the whole mixture with HCl, filter, then make the solution basic with NH_4OH again. On standing, the right kind of precipitate will form if $AsO_4^{\neg}$ is present.

† Both the magnesia-mixture test and the molybdate test are given by phosphates as well as by arsenates If the analytical separation has been clean-cut, however, phosphates will not be present at the time this test is made for arsenic.

When ammonium molybdate is used as a reagent for arsenates or phosphates, a large excess of the reagent must be used, as otherwise the products that form are soluble in the HNO_3 solution

When arsenates and phosphates are absent, a dirty white precipitate of molybdic acid, H_2MoO_4, is frequently obtained. Only yellow precipitates should be accepted as positive tests for these ions, therefore, when ammonium molybdate is used as the reagent.

Filter and wash the precipitate; then divide it into two portions.

Try dissolving one portion of the precipitate in 4 or 5 drops of $(NH_4)_2S$ solution.

To the second portion of SnS add 5 drops of concentrated HCl, and warm to see if the precipitate will dissolve.

b. Pass H_2S into 2 drops of Sn^{++++} test solution. Filter and wash the precipitate; then divide it into two parts.

Test the solubility of one part in hot $(NH_4)_2S$, and contrast the results with those obtained with the SnS above.

Dissolve the remainder of the SnS_2 precipitate in 10 drops of concentrated HCl. To this solution add the smallest possible granule of zinc. Heat until all the zinc is dissolved; then to half of the solution add a drop of $HgCl_2$ solution.* To the other half of the solution add 1 drop of gold (auric) chloride ($AuCl_3$), and note results. Colloidal gold is formed and is responsible for the color observed.

Compare these results with those obtained by mixing 1 drop of Sn^{++} test solution, 10 drops of water, and 1 drop of $AuCl_3$ solution.

c. To 1 drop of Sn^{++} solution add 2 or 3 drops of H_2O_2. Pass H_2S into the mixture, and note by the color whether the precipitate produced is SnS or SnS_2 (see Note 1).

Analytical Aspects

The cations in this group consist of those whose sulfides can be precipitated by H_2S from solutions whose acidity corresponds to that of 0.3*N* HCl. The conditions of acidity are critical, as some of the members of this group—notably tin and cadmium—are somewhat soluble in solutions whose acidity is only slightly greater than this whereas some of the members of Group III, especially zinc, give sulfide precipitates from solutions that are only slightly less acid. In fact, if the concentration of Zn^{++} in the unknown is moderately great, some ZnS will precipitate even from the 0.3*N* HCl solution.

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* The function of the zinc and HCl is to reduce Sn^{++++} to Sn^{++}, as Sn^{++++} does not have reducing properties.

The reduction of $HgCl_2$ to insoluble Hg_2Cl_2 then to black Hg^0 was used earlier in testing for mercury (which see). In that case, the reagent was a known solution of $SnCl_2$. In this case, the reagent is $HgCl_2$ which is to be used in testing for Sn^{++}.

The large number of cations in Group II makes it advisable to separate this group into smaller subgroups to make the chances of mutual interference less. This is done by taking advantage of the fact that only the sulfides of arsenic, antimony, and stannic ions are soluble in ammonium monosulfide, $(NH_4)_2S$, solution. These three elements constitute the *tin group;* the other elements are known as the *copper group.*

Lead is considered in this group as well as in Group I because its chloride is not extremely insoluble (at 20°C., 100 g. of water will dissolve about 1 g. of $PbCl_2$). Consequently, some lead will always slip through into Group II; and if the concentration of lead is low in the unknown, the lead may be missed entirely in Group I. The Group II analysis for lead is much more sensitive than is the Group I analysis.

Group II Analysis

Use the filtrate from the Group I precipitate (or, if a Group II unknown, take 1 ml. of the solution issued to you). Add 7 or 8 drops of H_2O_2 to the solution (Note 1). Evaporate the solution *barely* to dryness, add 5 or 6 drops of concentrated HCl to the residue, and evaporate again *very carefully* (see Notes 2 and 3). *Cool,* add 1 drop of conc. HCl, and tilt and rotate the test tube until the residue is moistened with the acid. Add 40 drops of water and stir. Pass H_2S into the solution *until precipitation is complete* (see Note 4). Add 2 or 3 small crystals of NH_4I (see Note 5), heat to boiling, and again pass in H_2S. Cool; complete the saturation; then filter (see Notes 6 and 7). Wash the precipitate with 1*N* NH_4NO_3 soln. through which H_2S has been passed for 1 or 2 min. (see Note 8).

Filtrate. Make strongly acid with HCl, and boil to half its volume to remove H_2S. Save for Groups III, IV, and V.	**Precipitate.** Contains sulfides of all Group II metals. Add 10 drops $(NH_4)_2S$ soln. (see Note 9), and heat on the steam bath for 1 or 2 min. with stirring. Filter, saving both the filtrate and precipitate. Repeat the treatment of the precipitate with successive portions of hot $(NH_4)_2S$ until no more precipitate seems to dissolve. Combine the filtrates. Wash the precipitate twice with 1*N* NH_4NO_3 soln. saturated with H_2S, discarding the second wash liquid.

Filtrate. Contains members of Group II*B* as thio ions $AsS_3^{=}$, $SbS_3^{=}$, and $SnS_3^{=}$. Treat as described for the subgroup.	**Precipitate.** Contains sulfides of Group II*A* metals. Treat as described for this subgroup.

GROUP IIA ANALYSIS

To the precipitate from the subgroup separation add 10 drops of 4*N* HNO_3, and heat almost to boiling. Keep the mixture hot for 2 or 3 min., stirring continuously; then filter. If much precipitate is left, repeat the treatment, combining the filtrates; then wash the precipitate with water.

Filtrate. Contains Pb^{++}, Bi^{+++}, Cu^{++}, and Cd^{++}. Add 3 drops of conc. H_2SO_4, and evaporate over a micro flame until *very dense* white fumes appear and only 2 or 3 drops of liquid remain (see Note 10). *Cool;* then add 1 ml. of cold water, and stir. Let stand 30 to 60 sec.; then filter. Wash the precipitate twice with cold water (see Note 11).

Precipitate. Contains sulfur and/or HgS. Add 3 drops of conc. HNO_3 and 9 drops of conc. HCl, warm on the steam bath with stirring 2 or 3 min. Then evaporate to dryness (see Note 15), removing the last 2 or 3 drops of liquid by heating on the steam bath. Dissolve the residue in 6 to 8 drops of water. Filter, and use the filtrate as follows:

To 3 drops add 1 drop of $SnCl_2$ soln.
WHITE or GRAY PPT.
indicates Hg^{++} present.

To the remainder of the filtrate add a *freshly* polished bit of metallic copper and let stand 5 to 10 min.
GRAY or SILVERY deposit
on the copper confirms Hg^{++}.

Filtrate. Contains Bi^{+++}, Cu^{++}, and Cd^{++}. Add an excess of 6*N* NH_4OH; stir; then filter even if no precipitate is visible (see Note 12). Wash any precipitate with dilute NH_4OH.

Precipitate. $PbSO_4$ (possibly some basic bismuth sulfate). Add 10 drops of 6*N* ammonium acetate and heat almost to boiling. Filter, then to the filtrate add 1 drop K_2CrO_4 soln.
YELLOW PPT.
indicates Pb^{++}.
Confirm by filtering and adding excess 6*N* NaOH to the precipitate.
PRECIPITATE DISSOLVING
confirms Pb^{++}.

Filtrate. Contains $Cu(NH_3)_4^{++}$ and $Cd(NH_3)_4^{++}$.
BLUE COLOR
indicates Cu^{++} present.
To 1 drop of the filtrate add 1 drop 6*N* $HC_2H_3O_2$ and 1 drop of $K_4Fe(CN)_6$ soln.
RED PPT.
confirms Cu^{++}.

Evaporate the remainder of the filtrate to one-third its volume, and filter if necessary. Cool the filtrate; then test for Cd^{++}. If Cu^{++} was present, add KCN soln. (*Caution:* KCN is exceedingly poisonous and must be handled with great care) drop by drop until the blue color of $Cu(NH_3)_4^{++}$ disappears; then add 3 or 4 drops in excess. If no Cu^{++} was present, proceed without using KCN. Pass in H_2S for 2 to 3 min., noting the color of any precipitate that forms.
YELLOW PPT.
indicates Cd^{++} (see Note 14).

Precipitate. $Bi(OH)_3$ [and possibly traces of $Pb(OH)_2$]. Dissolve in 5 or 6 drops 2*N* HCl. To 2 drops of the solution on filter paper add 1 drop of dil. NaOH and 2 drops of freshly prepared sodium stannite soln. (see footnote, page 221).
BLACK COLORATION indicates Bi^{+++} present (see Note 13).

GROUP IIB ANALYSIS

To the filtrate from the subgroup separation, add dil. $HC_2H_3O_2$ until it is just definitely acid (see Note 16) Heat for 2 or 3 min. on the steam bath; then filter, and wash the precipitate with NH_4NO_3-H_2S soln. (see Note 17).

Filtrate. Discard.

Precipitate. As_2S_3, Sb_2S_3, and SnS_2. Add 10 drops conc. HCl; warm on the steam bath, and stir for 1 min. Cool, and add 2 drops water. Filter, and wash the precipitate with 6*N* HCl.

Filtrate. Contains Sb^{+++} and Sn^{++++}. To 2 drops of the liquid add 2 drops (*exactly*) of water, and saturate with H_2S.

ORANGE PPT.

indicates Sb present (see Note 18).

To the remainder of the filtrate in a 100-mm. test tube, add 10 drops of water and 2 to 3 small aluminum filings. Suspend a 75-mm test tube two-thirds full of cold water in the larger test tube to act as a condenser. Heat the mixture *gently* keeping it just hot enough to promote rapid reaction. Continue until all the aluminum has dissolved, adding 2 or 3 drops conc. HCl, if necessary Examine the bottom of the large test tube carefully.

FINE BLACK PPT.

that is insoluble in HCl confirms antimony.

Filter the solution from the Al reduction, and divide the filtrate into two equal parts. Neutralize one part with dil. NH_4OH, then make it slightly acid with 1*N* HCl. Add 2 or 3 drops of H_2O_2, stir, then saturate with H_2S.

YELLOW PPT.

indicates tin.

On the remainder of the solution repeat the reduction with aluminum (see Note 19). Add more conc. HCl if reaction slows too much, and keep the mixture hot. *When all reaction has ceased,* divide the solution into two parts. To one part add 1 drop of $HgCl_2$ solution.

WHITE or GRAY PPT.

confirms Sn (see Note 20).

Precipitate. As_2S_3 and/or sulfur. To the precipitate add 7 or 8 drops of 6*N* NH_4OH and an equal volume of 3 per cent H_2O_2. Warm on the steam bath with stirring for 2 or 3 min. Filter if necessary; then divide the filtrate into two equal parts.

Evaporate one portion of the solution *almost* to dryness. Add 2 or 3 drops of water, about 8 drops of conc. HNO_3, and 6 or 8 drops of ammonium molybdate solution. Warm on the steam bath, with frequent stirring, for 10 to 15 min.

FINE YELLOW PPT.

indicates arsenic present (see footnote, page 223).

To the second portion of solution, add 2 or 3 drops of saturated NH_4Cl and 2 or 3 drops of $MgCl_2$ soln. Place on steam bath, and heat for 10 to 15 min., stirring frequently.

FINE WHITE PPT.

indicates arsenic present (see footnote, page 223).

Questions on Preliminary Experiments

1. Which of the metals of Group II form water-insoluble hydroxides? Which do not?

2. What is meant by the term *amphoteric hydroxide*? The hydroxides of which metals of Group II are amphoteric? Illustrate by equations.

3. What can you say as to the thermal stability of the hydroxides of the Group II metals? What usually is produced when the unstable hydroxides are heated?

4. Which metals of Group II form ammonia complexes? Illustrate by equations the formation of these complexes.

5. The dissolving of a water-insoluble iodide in excess KI or NaI indicates that the metal is capable of forming what kind of ion with iodide ion? Would the metal be expected to form similar ions with chlorides or bromides? Illustrate these answers with equations

6. Would you classify 4*N* HNO_3 as being a poor or a good solvent for HgS?

7. Why is it necessary to prepare aqua regia fresh at the time it is needed rather than keep a stock supply of the mixture? Illustrate your answer by equations.

8. Could you distinguish between Hg_2^{++} and Hg^{++} by the tests described in Preliminary Experiment 2*g*? Explain.

9. Do HgS and CuS dissolve in $(NH_4)_2S$? Which of the other members of the group behave similarly? Which of these cations form sulfides which are soluble in $(NH_4)_2S$? (See Note 16.)

10. How could the properties described in Question 9 be used to separate Group II metals into subgroups? Illustrate by typical equations.

11. What is the nature of the deposit that forms when iron is placed in the $Cu^{++} - Cd^{++}$ mixture? What is the precipitate that forms with the H_2S?

12. What is the color and the formula of the sulfide of each cation in Group II? What valences may each of these metals exhibit?

13. The salts of which metals in Group II hydrolyze to form insoluble compounds? What is the formula of the compound produced in each case?

Notes

1. It is necessary to oxidize any Sn^{++} present to the Sn^{++++} state, as otherwise the subgroup separation, which employs $(NH_4)_2S$ to dissolve the sulfides of arsenic, antimony, and tin, will not work for the tin. SnS is not significantly soluble in $(NH_4)_2S$ reagent.

2. One purpose of this evaporation is to destroy any oxidizing agents such as HNO_3, nitrates, etc. If this is not done, the oxidizing agents will attack the H_2S, for H_2S is a powerful reducing agent (see page 105) as is illustrated by the equation

$$NO_3^- + H_2S \rightarrow NO + 2H_2O + 2S$$

This destruction of the $S^=$ not only interferes with the precipitation of the sulfides of Group II but also produces a large quantity of sulfur, which interferes with the action of some of the reagents used later.

The other purpose of the evaporation is to remove any excess acid so that the addition of 1 drop of concentrated HCl and 40 drops of water will produce a solution whose acidity is close to that of 0.3*N* HCl.

3 The last few drops of liquid should always be evaporated on the steam bath If the residue is heated by direct flame there is danger (*a*) that volatile substances like $AsCl_3$ and $HgCl_2$ will be lost by vaporization and (*b*) that the hydrolysis of some of the salts will produce oxides, many of which, on being heated, change to forms not readily soluble in acids. Such insoluble residues would then be found mixed with the sulfides of Group II; and the net result would be to weaken the tests for many metals and to cause marked interference with the tests for the members of Group II. One troublesome example is iron, the aqueous solution of whose chloride yields, on being evaporated to dryness, the following products:

$$2FeCl_3 + 3H_2O \rightarrow Fe_2O_3 + 6HCl$$

the reaction going to completion because the HCl is lost by evaporation.

Partial hydrolysis of the chlorides of such metals as bismuth or antimony to form basic salts may occur even when the evaporation is performed properly. The products of the hydrolysis are white, in such cases; and though they are insoluble in the 0.3*N* HCl medium used in the precipitation, their presence need not worry the student. It is necessary only to continue adding H_2S until the sulfide precipitate contains no visible flecks of white and until the precipitation is otherwise complete.

4. It is essential that the precipitation with H_2S be complete before adding the next reagent, NH_4I. There are a number of reasons for this, but the most important is the fact that if any lead is present and this lead is not changed to the sulfide before the iodide is added, lead iodide will be formed. The lead iodide is exceedingly difficult to change to the sulfide and, unless it is so changed, does not follow cleanly the outlined procedure.

5. The precipitation of As_2S_5 from solutions of arsenic ion, As^{+++++}, by means of hydrogen sulfide is very slow except in hot strongly acid solutions. High acidity is prohibited in this separation, as the sulfides of some of the other Group II metals would not precipitate in highly acid solutions. Therefore, use is made of the fact that arsenious sulfide is easily precipitated from solutions of arsenious ion, arsenic ion being reduced by NH_4I to the arsenious state and then the H_2S being added.

6. If much precipitate forms, filter, saving both the filtrate and the precipitate Dilute the filtrate with an equal volume of water; then pass in a slow stream of H_2S for at least 3 min. If any *yellow* precipitate forms, continue until precipitation is complete; then filter and combine the precipitate with the first obtained. If a dark or white precipitate forms instead of the yellow, discontinue the precipitation and, without filtering, add 5 or 6 drops of concentrated HCl. Boil to half its volume as described under Filtrate, and save the mixture for Group III.

The reason for this dilution and precipitation is that during the original precipitation the acidity of the solution is increased by reactions such as

$$CuCl_2 + H_2S \rightarrow CuS + 2HCl$$

Consequently, the more soluble sulfides, such as those of cadmium and tin, may not precipitate completely unless the acidity is reduced by dilution.

7. Much information can be gleaned by observing the appearance of the mixture during various stages of the precipitation of the Group II sulfides. No precipitate, of course, means that these metals are all absent. A yellow precipitate, forming immediately upon adding H_2S to the solution after treatment with NH_4I, indicates the probable presence of As^{+++}.

These indications cannot be taken as tests for these ions, but their appearance often serves as a warning of something having gone wrong, if the test for the element does not appear later.

8. The sulfides of some metals (*e.g.*, cadmium, arsenic, cobalt, and nickel) *peptize* readily, *i.e.*, pass from the precipitated to the colloidal form. Others that are of only moderately low solubility (*e.g.*, cadmium and tin) partly redissolve in water. The wash solution described here opposes both these tendencies, the ions of the NH_4NO_3 tending to neutralize the charges on the colloidal particles and the $S^{=}$ from the H_2S opposing the dissolving of the sulfides, by means of the common ion effect.

As is usual, the first wash solution should be added to the filtrate in order to reduce loss of the metals of later groups.

9. If $(NH_4)_2S$ is not available, the reagent may be made by passing a rapid stream of H_2S through 1 ml. of dilute NH_4OH for 2 or 3 min.

The reagent loses strength rapidly and must be kept tightly stoppered and away from light. Unless kept in moderately large quantities, it should not be used more than one day after it is prepared; and even then it should be prepared fresh at least once each week.

10. The evaporation with H_2SO_4 drives off HNO_3 in which $PbSO_4$ is appreciably soluble and forms $Pb(HSO_4)_2$. The end point of the evaporation is indicated by the evolution of dense white fumes of SO_3. Some whitish fumes of steam and HNO_3 appear earlier and must not be confused with the SO_3, or the precipitation of $PbSO_4$, on dilution with water, will be incomplete.

11. This mixture must not be allowed to stand, after dilution, for more than 2 min., or the danger of a white precipitate of basic bismuth sulfate forming will be increased. The bismuth salt, if it appears, will give all the tests for lead except that the chromate formed with the bismuth will not dissolve in NaOH.

12. The hydroxide of bismuth is very transparent and gelatinous; and particularly if copper is present, the precipitate is often difficult to see.

13. An excellent confirmation test for Bi^{+++} is performed by adding to the remainder of the HCl solution 1 drop of cinchonine reagent. An orange precipitate will be obtained if as much as 0.00014 mg. of bismuth is present.

14. To check the test for cadmium the precipitate may be filtered, washed, and heated with a mixture of 5 drops of $6N$ H_2SO_4 and 5 drops of water for 3 or 4 min. Filter and discard any residue. Neutralize the filtrate, then acidify slightly with $6N$ $HC_2H_3O_2$. Use this solution for one of the Auxiliary Tests for cadmium (the thiosinamine test is recommended), or saturate it with H_2S to obtain a precipitate of CdS again.

This procedure is especially recommended when the precipitate obtained in the first test is dark in color. The dark color is due to the presence of

sulfides of the other metals which often slip through in traces and cause trouble at this point. The sulfides of these metals are not soluble in dilute H_2SO_4, however.

15. The mercuric chloride formed by the treatment of HgS with aqua regia is readily lost by sublimation unless the evaporation is performed with care.

16. When the sulfides of arsenic, antimony, or tin dissolve in $(NH_4)_2S$, the $S^=$ from the latter reacts with the sulfides to form thio ions, as illustrated by the equation

$$As_2S_3 + 3S^= \rightleftharpoons 2AsS_3^{\prime}$$

If the resulting solution is acidified weakly, the following type reaction occurs

$$2AsS_3^{\prime} + H^+ \rightleftharpoons As_2S_3 + 3HS^-$$

The H_2S is only moderately soluble, and its solubility is decreased by warming, consequently, the equilibrium shown is shifted to the right by heating, and the sulfides precipitate.

It is advisable to practice writing the equations for the reactions of the other sulfides, showing these steps.

17. If the precipitate refuses to settle or is very pale yellow (almost white), it is probably sulfur and the members of the tin group may be considered absent

18. A yellow precipitate forming here after some time may be considered an *indication* of the presence of *tin* It is probably stannic sulfide, which will precipitate under these conditions if tin is present in large concentration

19. This second reduction with aluminum is usually necessary to insure proper reduction of the stannic ion to stannous ion. This is especially true if antimony is present, since the aluminum will reduce the antimony to the metallic state instead of reducing the tin.

20. Other confirmation tests for tin may be performed, using the other half of the solution from the second reduction If a drop of a 0 05 per cent solution of auric (gold) chloride is added to 2 or 3 drops of the filtrate, a dirty green, purple, or black colloid of metallic gold will form If a drop of cacotheline reagent is used instead of the auric chloride, a violet coloration will be produced if even a trace of Sn^{++} is present

Questions on Analysis of Group II

1. Write equations for the reactions undergone by each cation during the precipitation of the Group II cations.

2. What is the function of each of the following in the precipitation of the Group II cations: (*a*) NH_4I, (*b*) the double evaporation, (*c*) the NH_4NO_3 in the wash solution, (*d*) the H_2S in the wash solution?

3. Why is it necessary to get rid of any HNO_3 or nitrates before precipitating with H_2S?

4. Why is it necessary to be so careful about the acid concentration in starting this separation?

5. Give at least one solvent for each of the following compounds of each metal in Group II: (*a*) nitrate, (*b*) chloride, (*c*) sulfate, (*d*) carbonate

6. Write the equations for the dissolving of As_2S_3, Sb_2S_3, and SnS_2 in $(NH_4)_2S$; also for the reprecipitation of these sulfides from this solution.

7. What is the basis of the separation of Hg from the rest of the Group II*A* metals?

8. What substances in aqua regia are responsible for its ability to dissolve highly insoluble compounds of mercury? Explain.

9. What reactions are used in getting the final test for Hg? Give equations for these reactions.

10. What is the basis for the separation of Bi from Cu and Cd?

11. Explain the reactions involved in getting the final Bi test.

12. In the separation of Cu^{++} and Cd^{++} in testing for the latter, what procedure is used? Give equations showing why this separation works

13. In case Cu is absent what difference is made in the procedure?

14. What is the basis for the separation of arsenic from antimony and tin?

Equations for Group II Analysis*

$$Hg^{++} + S^{=} \rightarrow HgS$$
$$HgS + H^{+} + NO_3^{-} + Cl^{-} \rightarrow HgCl_2 + H_2O + NO + S$$
$$HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$$
$$Hg_2Cl_2 + SnCl_2 \rightarrow Hg^0 + SnCl_4$$

$$Bi^{+++} + S^{=} \rightarrow Bi_2S_3$$
$$Bi_2S_3 + H^{+} + NO_3^{-} \rightarrow Bi^{+++} + NO + S + H_2O$$
$$Bi^{+++} + OH^{-} \rightarrow Bi(OH)_3$$
$$Bi(OH)_3 + HSnO_2^{-} \rightarrow Bi^0 + H_2O + SnO_3^{=}$$

$$Cu^{++} + S^{=} \rightarrow CuS$$
$$CuS + H^{+} + NO_3^{-} \rightarrow Cu^{++} + H_2O + NO + S$$
$$Cu^{++} + OH^{-} \rightarrow Cu(OH)_2$$
$$Cu^{++} + NH_4OH \text{ (excess)} \rightarrow Cu(NH_3)_4^{++} + H_2O$$
$$Cu(NH_3)_4^{++} + H^{+} \rightarrow Cu^{++} + NH_4^{+}$$
$$Cu^{++} + Fe(CN)_6^{\equiv} \rightarrow Cu_2Fe(CN)_6$$
$$Cu(NH_3)_4^{++} + CN^{-} \text{ (excess)} \rightarrow Cu(CN)_3^{-} + NH_3 + C_2N_2$$
$$Cu(CN)_3^{-} + H_2S \rightarrow \text{no reaction}$$

Cd^{++}—all reactions are similar to those of copper except the following:

$$Cd^{++} + Fe(CN)_6^{\equiv} \rightarrow Cd_2Fe(CN)_6$$
$$Cd(NH_3)_4^{++} + CN^{-} \rightarrow Cd(CN)_4^{=} + NH_3$$
$$Cd(CN)_4^{=} + H_2S \rightarrow CdS + CN^{-} + H^{+}$$

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* The student should balance each of these for practice, indicating precipitates by ($\downarrow$) and gases by ($\uparrow$). Also indicate the *colors* of any products.

$$As^{+++++} + I^- \rightarrow As^{+++} + I_2$$
$$As^{+++} + S^= \rightarrow As_2S_3$$
$$As_2S_3 + S^= \text{ (from } (NH_4)_2S) \rightarrow AsS_3^{\equiv}$$
$$AsS_3^{\equiv} + H^+ \rightarrow As_2S_3 + H_2S$$
$$As_2S_3 + H^+ \rightarrow \text{no reaction}$$
$$As_2S_3 + NH_4OH + H_2O_2 \rightarrow AsO_4^{\equiv} + NH_4^+ + H_2O + SO_4^=$$
$$AsO_4^{\equiv} + Mg^{++} + NH_4^+ \rightarrow MgNH_4AsO_4$$
$$AsO_4^{\equiv} + Ag^+ \rightarrow Ag_3AsO_4$$

$$Sb^{+++} + S^= \rightarrow Sb_2S_3$$
$$Sb_2S_3 + H^+ \rightarrow Sb^{+++} + H_2S$$
$$Sb_2S_3 + S^= \rightarrow SbS_3^{\equiv}$$
$$SbS_3^- + H^+ \rightarrow Sb_2S_3 + H_2S$$
$$Sb^{+++} + Al \rightarrow Sb^0 + Al^{+++}$$

$$Sn^{++++} + S^= \rightarrow SnS_2$$
$$SnS_2 + S^= \rightarrow SnS_3^=$$
$$SnS_3^= + H^+ \text{ (dilute)} \rightarrow SnS_2 + H_2S$$
$$SnS_2 + H^+ \rightarrow Sn^{++++} + H_2S$$
$$Sn^{++++} + Al \ (+ H^+) \rightarrow Sn^{++} + Al^{+++}$$
$$Sn^{++} + HgCl_2 \rightarrow Hg_2Cl_2 + Sn^{++++} + Cl$$
$$Sn^{++} + Hg_2Cl_2 \rightarrow Hg^0 + Sn^{++++} + Cl^-$$
$$Sn^{++} + AuCl_3 \rightarrow Sn^{++++} + Au^0 + Cl^-$$

GROUP III METALS

Chemical Characteristics*

Iron. Iron is a gray metal, having a melting point of 1535°C., a boiling point of 3000°C., and a density of 7.86. It is a moderately active metal, reacting rapidly at high temperatures with oxygen, to form Fe_3O_4; with sulfur, to form FeS, and with steam, to form Fe_3O_4 and hydrogen. It dissolves readily in HCl, H_2SO_4, or dilute HNO_3. Cold concentrated, or fuming HNO_3, however, changes pure iron to the "passive" state—a condition in which it will not show any of the usual reactions of iron.†

Compounds of Iron. Iron forms ferrous (Fe^{++}) and ferric (Fe^{+++}) compounds. The former may be readily oxidized to the ferric state by oxygen, bromine, chlorine, and other oxidizing agents. Many of the ferric compounds important in analysis are less soluble than the corresponding ferrous compounds, and most of the reactions used in identifying iron are those characteristic of Fe^{+++}, since the analytical procedure used involves oxidation previous to the tests for iron.

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* For other typical reactions that have application to analysis, see the section on Auxiliary Tests.

† It is believed that the HNO_3 forms a thin, unstable film of oxide on the surface of the iron and that this protects the iron from any reagents that may be applied. This film is destroyed by heating, scratching, or striking the iron sharply.

Ferrous Compounds. From solutions containing ferrous ion:

NH_4OH and alkalies precipitate $Fe(OH)_2$, white,* insoluble in water or excess alkali, but soluble in high concentrations of ammonium salts and in acids. $Fe(OH)_2$ quickly oxidizes to $Fe(OH)_3$ in the presence of air or other oxidizing agents such as H_2O_2 or Na_2O_2.

H_2S or $(NH_4)_2S$ precipitates FeS from neutral solutions or more quickly from alkaline solutions of ferrous ion. FeS is black, insoluble in water or alkalies, but soluble in quite dilute acids.

Soluble carbonates precipitate $FeCO_3$, white at first but turning green on standing, soluble in acids.

Alkali cyanides such as KCN precipitate yellowish $Fe(CN)_2$, soluble in excess cyanide [forming $Fe(CN)_6^{--}$] and in acids.

Potassium ferricyanide, precipitates blue $Fe_3[Fe(CN)_6]_2$ (Turnbull's blue).

Potassium ferrocyanide, $K_4Fe(CN)_6$, precipitates white $Fe_2Fe(CN)_6$ (usually tinged blue, owing to the fact that air oxidation causes small amounts of Prussian blue, $Fe_4[Fe(CN)_6]_3$, to form)

Thiocyanates give no perceptible reaction with Fe^{++}.

Dimethylglyoxime gives a red coloration which slowly fades as the Fe^{++} is oxidized by air to the ferric state.

Ferric Compounds. From solutions containing Fe^{+++}:

NH_4OH and alkalies precipitate red-brown $Fe(OH)_3$, even less soluble in water than is $Fe(OH)_2$ and insoluble in alkalies or in solutions of ammonium salts, soluble in acids.

H_2S or $(NH_4)_2S$ precipitates a mixture of sulfur and FeS, the sulfide first reducing the Fe^{+++} to Fe^{++} ions.

Soluble carbonates give a precipitate of a *basic ferric carbonate*, decomposed, by boiling, into $Fe(OH)_3$.

Disodium phosphate precipitates brown $FePO_4$, soluble in mineral acids.

Potassium iodide reduces Fe^{+++} to Fe^{++} with liberation of free iodine.

Potassium ferricyanide, $K_3Fe(CN)_6$, gives a brown coloration but no precipitate.

Potassium ferrocyanide, $K_4Fe(CN)_6$, gives a dark blue precipitate of $Fe_4[Fe(CN)_6]_3$ (Prussian blue).

KSCN gives no precipitate but yields a deep red color with solutions containing Fe^{+++}, owing to the formation of $Fe(SCN)_6^{---}$.†

* As usually precipitated, $Fe(OH)_2$ has a greenish color. This is due to the fact that it is very difficult to prepare or keep ferrous salts free of ferric compounds. The trace of $Fe(OH)_3$ that precipitates colors the $Fe(OH)_2$. It will be found that other ferrous compounds, as ordinarily precipitated, exhibit similar anomalies.

† The color does not form if fluorides, phosphates, oxalates, or tartrates are present, as these form very stable complex ions with the iron. If the cold solution is made acid with nitric acid, however, the test may be used successfully.

Acetates precipitate red-brown $Fe(OH)_2(C_2H_3O_2)$ from hot solutions of Fe^{+++} ions.

Aluminum. Aluminum is a silvery, rather soft metal, having a density of 2.7, a melting point of 648°C., and a boiling point of 1800° C. It is very active, but owing to the presence of a protective film of oxide that quickly forms on its surface, it is not appreciably attacked by oxygen or moisture at ordinary temperatures. The metal dissolves readily in HCl, in dilute H_2SO_4, or in solutions of alkalies (forming AlO_2^- and hydrogen), but it is unaffected by HNO_3.*

Compounds of Aluminum. The salts of aluminum hydrolyze quite extensively when in aqueous solution, many of them precipitating $Al(OH)_3$.

Active bases or ammonium hydroxide give, with solutions of Al^{+++}, $Al(OH)_3$, a colorless gelatinous precipitate, insoluble in water, in excess NH_4OH, or in acetic acid, soluble in excess NaOH or KOH† (forming aluminate, AlO_2^-) and in mineral acids.

Ammonium sulfide precipitates no Al_2S_3, as this compound is unstable in aqueous solutions and hydrolyzes completely. The product, therefore, is $Al(OH)_3$.

Carbonates precipitate $Al(OH)_3$ just as does $(NH_4)_2S$.

Phosphates precipitate $AlPO_4$, white, soluble in active bases or in mineral acids.

Acetates produce no precipitate with cold solutions of Al^{+++}, but with hot solutions a white basic acetate, $Al(OH)_2(C_2H_3O_2)$, is precipitated. This compound is readily soluble in acids and alkalies.

Certain *dyes*, such as *aluminon* (the ammonium salt of aurin tricarboxylic acid) and *alizarin*, form characteristic colored "lakes" with $Al(OH)_3$. It is probable that the dyes are adsorbed by the gelatinous precipitate of $Al(OH)_3$.

Chromium. Chromium is a silvery, rather brittle metal, having a melting point of 1615°C. and a density of 6.92. It dissolves in HCl, dilute H_2SO_4 or alkalies, but, like aluminum, is not dissolved by nitric acid. It is very similar to aluminum in many respects but differs in that chromium exhibits many different valences.

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* As in the case of iron, this phenomenon is usually attributed to the formation of a protective film of oxide. HCl readily destroys this film.

† It will be recalled that the hydroxides of some metals have weakly acidic, as well as basic, characteristics. For example, $Al(OH)_3$, $Cr(OH)_3$, and $Zn(OH)_2$ react, in solutions having a high concentration of OH^-, as if they were very weak acids. This behavior is better illustrated if one writes the formulas of these hydroxides as $HAlO_2 \cdot H_2O$, $HCrO_2 \cdot H_2O$, and H_2ZnO_2. Thus, if the hydroxides of these metals are treated with excess NaOH or KOH, the following reactions occur—just as if the hydroxides were acids:

$$HAlO_2 \cdot H_2O + OH^- \rightleftharpoons AlO_2^- + 2H_2O$$
$$HCrO_2 \cdot H_2O + OH^- \rightleftharpoons CrO_2^- + 2H_2O$$
$$H_2ZnO_2 + OH^- \rightleftharpoons HZnO_2^- + H_2O$$

For a more complete discussion see this subject in Chap. VIII.

Compounds of Chromium. Although chromium forms compounds corresponding to the oxides, CrO, Cr_2O_3, CrO_2, and CrO_3, the most common are those formed from Cr_2O_3 and CrO_3. The oxides CrO and Cr_2O_3 are basic anhydrides, though Cr_2O_3 is also somewhat amphoteric. CrO_3 is an acidic oxide dissolving in water to form chromic acid, H_2CrO_4. Its normal salts are the chromates; its acid salts are the dichromates. The chromous salts (salts of CrO) are strong reducing agents, reacting readily with oxygen and other oxidizing agents to give chromic, Cr^{+++}, ion.

Chromic Compounds. *With NH_4OH, $(NH_4)_2S$ (or H_2S and NH_4OH), alkalies, and carbonates,* chromic salts give a precipitate of $Cr(OH)_3$, green; slightly soluble in excess NH_4OH, especially if ammonium salts are present; readily soluble in excess alkali (forming chromite, CrO_2^-, ion) and in acids.

Alkaline solutions of chromites are oxidized to chromates (CrO_4^-) by addition of Na_2O_2, NaClO, Br_2, or Cl_2.

Acid solutions of chromic ion may be oxidized to form dichromate ion by use of strong oxidizing agents such as hot HNO_3 and/or $NaClO_3$ or $KClO_3$.

Fusion of chromic compounds with Na_2CO_3 and oxidizing agents (such as Na_2O_2, $KClO_3$, or KNO_3) converts the chromic compounds to Na_2CrO_4.

Soluble phosphates such as Na_2HPO_4 give a greenish precipitate of $CrPO_4$, soluble in acetic acid and mineral acids.

Acetates produce no precipitate except when considerable quantities of aluminum or iron are present. In this case, chromium coprecipitates with these two metals as the basic acetate.

The chromates are strong oxidizing agents, especially in acid solutions. Acids convert chromates to dichromates.* The process is reversible, dichromates changing to chromates if the solution is made slightly alkaline.

Cold, concentrated H_2SO_4 gives a red precipitate of CrO_3, with chromates. On heating, the mixture gives off oxygen and the CrO_3 is reduced to a green solution of Cr^{+++}.

Hydrogen peroxide gives, with acid solutions of dichromates, blue perchromic acid, H_3CrO_8 (?). The color rapidly disappears as the compound breaks down giving oxygen and Cr^{+++}. The perchromic acid is more stable in ether solutions than in water. If the reaction is carried out in acetic acid buffered with ammonium acetate, a brown solution is formed, the coloration remaining for several minutes

Many metals form characteristic, insoluble chromates. For these, see the discussions on silver, mercury, lead, barium, and strontium.

Manganese. Manganese is a gray or reddish-white, very hard, brittle metal having a density of 7.12 and a melting point of 1260°C. It is very similar to iron in activity, combining readily at high temperatures with

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* The dichromates are really dehydrated acid chromates The relationship may be shown by the equations for the reaction between H^+ and CrO_4^- ions.

$$CrO_4^- + H^+ \rightleftharpoons HCrO_4^-$$
$$2HCrO_4^- \rightleftharpoons Cr_2O_7^- + H_2O$$

oxygen, sulfur, chlorine, and many other nonmetals. Manganese dissolves readily in dilute acids.

Manganous Compounds. *Alkalies and NH_4OH* react with solutions of manganous ion to form $Mn(OH)_2$, white, insoluble in excess alkali, but soluble in solutions of ammonium salts and readily soluble in acids.

Soluble carbonates precipitate $MnCO_3$, white, insoluble in solutions of ammonium salts, but readily soluble in dilute acids.

Fusion of manganous compounds with Na_2CO_3 and an oxidizing agent (such as air, $KClO_3$, KNO_3, or Na_2O_2) yields green Na_2MnO_4 (sodium manganate). A solution of a manganate will, on acidification, change from green to violet or pink, and a brown precipitate of H_2MnO_3 will settle out. The reaction is

$$MnO_4^{-}{}_{(\text{manganate})} + 4H^+ \rightarrow MnO_4^{-}{}_{(\text{permanganate})} + H_2MnO_3 + H_2O$$

If the solution of the manganate is treated with Cl_2, the manganate is oxidized completely to MnO_4^-.

Soluble phosphates precipitate $Mn_3(PO_4)_2$, white, soluble in acetic and mineral acids.

Soluble cyanides give $Mn(CN)_2$, brown, soluble in excess of the reagent to form $Mn(CN)_6^{=}$.

Potassium ferrocyanide, $K_4Fe(CN)_6$, precipitates $Mn_2Fe(CN)_6$, white, insoluble in water but slightly soluble in HCl.

Potassium ferricyanide, $K_3Fe(CN)_6$, precipitates $Mn_3(Fe(CN)_6)_2$, brown, insoluble in water and most acids, but somewhat soluble in HCl.

Potassium chlorate (solid) or $NaClO_3$ with concentrated HNO_3 solutions of Mn^{++} gives, on heating, H_2MnO_3, brown, insoluble in HNO_3, soluble in HCl or aqua regia.

Ammonium persulfate (in the presence of $AgNO_3$ as catalyst) gives, with hot solutions of Mn^{++} in dilute HNO_3, violet or purple permanganic acid, $HMnO_4$. Lead dioxide or $KBrO_3$ in hot concentrated HNO_3 also oxidize Mn^{++} to $HMnO_4$.

Sodium bismuthate gives $HMnO_4$ with *cold* solutions of Mn^{++} in HNO_3; with *hot* solutions, the product is $MnO_2 \cdot H_2O$.

Permanganates. The permanganates are all quite soluble in water. The important uses of permanganates are based on the oxidizing properties of these compounds.

In alkaline solutions, permanganates are readily reduced, MnO_2 being produced. In acids the reduction of MnO_4^- yields Mn^{++}.

Zinc. Metallic zinc is a bluish-gray, rather soft metal, having a density of 7.14, a melting point of 419°C. It is quite active, burning readily in air to form white ZnO and combining with many nonmetals (such as chlorine) even at ordinary temperatures. It dissolves readily in dilute acids or alkalies, giving hydrogen.

Compounds of Zinc. *Alkalies and NH_4OH* react with solutions containing Zn^{++} precipitating $Zn(OH)_2$, white and gelatinous, soluble in excess alkali [giving zincate, $HZnO_2^-$, ion], in excess NH_4OH or solutions of ammonium salts [giving $Zn(NH_3)_4^{++}$], and in acids.

H_2S or $(NH_4)_2S$ precipitates ZnS from neutral, basic, ammoniacal, or acetic acid-sodium acetate solutions but not from more acid solutions (unless the concentration of zinc is unusually high) ZnS is white, insoluble in water or NH_4OH, but soluble in very dilute mineral acids.

Soluble carbonates precipitate mixed basic carbonates of the type $Zn_2(OH)_2CO_3$, white, soluble in NH_4OH or strong solutions of ammonium salts, in alkali carbonates, and in acids.

Phosphates precipitate $Zn_3(PO_4)_2$, white, soluble in NH_4OH or in acids.

Cyanides precipitate $Zn(CN)_2$, white, soluble in excess of the reagent to form $Zn(CN)_4^{=}$. The latter is readily decomposed by $(NH_4)_2S$ to form ZnS

$K_4Fe(CN)_6$ precipitates white $Zn_2Fe(CN)_6$

Cobalt and Nickel.* These elements are both gray metals, nickel being more silvery in appearance than is cobalt. Both have a density of 8 9 and a boiling point of 2900°C. The melting point of cobalt is 1180°C, whereas that of nickel is 1452°C.

Both dissolve easily in HNO_3; but although cobalt dissolves readily in dilute HCl and H_2SO_4, nickel dissolves in these acids with difficulty.

Both metals readily form a large variety of complex ions, and both are capable of existing in either the bivalent state or the trivalent state In both cases the most common ions are the bivalent form. However, cobalt is more easily oxidized to form the trivalent ion than is nickel.

Compounds of Nickel. *Alkalies* precipitate from solutions of nickelous ion (Ni^{++}) $Ni(OH)_2$, green, insoluble in excess alkali, but soluble in mixtures of ammonium salts and NH_4OH [forming $Ni(NH_4)_4^{++}$] and in acids.

NH_4OH precipitates a basic salt of the type, $Ni(OH)Cl$, soluble in the same reagents as is $Ni(OH)_2$.

Oxidizing agents such as Br_2, Cl_2, or NaClO oxidize alkaline suspensions of $Ni(OH)_2$ to black nickelic hydroxide, $Ni(OH)_3$, insoluble in NH_4OH or KCN, soluble in mineral acids.

H_2S or $(NH_4)_2S$ precipitates NiS from basic, neutral, or weakly acid (acetic acid-acetate) solutions. NiS is insoluble in $(NH_4)_2S$, very slowly soluble in cold 1*N* HCl, but readily soluble in aqua regia or in concentrated HNO_3.

Carbonates precipitate green $NiCO_3$, soluble in mixtures of ammonium salts and NH_4OH, in ammonium carbonate, and in acids.

Phosphates precipitate green $Ni_3(PO_4)_2$, soluble in dilute acids.

Potassium cyanide, KCN, precipitates green $Ni(CN)_2$, soluble in excess reagent to form relatively stable $Ni(CN)_4^{=}$. This is decomposed by acids. Solutions containing $Ni(CN)_4^{=}$ will give NiS with H_2S but with strong oxidizing agents will decompose, giving $Ni(OH)_3$ and cyanate (CNO^-) ion

$K_4Fe(CN)_6$ precipitates $Ni_2Fe(CN)_6$, green, almost insoluble in dilute HCl.

KSCN gives no visible reaction with nickel solutions.

* These metals are so similar in nature that is logical to consider them together in order to bring out their similarities and differences. They are also quite similar to iron in many respects.

Chromates precipitate a basic chromate from *hot*, nickelous solutions but react only slowly in the cold

Potassium nitrite gives no precipitate with dilute solutions of Ni^{++} (see Cobalt)

Compounds of Cobalt. *Alkalies or NH_4OH* precipitate a blue basic salt of the type $Co(OH)NO_3$, insoluble in excess reagent, but soluble in acids, in an excess of KCN, or in concentrated solutions of ammonium salts On being heated the basic salt hydrolyzes, forming pink $Co(OH)_2$. The latter changes to brown $Co(OH)_3$, slowly in air, but rapidly if oxidizing agents such as Br_2, Cl_2, H_2O_2, or NaClO are added.

H_2S or $(NH_4)_2S$ precipitates black CoS from neutral or basic solutions CoS is insoluble in $(NH_4)_2S$, and, if allowed to stand for a time, changes to a form that dissolves but slowly in cold dilute (1*N*) HCl. It dissolves readily, however, in hot concentrated HNO_3 or in aqua regia

Carbonates precipitate *basic cobalt carbonates*, red, soluble in NH_4OH or in ammonium carbonate solutions.

Phosphates precipitate blue-violet $Co_3(PO_4)_2$, soluble in NH_4OH.

Potassium cyanide precipitates $Co(CN)_2$, brown, soluble in excess reagent to form very stable cobaltocyanide, $Co(CN)_6$, ion. The latter oxidizes readily to cobalticyanide, $Co(CN)_6$, ion.

$K_4Fe(CN)_6$ precipitates $Co_2Fe(CN)_6$, green, almost insoluble in HCl, but soluble in NH_4OH.

Chromates precipitate a dark brown basic chromate* from cold solutions of Co^{++}. The precipitate is readily soluble in NH_4OH.

Potassium nitrite precipitates from solutions of Co^{++} on addition of acetic acid, a fine yellow precipitate of potassium cobaltinitrite, $K_4Co(NO_2)_6$. The reaction involves oxidation of the Co^{++} to Co^{+++}.

Preliminary Experiments†

1. General Comparisons. *a.* In separate depressions of a glass spot plate or on microscope slides place single drops of Fe^{+++}, Mn^{++}, Co^{++}, Ni^{++}, Al^{+++}, Cr^{+++}, and Zn^{++} test solutions. Lay the spot plate (or slides) on a sheet of paper on which the symbols of these elements are written so the identity of each drop will not be lost. In the case of the Al^{+++} and Zn^{++}, use a black background, as any precipitate formed will be light in color. Then to each solution add 1*N* NaOH until a precipitate forms. Describe each, using a chart to record these and later results.

* One of the separations of cobalt and nickel is based on the fact that cobalt gives a precipitate of the basic chromate from cold solutions whereas the corresponding salt of nickel precipitates very slowly.

† *Note to Teacher:* It is suggested that some of these preliminary experiments be omitted in short courses as the large number listed have been described in order to give adequate choice.

Next to each add 1 drop of 6*N* NaOH, and stir. Note and record which precipitates dissolve. Finally to each mixture add 1 drop of H_2O_2 or a few granules of Na_2O_2, and stir. Note and explain all color changes, both in precipitates and in solutions (see Note 6 and Question 1).

b. Precipitate the hydroxides of all seven of these metals as in *a*; then to each add 1 drop of a mixture of equal volumes of 6*N* NH_4Cl and 6*N* NH_4OH. Stir, and note which of the precipitates redissolve. Be sure that you know the difference in the reactions involved in the dissolving of metal hydroxides in excess NaOH as contrasted to those involved in the dissolving of hydroxides in excess NH_4OH (see Chap. VIII).

c. To each mixture in *b* add 1 drop of $(NH_4)_2S$ solution; stir, and note results.

2. Ferric and Ferrous Ions, Fe^{+++} and Fe^{++}.* Recall the properties of Fe^{+++} as determined in 1 above; then perform the following:

a. To 1 drop of Fe^{+++} solution add 1 drop of KSCN solution, and note results.

b. Repeat *a*, using $K_4Fe(CN)_6$ solution instead of KSCN.

c. Repeat *a*, using $K_3Fe(CN)_6$ solution instead of KSCN.

d. To 1 drop of Fe^{+++} add 1 drop of 0.1*N* KI solution. Observe and record the slow color change; then add 2 or 3 drops of *fresh* starch solution, or shake the mixture with CCl_4, and note the color obtained.

e. Prepare a solution of Fe^{++} by carefully selecting some small clean green crystals of ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2$, washing them, and dissolving two or three of them in 10 to 15 drops of hot water.† Using this solution, repeat the tests described in 2(*a*, *b*, and *c*), and contrast the results with those obtained with Fe^{+++}. (Question 3.)

If any color is produced with the KSCN, add 1 drop of stannous chloride solution to the mixture to reduce any traces of Fe^{+++} that may be present.

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* Solutions of ferrous ion are rapidly oxidized even in air, to form ferric ion; consequently when such solutions are prepared, they must be used *at once* or reactions observed will be partly those of ferric ions.

† Even when the precautions described here are used, it is difficult to get solutions of Fe^{++} that are absolutely free of Fe^{+++}. The results obtained will, therefore, seldom be exactly characteristic of ferrous ions.

3. Aluminum Ion, Al^{+++}. *a.* To 2 drops of Al^{+++} solution add 1*N* NaOH until a precipitate forms. Add 1 or 2 drops of 6*N* NaOH to redissolve the precipitate; then add 3 or 4 drops of 6*N* NH_4NO_3 or 6*N* $NH_4C_2H_3O_2$ solution, and stir. Heat on the steam bath 2 or 3 min., and note results (see Note 6). Filter and wash the precipitate; then dissolve it in 4 or 5 drops of 1*N* HCl, saving the solution.

b. To 2 drops of the solution obtained in *a* add 1 drop of 6*N* ammonium acetate and enough *freshly filtered* aluminon* reagent to give the solution a slight but distinct color; then make the solution *slightly* basic with dilute NH_4OH. Stir; warm on the steam bath 2 to 3 min.; then centrifuge. Note the color of the precipitate.

c. Treat the remainder of the solution in exactly the same way, except substitute alizarin blue for the aluminon.

4. Chromic Ion, Cr^{+++}. *a.* Repeat the experiment in 3*a*, using Cr^{+++} solution instead of Al^{+++}, and compare and contrast the results obtained.

b. To 2 drops of Cr^{+++} add 6*N* NaOH until the precipitate of $Cr(OH)_3$ that first forms redissolves. Then add H_2O_2 or Na_2O_2, a little at a time with stirring, until no further *color change* takes place. Add 3 or 4 drops of water; stir, and heat on the steam bath 4 or 5 min.

c. To 2 drops of the solution from *b* add 4*N* HNO_3 until it is definitely acid. Let stand 1 or 2 min.; then make the solution basic with NH_4OH. Stir; then centrifuge, and note the color of any precipitate, and compare it with the precipitate obtained by adding 1 drop of Cr^{+++} and 1 drop of dilute NH_4OH to 3 or 4 drops of water.†

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* Both aluminon reagent and alizarin S (blue) reagent tend to precipitate on standing in the reagent bottle. These reagents should be filtered, therefore, just before being used.

† The addition of sodium peroxide to water always results in the formation of small amounts of hydrogen peroxide. Hence, when sodium chromite solution is treated with an excess of either hydrogen peroxide or sodium peroxide, the result is a solution of chromate ion and hydrogen peroxide. If this is acidified, perchromic acid, a highly unstable, blue substance of uncertain formula, is formed, this rapidly decomposing to give oxygen and the original chromic ion, Cr^{+++}. For this reason, the separation of chromate ion from aluminum in such a mixture is best accomplished by use of a buffering agent to precipitate $Al(OH)_3$ from the solution instead of, as some

d. To the remainder of the solution from *b* add 2 or 3 drops of 6*M* NH_4NO_3; stir; then add 2 or 3 drops of $Ba(NO_3)_2$ solution. Stir, and centrifuge. Note the color of the precipitate, and note the change in color of the liquid.

e. Wash the precipitate of $BaCrO_4$ in cold water; then to the precipitate add 3 drops of 1*N* HNO_3, and heat on the steam bath for 2 or 3 min. Add 1 drop of K_2SO_4 solution; then filter, discarding the precipitate. To the filtrate add 1 or 2 drops of 2*N* ammonium acetate and 2 drops of 5 per cent $AgNO_3$. Stir; centrifuge, and note the color of the precipitate (Question 4).*

f. To 2 drops of Cr^{+++} add 4 or 5 drops of concentrated HNO_3 and 2 or 3 drops of saturated $NaClO_3$ solution. Boil very gently until the solution has undergone a definite change in color. Cool; add dilute NH_4OH until the solution is just basic; then make the solution slightly acid with 1*N* $HC_2H_3O_2$. Divide the solution into two parts. To one portion add 2 or 3 drops of $BaCl_2$ solution, and filter, noting results. To the other portion add 2 drops of 5 per cent $AgNO_3$. Explain all occurrences at each step in the procedure.

5. Manganese Ion, Mn^{++}. Recall the results obtained with Mn^{++} under General Comparison; then perform the following:

a. Precipitate some $Mn(OH)_2$ by adding 1*N* NaOH to some Mn^{++} solution. Let stand, and note the effects of air oxidation on the precipitate.

b. Precipitate some $Mn(OH)_2$ as in *a*; then add a little Na_2O_2 or 4 or 5 drops of H_2O_2, and stir. Warm on the steam bath until bubbling action ceases; then filter. Wash the precipitate carefully; then treat the precipitate with concentrated HNO_3, and warm to see if it will dissolve. Finally, add 2 or 3 drops of H_2O_2 or 1 drop of 1*N* HCl, and stir.

c. To 1 drop of Mn^{++} add 5 or 6 drops of concentrated HNO_3. To this add 2 or 3 drops of saturated $NaClO_3$ solution; then boil

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procedures direct, first acidifying and then making the solution alkaline with ammonium hydroxide.

* Barium chromate is appreciably soluble in mineral acids owing to the conversion of CrO_4^- to $Cr_2O_7^-$. The HNO_3, therefore, dissolves the $BaCrO_4$. The K_2SO_4 which is then added reacts with the Ba^{++} to produce the very insoluble $BaSO_4$. When the latter is filtered off, the remaining solution contains all the chromium as $Cr_2O_7^-$. Since Ag_2CrO_4 is soluble in even weak acids, it is necessary to buffer the acid by adding ammonium acetate before a precipitate will form with $AgNO_3$.

gently. Note and explain the formation of the precipitate. Filter; then add more $NaClO_3$ solution to the filtrate, and heat to be sure that all the Mn^{++} has been precipitated. (*Caution: Never add $NaClO_3$ to the acid solution while the solution is boiling, as an explosion may result.* Cool first; add the $NaClO_3$; then heat.) Divide the precipitate into two portions, and use in *d* and *e*.

d. To one portion of the precipitate add 4 or 5 drops of 6*N* HNO_3, 1 drop of 5 per cent $AgNO_3$ solution, and a volume of ammonium persulfate, $(NH_4)_2S_2O_8$, the size of a match head. Quickly heat just to boiling. Add a little more ammonium persulfate, if necessary; then centrifuge, and note the color of the liquid portion.*

e. In the end of a bit of platinum or nichrome wire form a small closed loop by bending the tip of the wire around a matchstick. Heat this loop red-hot, and at once dip it into a small heap of sodium carbonate, Na_2CO_3. Some of the solid will cling to the loop. Heat the loop in the flame, and repeat the process until a molten bead or droplet forms in the loop. Finally touch the hot bead to some of the precipitate of $MnO_2 \cdot H_2O$ from *c*; heat; then touch the molten mass to a little solid $KClO_3$. Heat strongly; then cool. Note the color of the bead. If the color is too dark to be recognized, dissolve the bead in 2 or 3 drops of hot water, and note the color of the solution. See Manganese, Chemical Characteristics of, for an explanation of this reaction.

6. Zinc Ion, Zn^{++}. Recall the results of the tests on Zn^{++} performed under General Comparison; then perform the following:

a. To 2 drops of Zn^{++} solution in a test tube add 1 drop of 1*N* NaOH solution; then dissolve the precipitate of $Zn(OH)_2$ by adding 1 drop of 6*N* NH_4Cl and 1 or 2 drops of dilute NH_4OH. Now add 6 or 7 drops of water and an equal volume of saturated Na_2CO_3 solution, and heat on the steam bath until all NH_3 is expelled. Note the results, and explain. Filter, and wash the precipitate. Dissolve in 3 or 4 drops of 6*N* $HC_2H_3O_2$; add 1 or 2 drops of 6*N* $NH_4C_2H_3O_2$, and saturate with H_2S. Explain results.

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* The reaction is

$$MnO_2 \cdot H_2O + H^+ + S_2O_8^{=}(+Ag^+) \rightarrow MnO_4^- + H_2O + SO_4^{=}$$

b. To 1 drop of Zn^{++} solution add 1 drop of 1*N* HCl and 1 drop of 0.1 per cent $CuSO_4$ solution. Stir; then add 2 drops of ammonium mercuric thiocyanate, $(NH_4)_2Hg(SCN)_4$, reagent. Rub the inside of the container with a stirring rod; let stand for a short time, and note the precipitate.*

7. Cobalt and Nickel Ions, Co^{++} and Ni^{++}. Recall the experiments under General Comparisons.

a. To 1 drop of Co^{++} solution add 1 drop of 1*N* K_2CrO_4, and stir, noting results.

Repeat, using Ni^{++} instead of Co^{++}. Heat the solution to boiling, and note the difference in conditions needed for the two reactions.

b. To 1 drop of Co^{++} on a piece of filter paper add 1 drop of 1*N* NH_4OH and 2 or 3 drops of α-nitroso-β-naphthol. Note the color of the spot produced; then add 1 drop of dilute H_2SO_4, observing whether or not this produces any change.

Repeat, using Ni^{++} instead of Co^{++}.

c. On separate spots on filter paper place 1 drop of Co^{++} and 1 drop of Ni^{++} solution. To each add 1 drop of dimethylglyoxime solution; then add 1 drop of 1*N* NH_4OH, and record results.†

d. Make 1 drop of Co^{++} faintly acid with dilute HCl; then add 1 drop of Zn^{++} solution and 1 drop of $(NH_4)_2Hg(SCN)_4$ solution. Rub the inside of the container with a stirring rod, and note results.‡

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* The test described here makes practical use of *coprecipitation* (see p. 160). If zinc ion and $(NH_4)_2Hg(SCN)_4$ are mixed alone, a white precipitate of $ZnHg(SCN)_4$ forms.

When Cu^{++} ions are used with the zinc, the results are variable. Minute traces of Cu^{++} will color the precipitate lavender; more Cu^{++} turns it black, and if the quantity of Cu^{++} exceeds that of Zn^{++}, an apple-green precipitate forms.

† Cobalt gives a very light brownish color with dimethylglyoxime if the Co^{++} is present in high concentration. This coloration, however, is so weak that it will not interfere with the test for nickel in any ordinary analysis. The test for nickel as described here is sensitive to one part in a million. Dimethylglyoxime is a reagent for several other metallic ions, but the interfering ions are removed before this point in the procedure.

‡ In using $(NH_4)_2Hg(SCN)_4$ to test for Zn^{++} or for Co^{++} in unknowns, a pink or red solution is sometimes produced. This may be due to a trace of

Repeat this test, omitting only the Co^{++} solution, and compare results.

Repeat the test, using Ni^{++} instead of Co^{++}.

c. Bend the tip of a platinum wire around a matchstick to form a closed loop. Heat this loop until it is red-hot; then quickly dip it into some borax. Heat again to fuse the borax that clings to the wire; then repeat the dipping and heating until a transparent bead fills the loop. Cool; touch to a drop of Co^{++} solution; then heat strongly until the bead melts and becomes homogeneous. Allow to cool; then holding the bead between yourself and the window, observe its color.

Repeat this test, using Ni^{++} solution instead of Co^{++}.

Analytical Aspects

Group III consists of those metals whose sulfides or hydroxides precipitate on addition of NH_4OH and H_2S or of $(NH_4)_2S$. To prevent the precipitation of the hydroxides of the fourth group metals and magnesium, it is necessary that the hydroxyl ion concentration, during the precipitation of Group III, be kept low yet constant. For this reason, an excess of NH_4OH buffered with ammonium chloride is used to furnish the necessary alkalinity.

On making the solution alkaline, the hydroxides of all the metals of Group III precipitate, with the exception of those of zinc and nickel, which remain in solution as ammonia complexes. When H_2S is passed into this solution, the zinc and nickel complexes and the hydroxides of iron, manganese, and cobalt are converted into sulfides. The sulfides of aluminum and chromium are peculiar in that even if they were formed momentarily, they would at once hydrolyze to form hydroxides again. This is easily understood if one recalls the fact that the sulfides of these metals belong to that class of salts where hydrolysis is most

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Fe^{+++} slipping through and, if so, may be removed by the addition of a little microcosmic salt or some sodium fluoride. Occasionally the solution turns pink, and the precipitate slowly dissolves with evolution of a gas. This indicates the presence of nitrites, which decompose the SCN^-. When this occurs, boil the solution until it becomes quite colorless and evolves no more gases; then cool and add more of the $(NH_4)_2Hg(SCN)_4$ reagent.

complete, *i.e.*, salts of very weak acids and very weak bases (see Chap. VII).

In one of the two analytical procedures suggested here the metals of this group are divided into two subgroups. This division is based on the fact that treating a solution containing these ions with excess alkali will cause the amphoteric hydroxides of aluminum, chromium, and zinc to dissolve, while the hydroxides of iron, nickel and cobalt and the hydrated oxide of manganese, being insoluble in excess alkali, may be filtered off.

Group III Analysis

(Option I)

In a general unknown, the solution used here will be the filtrate from the precipitation of the sulfides of Group II. If a Group III unknown is being run, use 1 ml. of the solution issued by the instructor.

Add about 15 drops of 6*N* NH_4NO_3, then add 6*N* NH_4OH, drop by drop, until precipitation of any hydroxides seems complete. Finally, add about 5 drops more of the 6*N* NH_4OH (see Notes 1 and 2). Dilute the mixture with an equal volume of water, then heat almost to boiling, and pass in H_2S until precipitation is complete (see Note 3). Wash the precipitate at least twice with NH_4NO_3—H_2S soln., adding the *first* wash portion to the filtrate.

Filtrate. Acidify *at once* with HCl, and boil to half its volume to eliminate $S^=$ (see Note 4). Save for Groups IV and V.

Precipitate: Consists of FeS, ZnS, MnS CoS, NiS, $Al(OH)_3$, and $Cr(OH)_3$ Add about 10 drops of conc. HNO_3 and 1 drop of dil. HCl and warm the mixture until the precipitate dissolves. Filter, and discard any sulfur; then add 1 ml of 3 per cent H_2O_2 or 15 to 20 drops of 8 per cent H_2O_2.* Make the solution basic with 6*N* NaOH, then add 5 or 6 drops in excess. Stir; observe the mixture for about 1 min.; then if no bubbling action is noticeable at the end of that time (see Note 5), add more H_2O_2. Dilute with 15 or 20 drops of water; stir; then warm on the steam bath until no more bubbles of oxygen form in the mixture. Filter, and wash the precipitate with cold water.

Filtrate. Contains AlO_2^-, CrO_4^-, and $HZnO_2^-$. Analyze as directed under the heading, Group III*A*.

Precipitate. Consists of $Fe(OH)_3$, MnO_2, $Ni(OH)_3$, and $Co(OH)_3$. Analyze as directed for Group III*B*.

* Sodium peroxide may be used instead of H_2O_2 if desired In that case make the solution just basic with NaOH, then add solid Na_2O_2, little by little with stirring until vigorous bubbling action continues for at least 1 min. (see Note 5). Then dilute with water, heat, and continue as instructed.

GROUP IIIA ANALYSIS

(Option I)

To the filtrate from the subgroup separation add 8 or 10 drops of 6*M* ammonium acetate soln., stir, and heat for 3 or 4 min. on the steam bath. If no precipitate forms (see end of Note 6), add 6 or 8 drops more of ammonium acetate, stir, and heat again. Filter, and wash the precipitate with cold water.

Filtrate. Contains $CrO_4^{=}$ and $Zn(NH_3)_4^{++}$ (see Note 7) Add $Ba(NO_3)_2$ soln until precipitation is complete. Filter, and wash the precipitate twice with cold water.

Precipitate. $Al(OH)_3$. Dissolve in 6 to 10 drops of 2*N* HCl, then divide the solution into two portions.

To 1 portion add *freshly filtered* aluminon reagent, until the solution is just definitely pink. Add 1 drop of 6*N* ammonium acetate; then make the solution *slightly* basic with NH_4OH. Heat on the steam bath 4 or 5 min. then centrifuge.

RED PPT.

indicates Al^{+++}.

With the second portion of the soln. repeat the test just described using alizarin blue instead of aluminon reagent.

BLUE PPT.

confirms Al^{+++}

Filtrate. Contains $Zn(NH_3)_4^{++}$ Make slightly acid with acetic acid; then evaporate to 1 ml. volume, and filter, discarding any precipitate Test for Zn^{++} as follows:

To 2 drops of the soln. add 1 drop of $K_4Fe(CN)_6$ soln.

WHITE PPT.

indicates Zn^{++}.

Pass H_2S into half of the remaining solution for 1 min.

WHITE PPT.

confirms Zn^{++} (see Note 8) See Preliminary Experiment 6*b* and Auxiliary Tests for other confirmation tests.

Precipitate. $BaCrO_4$ (and/or $BaSO_4$) (see Note 13).

YELLOW PPT.

indicates Cr^{+++} present.

To the precipitate add 6 or 7 drops of 1*N* HNO_3, and warm on the steam bath 1 or 2 min Add 2 drops of K_2SO_4 soln., stir, and filter Divide filtrate into two equal parts.

To one part in a small test tube add diethyl ether until it forms a layer 1 cm. deep. Be sure that the solution is *cold*, then add 1 drop of 3 per cent H_2O_2, and *at once* shake the mixture

BLUE ETHER LAYER

(usually present only *momentarily*) confirms chromium.

To the remainder of the filtrate add an equal volume of 2*N* ammonium acetate and 2 drops of 5 per cent $AgNO_3$ soln.

PURPLISH-BROWN PPT.

confirms chromium present.

GROUP III*B* ANALYSIS

(Option I)

Dissolve the precipitate from the subgroup separation in about 10 drops of concentrated HNO_3, warming if necessary (see Note 9). Place the solution in a crucible, boil gently until most of the liquid has evaporated, then cool. Add about 2 ml. of concentrated HNO_3, then add 8 drops of saturated $NaClO_3$ solution. Stir, then boil *gently* over a micro flame until the liquid is reduced to half its volume. If a brown or black precipitate forms (see Note 10), filter, saving the precipitate. To the *cool* filtrate add 5 or 6 drops more of the $NaClO_3$ solution and 1 ml. of concentrated HNO_3, and heat again. Repeat this treatment until no further brown precipitate forms. Combine the precipitates, and wash them with hot water. Combine the *first* wash water with the filtrate.

Filtrate. Contains Fe^{+++}, Co^{++}, and Ni^{++}. *Boil to half its volume* to destroy any remaining chlorate (see Note 11); dilute with water if necessary, and make strongly basic with dil. NH_4OH. Stir; then filter.

Filtrate. Contains $Ni(NH_3)_4^{++}$ and $Co(NH_3)_6^{++}$.

To 1 drop of the filtrate on a piece of filter paper add 1 drop of dimethylglyoxime soln.

RED SPOT
shows Ni^{++} present.

To another drop of the filtrate on a piece of filter paper add 1 drop of α-nitroso-β-naphthol soln. and 1 drop of $6N$ H_2SO_4.

REDDISH SPOT
indicates Co^{++} present.

To 3 drops of the filtrate in a test tube add 2 drops of $6N$ HCl, 1 drop of Zn^{++} test solution, and 1 drop of $(NH_4)_2Hg(SCN)_4$ soln. Scratch the inside of the test tube to cause precipitation and let stand.

BLUE PPT.
confirms presence of Co^{++}.

Precipitate. $Fe(OH)_3$ [and any manganese that slipped through, as $Mn(OH)_2$ and $MnO_2 \cdot H_2O$].

Dissolve the precipitate in $3N$ HCl. To 1 drop of this solution add 1 drop of KSCN soln.

DEEP RED
solution indicates iron present (see Note 12).

To a second drop of the solution add 1 drop of $K_4Fe(CN)_6$ soln.

DARK BLUE
solution confirms presence of iron (see Note 12).

Precipitate. $MnO_2 \cdot H_2O$ DARK BROWN PPT. indicates Mn^{++} present.

Confirm as described in Preliminary Experiment 5*e*.

To half of the precipitate add 7 or 8 drops of $3N$ HNO_3 and stir. Now add 1 drop of Ag^+ soln and a volume of solid ammonium persulfate the size of a match head, then quickly heat almost to boiling. Centrifuge if necessary.

PINK OR VIOLET SOLUTION
confirms Mn^{++}.

GROUP III ANALYSIS

(Option II)

To the unknown add about 15 drops of 6*N* NH_4NO_3; then add 6*N* NH_4OH, drop by drop, until precipitation of any hydroxides seems complete. Finally, add about 5 drops more of the 6*N* NH_4OH (see Notes 1 and 2). Dilute the mixture with an equal volume of water, then heat almost to boiling, and pass in H_2S until precipitation is complete (see Note 3). Wash the precipitate at least twice with NH_4NO_3-H_2S soln., adding the *first* wash portion to the filtrate.

Filtrate. Acidify at once with HCl, and boil to half its volume (see Note 4) Save for Groups IV and V.

Precipitate. Consists of FeS, ZnS, MnS, CoS, NiS, $Al(OH)_3$, and $Cr(OH)_3$. Add 10 or 12 drops of conc HNO_3 and 1 drop dil HCl, and warm until the precipitate dissolves. Filter, discarding any sulfur, then evaporate to one-fourth its volume Cool, add 2 ml. of conc. HNO_3 and 8 drops of saturated $NaClO_3$ soln., and evaporate the mixture over a micro flame to half its volume If a brown or black precipitate forms (see Note 10), filter, saving the precipitate. Cool the filtrate, add 5 or 6 drops more $NaClO_3$ soln and 1 ml more of the conc. HNO_3, and heat again Repeat the process until no more brown precipitate forms; then combine the precipitates and wash them with hot water.

Filtrate. Contains Fe^{+++}, Al^{+++}, CrO_4^-, Zn^{++}, Co^{++}, and Ni^{++}.
Add 6*N* NH_4OH until the solution is just basic; then add 4 or 5 drops in excess Stir, then filter. Wash the precipitate twice with 1*N* NH_4OH.

Precipitate. $MnO_2 \cdot H_2O$.
DARK BROWN PPT.
indicates Mn.

To half the precipitate add 7 or 8 drops of 6*N* HNO_3 and stir. Add 1 drop 5 per cent $AgNO_3$ and a volume of solid ammonium persulfate the size of a large match head, then quickly heat almost to boiling Centrifuge if necessary.
PINK OR VIOLET SOLUTION
confirms Mn
Confirm also by Preliminary Experiment 5*e*.

Filtrate. Contains $Zn(NH_3)_4^{++}$ $Co(NH_3)_6^{++}$ $Ni(NH_3)_4^{++}$ CrO_4^- (see next page)

Precipitate. Contains $Fe(OH)_3$ and $Al(OH)_3$
To the precipitate add 5 or 6 drops of water and an equal volume of 6*N* NaOH. Stir thoroughly; then filter.

Filtrate. Contains AlO_2^-.
Acidify with HCl, add 2 drops of 6*N* ammonium acetate, and divide into two parts.

To 1 portion add just enough *freshly filtered* aluminon to color the soln pink. Make the solution *slightly* basic with dil. NH_4OH. Heat on the steam bath 4 or 5 min.; then centrifuge.

RED PPT.
confirms Al^{+++}.

To the other portion add freshly filtered alizarin blue soln. until the liquid is faintly blue; then make the solution *slightly* basic with dil. NH_4OH. Warm on the steam bath 4 or 5 min. then centrifuge.

BLUE PPT.
confirms Al^{+++}.

Precipitate. $Fe(OH)_4$ Dissolve in 3*N* HCl. To 1 drop of the solution add 1 drop of KSCN.
DEEP RED
solution indicates iron (see Note 12).

To another drop add 1 drop $K_4Fe(CN)_6$ solution.
DARK BLUE
solution confirms iron (see Note 12).

(See Note 7.) To the solution containing the $CrO_4^{=}$, $Zn(NH_3)_4^{++}$, $Co(NH_3)_6^{++}$, and $Ni(NH_3)_4^{++}$, add 3 or 4 drops of $6N$ NH_4NO_3; stir, then add $Ba(NO_3)_2$ soln. until precipitation is complete. Filter, and wash the precipitate.

Filtrate. Contains ammines of zinc, cobalt and nickel. Pass in H_2S until precipitation is complete. *Without filtering* heat the mixture on the steam bath for at least 5 min, replacing with hot water any liquid lost by evaporation. Filter, discarding the filtrate. Wash the precipitate twice. *Let the precipitate become cold*, then add 10 drops of *cold* $1N$ HCl, stir, and *filter at once* (see Note 14). Do not wash the precipitate.

Filtrate. Contains Zn^{++} (and possibly traces of Ni^{++} and Co^{++}.)

To half the filtrate add 2 drops of $6M$ ammonium acetate; then pass in H_2S (see Note 8) for 1 min.

WHITE PPT.
indicates zinc.

Boil the remainder of the filtrate almost to dryness, then add $1N$ HCl to make up the lost volume. Using this liquid test for Zn by tests described in Preliminary Experiment 6*b* and *c*, and in Auxiliary Tests.

Precipitate. CoS and NiS.

Dissolve in 8 or 10 drops of conc. HNO_3 and 1 drop of dil. HCl. Evaporate to half its volume; then cool. Make the solution basic with dil NH_4OH, and test it as follows:

To 1 drop of the solution on filter paper add 1 drop of dimethylglyoxime soln.

RED SPOT
shows nickel present.

To another drop on filter paper add 1 drop of α-nitroso-β-naphthol and 1 drop of $6N$ H_2SO_4.

REDDISH SPOT
indicates Co.

To 3 drops of the solution in a test tube add 2 drops of dilute HCl, 1 drop of Zn^{++} solution, and 1 drop of $(NH_4)_2Hg(SCN)_4$ solution. Rub the inside of the container with a stirring rod, and let stand.

BLUE PPT.
confirms cobalt.

Precipitate. $BaCrO_4$ (and $BaSO_4$. See Note 13.)

YELLOW PPT.
indicates chromium.

To the precipitate add 6 or 7 drops of $1N$ HNO_3; stir, and warm on the steam bath 2 or 3 min. Add 2 drops of K_2SO_4 soln., stir, and filter. Divide the filtrate into two parts.

To one part add an equal volume of $2N$ ammonium acetate and 2 drops of 5 per cent $AgNO_3$ soln.

PURPLE-BROWN PPT.
confirms Cr.

To the second portion of *cold* filtrate in a test tube add diethyl ether to a depth of 1 cm. Add 1 drop of 3 per cent H_2O_2 and *at once* shake the mixture.

BLUE ETHER LAYER
confirms chromium.

Questions on Preliminary Experiments

1. What is meant by the term *amphoteric*? Which elements in Group III are amphoteric?

2. Which elements in this group form ammonia complexes? What is the formula of the complex formed by each?

3. How could you identify Fe^{++} and Fe^{+++} in solutions?

4. Explain, by means of the solubility product principle:

a. Why $BaCrO_4$ precipitates when $Ba(NO_3)_2$ is added to a neutral or slightly basic solution of a chromate.

b. Why strong mineral acids will dissolve $BaCrO_4$

c Why the addition of a solution of sodium sulfate to a precipitate of $BaCrO_4$ will produce some $BaSO_4$ and leave a solution containing some CrO_4^-

5. What valence is each of the elements in Group III capable of having? Illustrate with formulas.

6. Show by equations why a slightly basic solution of $NiCl_2$ tends to become acidic if it is treated with H_2S?

NOTES

1. During this precipitation, it is necessary that a moderate excess of base be present. The reaction of a salt with hydrogen sulfide results in excess hydrogen ion being formed—as illustrated here:

$$Ni(NO_3)_2 \rightarrow Ni^{++} + 2NO_3^-$$
$$H_2S \rightarrow S^= + 2H^+$$
$$\downarrow$$
$$NiS$$

This acid must be neutralized by the base in order to prevent reversal of the reaction. At the same time, the hydroxyl ion concentration must be kept low to prevent precipitation of the hydroxides of barium, calcium, strontium, and magnesium with the metals of Group III These apparently opposing conditions are brought about by the use of NH_4OH buffered with NH_4NO_3. This gives a large reserve of base but a low immediate hydroxyl ion concentration. For a more complete discussion of buffered bases see page 68

2 Helpful information can be gained by carefully watching the changes that occur in the unknown on the addition of the NH_4OH. A gelatinous, reddish-brown precipitate, insoluble in excess NH_4OH, may indicate that iron is present. A colorless, gelatinous precipitate that fails to dissolve in excess NH_4OH indicates the probable presence of aluminum No precipitate at all, in excess NH_4OH, means that both iron and aluminum are absent. If on the addition of H_2S a white precipitate appears with no other colored precipitate forming, zinc is probably present and iron, nickel, and cobalt are absent

3. After precipitation is apparently complete, test the solution with litmus. It should be strongly basic. If the solution is *weakly* basic or acidic, add 2 or 3 drops more 6*N* NH_4OH solution, stir, and add more H_2S.

4. The removal of the $S^=$ by acidification and boiling is necessary because if a solution of a sulfide is allowed to stand, some of the sulfide is slowly oxidized by oxygen of the air to form $SO_4^=$. This would result in part of any barium and possibly some of any strontium in Group IV being precipitated as the very insoluble sulfates In such case the tests for these cations would be weakened, if not entirely missed.

5. The peroxide is added primarily to oxidize any chromite, CrO_2^-, to chromate, $CrO_4^=$. At the same time, however, any $Fe(OH)_2$ is oxidized to $Fe(OH)_3$; $Ni(OH)_2$ to $Ni(OH)_3$, $Mn(OH)_2$ to $MnO_2\,H_2O$, and $Co(OH)_2$ to $Co(OH)_3$. This means that care must be taken to add enough peroxide to complete all these oxidations, as otherwise some of the CrO_2^- may not be oxidized. Sometimes the quantity of peroxide required is comparatively large, especially if the peroxide has partly decomposed. The best procedure is to add the peroxide a little at a time until, after stirring, *the bubbling action continues for at least 1 min.* When this occurs, it may be considered that sufficient peroxide has been added.

6. During the subgroup separation the Al^{+++}, Zn^{++}, and Cr^{+++} react with an excess of NaOH (some of which is produced also when Na_2O_2 reacts with water) to form AlO_2^-, $HZnO_2^-$, and CrO_2^-. The last may then be oxidized to $CrO_4^=$ by H_2O_2 or Na_2O_2, thus assuming a form from which $Cr(OH)_3$ cannot be obtained without reduction taking place first. The other two ions remain stable as long as the concentration of OH^- is high, but if the OH^- concentration is reduced to a point only slightly greater than would be present in a neutral solution, the hydroxides of aluminum and zinc will precipitate.

When ammonium acetate is added to such a mixture, the OH^- concentration is reduced by the buffering action of the ammonium salt:

$$NH_4^+ + C_2H_3O_2^- + OH^- \rightleftharpoons NH_4OH + C_2H_3O_2^-$$

Consequently, the aluminum precipitates as $Al(OH)_3$ when sufficient $NH_4C_2H_3O_2$ is added. The zinc, however, does not precipitate, as its hydroxide is soluble in mixtures of NH_4OH and ammonium salts to form $Zn(NH_3)_4^{++}$.

To precipitate all the aluminum effectively it is necessary to add an excess of $NH_4C_2H_3O_2$ over the NaOH present in the solution. If much Na_2O_2 is used, more buffer must be used owing to the fact that the Na_2O_2 reacts with water to produce NaOH.

7. The color of the filtrate should be noted carefully at this point. Any yellowish coloration (best observed by looking *down into* the test tube toward a white background) that disappears after the $Ba(NO_3)_2$ treatment is excellent evidence of the presence of $CrO_4^=$—and therefore of chromium—in the unknown.

8. If the solution turns milky within about 30 sec upon the addition of H_2S, the presence of Zn^{++} is indicated. Frequently, the white precipitate will form but will then turn gray or black. This is due to the formation of NiS or CoS formed with Co^{++} or Ni^{++} which has not been properly removed during the separation. The ZnS will usually form first, however, since only traces of the other two metals will normally have slipped through.

9. A dark brown precipitate that resists the dissolving action of the HNO_3 is usually $MnO_2\,H_2O$ and indicates the presence of manganese in the unknown. The precipitate may be dissolved by adding 1 drop of 6*N* HCl to the mixture. If this procedure is followed, however, all the Cl^- must be destroyed before adding the $NaClO_3$, for otherwise the Cl^- will slow and may prevent the precipitation of the $MnO_2{\cdot}H_2O$ in the next step. The

evaporation of the solution as described, however, will destroy the Cl^- effectively.

10. Quite often a white crystalline precipitate will form at this stage of the procedure, either alone or mixed with the brown $MnO_2 \cdot H_2O$. This consists of the nitrates of sodium and the metals of this subgroup and forms owing to the fact that these nitrates are less soluble in concentrated HNO_3 than in water. This precipitate must be kept in the mixture in order to avoid loss or weakening of tests. Washing any brown precipitates with hot water will dissolve these nitrates, and the first portion of wash water should therefore be combined with the final filtrate.

11. If any chlorate or any of its active decomposition products remains in the solution, it will, when the solution is made ammoniacal, oxidize any Co^{++} present to Co^{+++}. Trivalent cobalt ion reacts readily with NH_3 to form complex ions of such great stability that the usual tests for Co^{++} give no indication of the presence of cobalt. Such a solution can sometimes be recognized by the fact that it is pink in color but refuses to give satisfactory tests for cobalt. In such cases it is best to pass H_2S into the solution until the cobalt is completely precipitated as CoS, then dissolve the precipitate in aqua regia, evaporate partly, and run the tests for cobalt on this solution.

12. Some manganese occasionally slips through the $NaClO_3$-HNO_3 separation and appears mixed with the $Fe(OH)_3$. The manganese is in a form that gives a greenish precipitate with $K_4Fe(CN)_6$ and a light red precipitate with KSCN. If, therefore, *precipitates* of this description are obtained when the tests are made for iron, it is probably manganese, and iron is absent. If even a very small amount of iron is present, the red and blue colorations produced will be so deeply colored that no precipitate can be seen.

13. When sulfides are dissolved in concentrated HNO_3 (as at the beginning of this analysis), some of the sulfide is always converted to sulfate. Consequently, since the solubility of $BaSO_4$ is very low, a precipitate of white $BaSO_4$ usually forms at this point, either alone or, if CrO_4^- is present, mixed with $BaCrO_4$.

14. If the sulfides of cobalt and nickel are heated for some time (as in this procedure), they change to a crystalline form that is only *slowly* soluble in 1*N* HCl. Zinc sulfide undergoes no such change. Consequently, zinc may be separated from cobalt and nickel by precipitating the sulfides of these metals, heating for a time, filtering, then treating the mixed sulfides with *cold* 1*N* HCl. The sulfide of zinc dissolves at once; those of cobalt and nickel, more slowly. If the mixture is filtered quickly, the separation will usually be good.

Questions on Analysis of Group III

1. What metals are found in Group III? In subgroup *A*? In subgroup *B*?

2. The members of Group III have what characteristics that cause them to fall in this group?

3. Write flow sheets showing the precipitation of Group III and the separation and identification of the metals therein.

4. What precautions must be used in testing for completeness of precipitation at the beginning of the analysis?

5. Write equations showing the changes undergone by each cation from the beginning of the analysis to its final identification.

6. What are the functions of each of the following reagents in the analysis of this group (illustrate with equations where possible):

(*a*) NH_4NO_3 at the beginning?

(*b*) NH_4OH at the beginning?

(*c*) Na_2O_2 or H_2O_2 in the separation of the subgroups?

(*d*) $NH_4C_2H_3O_2$ in the precipitation of $Al(OH)_3$ at the beginning of subgroup *A*?

(*e*) NH_4NO_3 and H_2S in the wash solution?

(*f*) Aluminon and alizarin blue in testing for aluminum?

7. Which of the reactions given in Question 6 are oxidation-reduction reactions? What is oxidized and what reduced in each case?

8. Why does not $Zn(OH)_2$ precipitate with the $Al(OH)_3$ when ammonium acetate is added to the alkaline subgroup *A* solution?

9. Why do we use the identification reactions for Fe^{+++} as tests for iron rather than using those for Fe^{++}?

10. Explain the reactions that occur at each step in an analysis following Option II.

11. What two functions does the $NaClO_3$ have in Option II?

12. Explain the reactions used

a. In separating aluminum from iron in Option II

b. In separating zinc from cobalt and nickel.

c. In separating chromium from iron, cobalt, nickel, zinc, and aluminum

Equations for Group III Analysis*

$$Fe^{+++} + OH^- \rightarrow Fe(OH)_3$$
$$Fe(OH)_3 + S^= \rightarrow FeS + S + OH^-$$
$$FeS + H^+ \rightarrow Fe^{++} + H_2S$$
$$Fe^{++} + OH^- \rightarrow Fe(OH)_2$$
$$Fe(OH)_2 + H_2O_2 \rightarrow Fe(OH)_3$$
$$Fe(OH)_3 + H^+ \rightarrow Fe^{+++} + H_2O$$
$$Fe^{+++} + Fe(CN)_6^{\equiv} \rightarrow Fe_4[Fe(CN)_6]_3$$
$$Fe^{+++} + SCN^- \rightarrow Fe(SCN)_6^{\equiv}$$

$$Mn^{++} + OH^- \rightarrow Mn(OH)_2$$
$$Mn(OH)_2 + H_2O_2 \rightarrow MnO(OH)_2 + H_2O$$
$$Mn(OH)_2 + S^= \rightarrow MnS + OH^-$$
$$MnS + H^+ \rightarrow Mn^{++} + H_2S$$
$$Mn^{++} + ClO_3^- \rightarrow MnO_2 + ClO_2$$
$$MnO_2 + H_2O + S_2O_3^= (+Ag^+) \rightarrow MnO_4^- + H^+ + SO_4^=$$
$$Mn^{++} + Na_2CO_3 + KClO_3 \rightarrow Na_2MnO_4 + CO_2 + KCl$$

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* The student should balance each of these for practice, indicating precipitates by (↓) and gases by (↑). Also indicate the *colors* of any products.

$$Cr^{+++} + OH^- \rightarrow Cr(OH)_3$$
$$Cr(OH)_3 + S^= \rightarrow \text{no reaction}$$
$$Cr(OH)_3 + H^+ \rightarrow Cr^{+++} + H_2O$$
$$Cr(OH)_3 + OH^- \text{ (strong NaOH)} \rightarrow CrO_2^- + H_2O$$
$$CrO_2^- + H_2O_2 + OH^- \rightarrow CrO_4^= + H_2O$$
$$CrO_4^= + Ba^{++} \rightarrow BaCrO_4$$
$$BaCrO_4 + H^+ \rightarrow Ba^{++} + Cr_2O_7^= + H_2O$$
$$CrO_4^= + Ag^+ \rightarrow Ag_2CrO_4$$

$$Al^{+++} + OH^- \rightarrow Al(OH)_3$$
$$Al(OH)_3 + S^= \rightarrow \text{no reaction}$$
$$Al(OH)_3 + OH^- \rightarrow AlO_2^- + H_2O$$
$$Al(OH)_3 + H^+ \rightarrow Al^{+++} + H_2O$$

$$Zn^{++} + OH^- \rightarrow Zn(OH)_2$$
$$Zn(OH)_2 + NH_4OH \rightarrow Zn(NH_3)_4^{++} + H_2O + OH^-$$
$$Zn(NH_3)_4^{++} + S^= \rightarrow ZnS + NH_3$$
$$ZnS + H^+ \rightarrow Zn^{++} + H_2S$$
$$Zn(OH)_2 + OH^- \rightarrow HZnO_2^- + H_2O$$
$$Zn^{++} + Fe(CN)_6^{----} \rightarrow Zn_2Fe(CN)_6$$

$$Co^{++} + OH^- \rightarrow Co(OH)_2$$
$$Co(OH)_2 + H_2O_2 \rightarrow Co(OH)_3$$
$$Co(OH)_2 + NH_3 \rightarrow Co(NH_3)_6^{++} + OH^-$$
$$Co(NH_3)_6^{++} + S^= \rightarrow CoS + NH_3$$
$$CoS + HNO_3 + HCl \rightarrow Co^{++} + Cl^- + NO + H_2O + S$$

$$Ni^{++} + OH^- \rightarrow Ni(OH)_2$$
$$Ni(OH)_2 + NH_3 \rightarrow Ni(NH_3)_4^{++} + OH^-$$
$$Ni(NH_3)_4^{++} + S^= \rightarrow NiS + NH_3$$
$$NiS + HCl + HNO_3 \rightarrow Ni^{++} + S + H_2O + NO + Cl^-$$

GROUP IV METALS

Chemical Characteristics

Barium. Barium is a silvery metal having a density of 3.5 and a melting point of 850°C. It is extremely active, tarnishing quickly in air and reacting readily with most nonmetals. It reacts with cold water, giving hydrogen and a precipitate of $Ba(OH)_2$, and reacts vigorously with dilute acids. As its acetate, nitrate, and chloride are readily soluble, the best solvent for the metal is very dilute $HC_2H_3O_2$, HCl, or HNO_3.

Compounds of Barium. *Sodium or potassium hydroxide* precipitates some $Ba(OH)_2$ from concentrated solutions of Ba^{++}. The precipitate is white, insoluble in excess alkali, but soluble in acetic acid, dilute HCl, or HNO_3.

Hydrogen sulfide, ammonium sulfide, ammonium hydroxide, and chlorides cause no precipitation with solutions containing Ba^{++}.*

* BaS is not precipitated from aqueous solutions on the addition of H_2S, owing to the fact that the salt hydrolyzes and forms the acid salt $Ba(HS)_2$,

Soluble carbonates precipitate $BaCO_3$, white, insoluble in NH_4OH or alkalies, but soluble in acetic acid, HCl, and HNO_3.

Soluble phosphates precipitate $Ba_3(PO_4)_2$, white, soluble in mineral acids.

Soluble chromates precipitate yellow $BaCrO_4$, soluble in mineral acids but only slightly soluble in acetic acid.*

Soluble sulfates precipitate $BaSO_4$, white, extremely insoluble in water, alkalies, or acids, slightly soluble in hot, concentrated H_2SO_4 †

Oxalates such as $K_2C_2O_4$, give a white precipitate of BaC_2O_4, only slightly soluble in water but soluble in hot dilute acetic acid

Potassium ferrocyanide, $K_4Fe(CN)_6$ gives a white precipitate of $Ba_2Fe(CN)_6$ or $BaK_2Fe(CN)_6$, depending on the relative amounts of Ba^{++} and reagent present

The nitrates and chlorides of barium are soluble in water but are insoluble in absolute alcohol or acetone.

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a fairly soluble substance As $Ba(OH)_2$ is moderately soluble, NH_4OH does not furnish a concentration of OH^- sufficiently large to cause its precipitation from any but the most concentrated solutions of Ba^{++}.

* Solutions of chromates contain chromate (CrO_4^-) ion in equilibrium with dichromate ($Cr_2O_7^-$) ion, according to the equation

$$2CrO_4^- + 2H^+ \rightleftharpoons Cr_2O_7^- + H_2O$$

The addition of hydrogen ion favors the formation of dichromate ion and lowers the concentration of the chromate ion.

Acetic acid, being only slightly ionized, does not furnish H^+ in sufficient concentration to repress the concentration of chromate ions to the point where $BaCrO_4$ will dissolve to any great extent. If the $HC_2H_3O_2$ is buffered, the $BaCrO_4$ is even less soluble in it

Unbuffered HCl or HNO_3, however, will dissolve $BaCrO_4$ readily.

† To get the barium of $BaSO_4$ into solution, any one of three methods may be used:

1. Digest the $BaSO_4$ in hot, saturated Na_2CO_3 solution for several minutes, then filter. Treat the precipitate with a fresh portion of Na_2CO_3 solution as before, and again filter. The reaction taking place is

$$BaSO_4 + CO_3^- \rightleftharpoons BaCO_3 + SO_4^-$$

The precipitate will contain the $BaCO_3$ which, though insoluble in water, is readily soluble in $HC_2H_3O_2$, HCl, or HNO_3. The sulfate will be in the combined filtrates, mixed with unused sodium carbonate

2. A more rapid and complete reaction between $BaSO_4$ and Na_2CO_3 can be obtained by mixing the two dry solids and heating the mixture at a dull red temperature for several minutes. The reaction is similar to that above but is more complete. The Na_2SO_4 that is formed may be dissolved from the mixture with hot water, leaving the $BaCO_3$ as a solid residue.

3. If a mixture of $BaSO_4$, Na_2CO_3, and powdered charcoal is heated on a charcoal block in the reducing flame of a blowpipe, the $BaSO_4$ is reduced to BaS. The latter is readily soluble in acids.

Strontium and Calcium. These metals are very similar to each other and to barium. They are both very active metals, reacting with the same reagents and in the same manner as does barium. Calcium is a rather soft metal, being only slightly harder than lead. It has a density of 1.55 and a melting point of 752°C. The solvents for these metals are the same as for barium, *i.e.*, acetic acid, very dilute HCl, or very dilute HNO_3.

Compounds of Strontium and Calcium. With few exceptions, solutions of Ca^{++} or of Sr^{++} give the same type of compounds as do solutions of Ba^{++}. The most notable exceptions are as follows:

Chromates do not give precipitates with neutral or acid solutions of Ca^{++} or Sr^{++}. If the solution is slightly alkaline, however, Sr^{++} gives $SrCrO_4$, yellow; readily soluble in acetic acid, HCl, or HNO_3, but only slightly soluble in alcohol or alcohol-water mixture.

Sulfates precipitate $SrSO_4$ from solutions containing Sr^{++} but give no precipitate with Ca^{++} unless the latter is present in very high concentrations.

Oxalates precipitate SrC_2O_4 and CaC_2O_4, neither of which dissolves readily in acetic acid, but both of which are soluble in mineral acids.

Potassium ferrocyanide gives no precipitate with either Ca^{++} or Sr^{++}.

The anhydrous chloride and nitrate of strontium are insoluble in either absolute alcohol or anhydrous acetone. The corresponding salts of calcium, however, are soluble in both of these solvents.

Preliminary Experiments

General Comparison. *a.* In test tubes or on a spot plate place separate drops of Ba^{++}, Sr^{++}, Ca^{++}, and Mg^{++}.* To each add 1 drop of Na_2CO_3 solution. Observe results against a black background. To each add 1 drop of $6M$ NH_4Cl solution, and stir, noting results.

Now add dilute $HC_2H_3O_2$ to each *precipitate* remaining, and stir.

b. To separate solutions of the four ions add 1 drop of K_2SO_4 solution, and note results.

c. To separate drops of Ba^{++}, Sr^{++}, Ca^{++}, and Mg^{++} on a spot plate add 1 drop of $1N$ K_2CrO_4. Note in which cases precipitates form; then to each add 1 drop of $1N$ NH_4OH and 1 drop of ethyl alcohol, noting results.

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* Magnesium, though belonging to Group V, is compared here with the members of Group IV to illustrate the fact that the separation of Mg^{++} from Ba^{++}, Sr^{++}, and Ca^{++} is dependent on careful control of the unknown while Group IV is being precipitated. Frequently, careless work results in magnesium being precipitated in Group IV, where it sometimes gives false tests for Ca^{++}, while if Group IV is incompletely precipitated, false tests are often obtained for magnesium. The results of these experiments should show what conditions are necessary to avoid such difficulties.

In the cases where precipitates formed, withdraw the liquid by touching the edge of the drop with the edge of a piece of filter paper. Then add to each precipitate 1 drop of a mixture of equal volumes of 2.5*N* $NH_4C_2H_3O_2$ and 1*N* $HC_2H_3O_2$, noting any differences in behavior of the precipitates toward this mixture. Try reprecipitating any that dissolved, by adding 2 drops of 1*N* NH_4OH and 1 drop of alcohol.

d. To separate drops of solutions of these ions, add 1 drop of $K_2C_2O_4$ solution.

e. To a mixture of Ba^{++} and Sr^{++} add K_2SO_4 until precipitation is complete. Filter; then to the filtrate add 1 drop of $K_2C_2O_4$. Rub the inside of the test tube, and let stand at least 15 min.; then examine.

Meanwhile, perform this same series of tests on a solution containing only Ca^{++}. Contrast the results.

f. Obtain a platinum flame-testing wire, and wash it carefully with water. Make a tiny loop in the end of the wire; rinse the wire in distilled water; then heat to redness in a Bunsen flame adjusted for maximum heat. While the wire is red-hot, plunge it into *clean* concentrated HCl in a test tube and heat again. Repeat until the wire, after becoming dry in the flame, imparts no color to the flame. Finally, dip the loop in a mixture of 1 drop of Ba^{++} solution and 1 drop of concentrated HCl; then hold it in the flame. Carefully observe the faintly greenish flame characteristic of Ba^{++}. Clean the wire carefully; then repeat the test, using first Ca^{++}, then Sr^{++}.

Analytical Aspects

Since the chlorides of barium, strontium, and calcium are very soluble, and their sulfides cannot be precipitated from aqueous solutions, these cations are not precipitated normally with Group I, II, or III. However, their carbonates are precipitated by addition of ammonium carbonate to a basic solution of their ions. Magnesium carbonate is also precipitated under these conditions; but if the OH^- concentration of the solution is lowered by addition of an ammonium salt, magnesium carbonate will not precipitate.

The identification of these elements is based upon (1) the low solubility of their carbonates, (2) the difference in solubility of their chromates (see Note 5), and (3) the low solubility of calcium oxalate.

GROUP IV ANALYSIS

To the group unknown (see Note 1) or the filtrate from Group III, add dilute NH_4OH until the solution is faintly basic to litmus. Heat the mixture on the steam bath (see Note 2), and add ammonium carbonate reagent, drop by drop with stirring, until precipitation is complete (see Note 3) Filter, and wash the precipitate twice with cold water.

Filtrate. Save for Group V

Precipitate. Contains $BaCO_3$, $SrCO_3$, and $CaCO_3$. Dissolve in the smallest possible volume of 6*N* acetic acid (see Note 4), warming if necessary. Evaporate the solution just to dryness, finishing the evaporation on the steam bath; then let the residue cool. Dissolve the residue in about 20 drops of a mixture of equal volumes of 1*N* acetic acid and 2.5*N* ammonium acetate soln To the resulting solution add 1*N* K_2CrO_4 soln , a drop at a time with stirring, until the clear liquid, after centrifuging, has a faint orange-yellow color (see Note 5) Filter, and wash the precipitate *twice* with 10-drop portions of a mixture of equal volumes of 1*N* $HC_2H_3O_2$ and 2.5*N* $NH_4C_2H_3O_2$, combining the first wash liquid with the filtrate (Note 6).

Filtrate. Contains Sr^{++}, Ca^{++} (and $CrO_4^{=}$) Add 6 or 7 drops of 6*N* NH_4OH and a volume of ethyl alcohol equal to about three-fourths the volume of this mixture (see Note 9). Stir; then centrifuge. Note the color of the clear liquid It should be faintly yellow. If not, add more K_2CrO_4 soln. stir, and centrifuge, repeating until the liquid remains yellow. Filter, and wash the precipitate with a mixture of 5 drops of water, 5 drops of ethyl alcohol and 1 drop of dil. NH_4OH

Precipitate. $BaCrO_4$.
YELLOW PPT.
indicates Ba^{++} Dissolve in 6 or 8 drops of conc HCl (see Note 7), evaporate until only 2 or 3 drops of liquid remain. Confirm the presence of barium by applying the flame test to this residual liquid (Note 8).

Filtrate. Contains Ca^{++} and $CrO_4^{=}$ (and possibly small quantities of Sr^{++}). Add 1*N* K_2SO_4 soln., drop by drop, with stirring until precipitation is complete (Note 10). Add 1 drop more of the K_2SO_4; then place on the steam bath, and heat (see Note 11), with stirring for 8 or 10 min. Cool, then filter, discarding the precipitate.

Precipitate. $SrCrO_4$
YELLOW PPT.
indicates Sr^{++} Confirm by dissolving in 6 or 8 drops of conc. HCl, evaporating to half its volume, then applying the flame test for Sr^{++} (see Notes 8 and 13).

To the clear filtrate, add half its volume of water and about 2 drops of 1*N* $K_2C_2O_4$ soln , then heat almost to boiling, and let stand for about 15 min. Centrifuge.

WHITE PPT.

indicates Ca^{++} present (see Note 12). Dissolve the precipitate in 2 or 3 drops of conc. HCl, and try the flame test for Ca^{++}, using this solution (Note 8).

NOTES

1. If a Group IV unknown is to be analyzed, use 1 ml. of the unknown and to it add 8 or 10 drops of 6*M* NH_4Cl or NH_4NO_3 solution before proceeding as described. Ammonium salts are needed to buffer the solution so the OH^- concentration cannot be sufficiently high to permit precipitation of $Mg(OH)_2$ or $MgCO_3$.

If the filtrate from the Group III precipitation is to be used for Group IV, sufficient NH_4^+ is already present, since NH_4NO_3 was added as buffering agent at the beginning of the precipitation of Group III.

2 Heating during the addition of reagents often aids by causing the formation of larger crystals, thus making filtrations easier.

3 Caution should be used to add enough reagent and allow sufficient time for precipitation to become complete, otherwise some of Group IV may slip through and give a false phosphate test for magnesium in Group V On the other hand, too great excess of the $(NH_4)_2CO_3$ reagent may cause the precipitation of some of the magnesium. There is usually sufficient leeway between these two points, but time and care must be taken in the precipitation

4. A modification of this procedure is to dissolve the precipitate in HNO_3 instead of $HC_2H_3O_2$, then evaporate to dryness Heat the residue (do not fuse it) with a micro flame to dehydrate it, then cool, and extract the residue with *anhydrous* acetone two or three times. The $Ca(NO_3)_2$ will dissolve in the acetone. By dissolving the residue in dilute acetic acid and proceding with the outlined procedure using K_2CrO_4, Ba^{++} and Sr^{++} may be identified. The combined acetone solutions may be evaporated on the steam bath, the residue dissolved in water, and the oxalate and flame tests for Ca^{++} applied.

5. $BaCrO_4$ is the least soluble of the chromates of these metals, calcium chromate being soluble to the extent of about 16 g in 100 ml of water at 16°C, while $SrCrO_4$ is soluble to the extent of about 0 12 g at this temperature—about 500 times as soluble as $BaCrO_4$. The presence of a low concentration of H^+ ion in the solution (1*N* acetic acid buffered with an equal volume of 2 5*N* ammonium acetate) reduces the concentration of CrO_4^{--} from the K_2CrO_4 by the reaction

$$2CrO_4^{--} + 2H^+ \rightleftharpoons Cr_2O_7^{--} + H_2O$$

and permits the precipitation of $BaCrO_4$ without precipitating $SrCrO_4$ or $CaCrO_4$, unless the concentration of Sr^{++} is unusually great If the filtrate from this reaction is made slightly basic, the above equilibrium shifts to the left and the concentration of CrO_4^{--} increases. This permits any Sr^{++} to precipitate as $SrCrO_4$, leaving the Ca^{++} still in the solution

6. By washing the $BaCrO_4$ precipitate with the buffered acid solution, any $SrCrO_4$ that might have precipitated owing to an unusually high concentration of Sr^{++} in the unknown will be dissolved.

7. Although $BaCrO_4$ is insoluble in buffered acetic acid, it is readily soluble in HCl. When this mixture is heated, reduction of the chromate occurs, since CrO_4^{--} or $Cr_2O_7^{--}$ is oxidizing and HCl is reducing in action. The result of this reaction is to convert the barium to its chloride and the chromate to Cr^{+++}.

8. The chromates, sulfates, and oxalates of the metals are not sufficiently volatile to give good flame tests. The chlorides, on the other hand, give excellent results. Moistening or dissolving a precipitate in concentrated HCl before testing intensifies the flame coloration obtained

9. In general, electrolytes are much less soluble in ethyl alcohol or alcohol-water mixtures than in water alone The addition of alcohol here, and to the wash water used later, reduces the solubility of the $SrCrO_4$ and in this way makes the precipitation much more efficient.

10. As $SrCrO_4$ is not so insoluble as might be desired, some of the Sr^{++} usually slips over into this filtrate The addition of K_2SO_4 at this point is for the purpose of precipitating the remaining Sr^{++} as $SrSO_4$ Plenty of time for this precipitation must be allowed as, owing to the low concentration of Sr^{++}, the process is slow

Usually a large part of any Ca^{++} present is also precipitated as $CaSO_4$ Sufficient Ca^{++} will remain, however, to give a good test

11. The first of this heating must be done cautiously, as much of the alcohol added earlier will boil away and the vigorous boiling may cause some of the solution to be thrown out of the container

12. Calcium oxalate, though very insoluble, has a strong tendency to form supersaturated solutions It is necessary, therefore, to heat the solution, rub the inside of the container with the tip of a stirring rod, and let the mixture stand

The precipitate should be very granular and fine and *should not precipitate quickly* A mass of semitransparent, needle-like crystals is usually the reagent, $K_2C_2O_4$, which has crystallized owing to loss of liquid by evaporation If such a precipitate forms, add distilled water to dissolve it. Any CaC_2O_4 will remain undissolved A gramy precipitate that forms *quickly* on addition of the $K_2C_2O_4$ is usually SrC_2O_4, and indicates incomplete removal of Sr^{++}. More rarely such a rapid precipitation indicates an unusually high concentration of Ca^{++} which was not sufficiently reduced by the addition of K_2SO_4 solution.

13 An additional confirmation of the presence of Sr^{++} can be secured, using the solution obtained by treating the $SrCrO_4$ with HCl. Dilute the remainder of this solution with 2 or 3 drops of water; add 1 drop of dilute NH_4OH, stir, and filter. To the filtrate add 1 drop of K_2SO_4 solution, stir, and let stand. A white precipitate of $SrSO_4$ confirms Sr^{++}.

QUESTIONS

1. Explain, by ionic equations and discussion, what happens to the OH^- concentration of an alkaline solution when ammonium salts are added

Next show by means of the equations for the ionization of carbonic acid, H_2CO_3, what effect would be produced on the CO_3^{--} concentration of a solution by a decrease in the OH^- concentration

Finally, using the foregoing information, explain why $MgCO_3$ will not precipitate from basic mixtures of Mg^{++} and CO_3^{--} when a moderately high concentration of NH_4Cl is present

2. By ionic equations show the effect produced on the H^+ concentration of acetic acid by the addition of ammonium acetate.

Show also the effect of an increase or decrease of H^+ on the CrO_4^- concentration of a solution.

Using the information given above, explain why $BaCrO_4$ precipitates from mixtures of Ba^{++}, Sr^{++}, and CrO_4^- containing $HC_2H_3O_2$ and $NH_4C_2H_3O_2$ whereas $SrCrO_4$ does not.

3. Outline briefly the precipitation, separation, and identification of the members of Group IV

4. What is the function

a. Of the NH_4OH in the precipitation of the carbonates of this group?

b. Of the ammonium chloride in the precipitation of this group?

c. Of each, the ammonium acetate and acetic acid, in the separation of Ba^{++} from Sr^{++} and Ca^{++}?

d. Of the alcohol in separating Sr^{++} from Ca^{++}?

e Of the K_2SO_4 that is added before testing for Ca^{++}?

5. Write equations for the reactions undergone by each of these cations during the complete Group IV analysis

6. Why is it suggested that concentrated HCl be used in making the flame tests for these metals?

7. Describe the color given a flame by each of these metals.

Equations for Group IV Analysis*

$$Ba^{++} + CO_3^- \rightarrow BaCO_3$$
$$BaCO_3 + H^+ \rightarrow Ba^{++} + H_2O + CO_2$$
$$Ba^{++} + CrO_4^- \rightarrow BaCrO_4$$
$$BaCrO_4 + H^+ + Cl^- \rightarrow Ba^{++} + Cr^{+++} + Cl_2 + H_2O$$

$Sr^{++} \rightarrow$ (same reactions as Ba^{++}); then

$$Sr^{++} + SO_4^- \rightarrow SrSO_4$$

$$Ca^{++} + CO_3^- \rightarrow CaCO_3$$
$$CaCO_3 + H^+ \rightarrow Ca^{++} + H_2O + CO_2$$
$$Ca^{++} + CrO_4^- \rightarrow \text{no reaction}$$
$$Ca^{++} + SO_4^- \rightarrow CaSO_4 \text{ (more soluble than } SrSO_4)$$
$$Ca^{++} + C_2O_4^- \rightarrow CaC_2O_4$$

GROUP V METALS

Chemical Characteristics

Magnesium. Metallic magnesium is a silvery metal having a density of 1.74, a melting point of 651°C, and a boiling point of 1110°C. It is quite active, reacting slowly with boiling (but not cold) water to give hydrogen and the rather insoluble magnesium hydroxide, $Mg(OH)_2$. It combines easily with oxygen and at high temperatures reacts readily with such nonmetals as the halogens, sulfur, and even nitrogen (the last reaction resulting

* The student should balance each of these for practice, indicating precipitates by (↓) and gases by (↑). Also indicate the *colors* of any products.

in the formation of magnesium nitride, Mg_3N_2). The metal dissolves readily in dilute acids, forming hydrogen and Mg^{++}.

Compounds of Magnesium. The compounds of magnesium have properties very similar to those of calcium, for which it is often mistaken in analyses. The *chromate*, $MgCrO_4$; the *ferrocyanide*, $Mg_2Fe(CN)_6$, the *chloride*, $MgCl_2$, and the *nitrate*, $Mg(NO_3)_2$, are very soluble in water. The *sulfide* cannot be precipitated from aqueous solutions, as hydrolysis of the sulfide readily occurs.

NH_4OH or *alkali hydroxides* produce a precipitate of $Mg(OH)_2$, white, gelatinous, insoluble in excess alkali, but soluble in solutions of ammonium salts and in acids.

Soluble carbonates produce a precipitate of $MgCO_3$, white, insoluble in NH_4OH, but soluble in solutions of ammonium salts (even in the presence of NH_4OH) and in acids.

Soluble phosphates precipitate $Mg_3(PO_4)_2$ from neutral or slightly basic solutions of Mg^{++}. From ammoniacal solutions of Mg^{++} containing a large concentration of ammonium salts, white, crystalline $MgNH_4PO_4$ precipitates. The latter is soluble in acids.

Soluble arsenates give white $Mg_3(AsO_4)_2$ with neutral solutions of Mg^{++} or white, crystalline $MgNH_4AsO_4$ with ammoniacal solutions of Mg^{++} containing ammonium salts.

Soluble oxalates precipitate, from fairly concentrated solutions of Mg^{++}, MgC_2O_4, white, soluble in acids and in excess alkali oxalate.

Soluble sulfates produce no precipitate, as $MgSO_4$ is very soluble in water.

Potassium, Sodium, and Ammonium.* Sodium and potassium are very soft metals, having, when freshly cut, a silvery luster. The former has a density of 0.97, a melting point of 97.5°C., and a boiling point of 880°C. Potassium has a density of 0.86, a melting point of 62.3°C., and a boiling point of 760°C. Both are extremely active metals, potassium being slightly the more active. Both tarnish almost instantly in air, forming the oxides, Na_2O_2, K_2O_4, and K_2O; both react vigorously with water, giving the hydroxide and hydrogen; both combine readily with non-metals, many of them at ordinary temperature. With acids, their reaction is so rapid as to be dangerous. The safest solvent is ethyl alcohol.

Potassium and sodium are monovalent in all their compounds.

* Although ammonium is not an element, the radical, NH_4, exhibits certain peculiarities that justify its treatment as a metal. Its base- and salt-forming properties are already familiar to the student. In addition, however, it has the ability to form an amalgam with mercury. This is easily demonstrated by either electrolyzing a strong solution of NH_4Cl, using a pool of mercury as the cathode, or by adding some sodium amalgam (a solution of metallic sodium in mercury) to a saturated solution of NH_4Cl. If either of these operations is carried out at a low temperature, an amalgam of ammonium is formed, the truth of this being demonstrated by allowing the amalgam to warm and noting the escape of hydrogen and NH_3 gases from the mass.

Compounds of Potassium, Sodium, and Ammonium. Practically all the compounds of these three ions are soluble to a greater or less extent. The *hydroxides, sulfates, chlorides, nitrates, carbonates, phosphates, arsenates, chromates, sulfides,* and *ferrocyanides* are all very soluble. However, NH_4OH is very unstable toward heat and breaks up, giving NH_3 and water. *Sodium oxalate* is less soluble than the oxalates of the other two ions.

A few of the compounds of sodium, potassium, and ammonium are sufficiently insoluble to make feasible their use in analysis

Sodium cobaltinitrite, $Na_3Co(NO_2)_6$, gives yellow precipitates with K^+ and with NH_4^+. These precipitates vary in composition, depending upon the relative amounts of ion and reagent, typical compositions being $K_2NaCo(NO_2)_6$ and $(NH_4)_2NaCo(NO_2)_6$. If the precipitation is performed in the presence of Ag^+, a very insoluble precipitate of yellow $K_2AgCo(NO_2)_6$ or $(NH_4)_2AgCo(NO_2)_6$ is formed.

If $(NH_4)_2NaCo(NO_2)_6$ is heated, the ammonium ion is decomposed, the corresponding potassium compound is also decomposed by heating, but the potassium ion remains in the solution and can be reprecipitated by cooling and adding more sodium cobaltinitrite

Perchloric acid with concentrated solutions of K^+ or NH_4^+ give white $KClO_4$ or NH_4ClO_4. If alcohol is added to the mixture, these compounds precipitate from even very dilute solutions. The alcoholic mixture must not be heated, however, as a violent explosion may result. Sodium does not give this reaction.

Tartaric acid, $H_2C_4H_4O_6$, precipitates white $KHC_4H_4O_6$ or $NH_4HC_4H_4O_6$ from solutions of K^+ or NH_4^+. Like most compounds of these two cations, the precipitate usually forms only on long standing Sodium gives no precipitate.

Chloroplatinic acid, H_2PtCl_6, yields K_2PtCl_6 and $(NH_4)_2PtCl_6$ with K^+ and NH_4^+; with Na^+, no precipitate forms.

If either precipitate is ignited, decomposition takes place

$$3(NH_4)_2PtCl_6 \rightarrow 2N_2 + 2NH_3 + 3Pt + 18HCl$$
$$K_2PtCl_6 \rightarrow 2KCl + Pt + 2Cl_2$$

Potassium pyroantimonate, $K_2H_2Sb_2O_7$, gives a white precipitate of $Na_2H_2Sb_2O_7$ with Na^+. Acids and all cations except those of the alkali family interfere.

Zinc uranyl acetate, magnesium uranyl acetate, and *cobalt uranyl acetate* give yellowish precipitates with Na^+ The formulas of the product are of the type $NaCo(UO_2)_3(C_2H_3O_2)_9$.

On ignition, ammonium compounds readily decompose, the NH_4^+ being destroyed.

Preliminary Experiments

1. Magnesium Ion, Mg^{++}. Recall the tests performed on Mg^{++} in the Preliminary Experiments, Group IV. Then perform the following:

a. To 1 drop of Mg^{++} solution in a test tube add 1 drop of dilute NH_4OH. Note results; then add 1 drop of 6*N* NH_4Cl, stir, and explain results (see Question 1).

b. To the solution from *a* add 1 or 2 drops of Na_2HPO_4 solution, and rub the inside of the glass container with the tip of a stirring rod. Let stand 10 or 15 min.; then note results (see Note 1).

c. Repeat *a* and *b*, using Ca^{++} instead of Mg^{++} (see Question 2).

d. To 1 drop of Mg^{++} solution add 3 or 4 drops of water, 1 drop of *p*-nitrobenzeneazoresorcinol reagent, and 1 drop of NaOH solution. Stir; centrifuge, and note results.

Repeat, but add 1 drop of 6*M* NH_4Cl before adding the reagent. Examine closely, noting especially the color of the solution. Finally, add 6*N* NaOH, drop by drop with stirring, until the solution turns violet or blue. Centrifuge once more, and note results.

2. Potassium, K^+, Sodium, Na^+, and Ammonium, NH_4^+, Ions. Since ammonium and potassium ions are very similar in their reactions, and since the tests for K^+ and Na^+ must be performed in the presence of each other, it is best to consider these three ions simultaneously in order to obtain a clearer picture of their similarities and differences. In each of the following precipitation reactions if a precipitate fails to appear, rub the inside of the container with the tip of a stirring rod. In some cases the solubility of the product is not extremely low, and usually the substances readily form supersaturated solutions.

a. To 2 drops of K^+ solution in a test tube add 2 drops of *freshly prepared* sodium cobaltinitrite reagent (Note 3), and note results (see Note 4). Dissolve the precipitate by boiling; *cool;* filter; then test the filtrate for K^+ as before.

Repeat, using NH_4^+ instead of K^+.

b. To 1 drop of K^+ solution add 1 drop of tartaric acid solution; stir; let stand; and note results. (Question 4.)

Repeat using NH_4^+; then again, using Na^+.

c. In similar manner test the action of zinc uranyl acetate reagent on separate drops of K^+, NH_4^+, and Na^+ solutions.

d. Using the procedure described in the Preliminary Experiments, Group IV (*f*) try a flame test on K^+ solution.

Repeat, viewing the flame through a piece of blue (cobalt) glass. Note that the coloration seems to stream upward in the flame from the wire.

Clean the wire carefully, then perform the flame test on Na^+ with and without the blue glass. Note the masking effect of the glass (see Note 5).

Finally test a mixture of K^+ and Na^+, with the glass and without the glass. The flame test is capable of detecting as little as 0.0006 mg. of K^+ or 0.000003 mg. of Na^+.

e. In the test tube of a gas evolution apparatus (see Fig. 26), place about 3 drops of NH_4^+ test solution. Evaporate the solution barely to dryness (see Note 8), *cool*, then add 1 or 2 drops of 6*N* NaOH. Assemble the apparatus, and put a piece of moist red litmus paper in the upper part. Close the top of the upper tube with a loose plug of cotton; then place the apparatus on the *steam bath* for 4 or 5 min., noting any changes in the litmus paper (see Note 9).

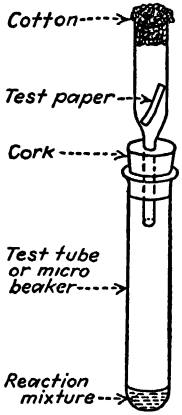


FIG. 26.—Gas-evolution apparatus.

ANALYTICAL ASPECTS

The members of this group remain in solution throughout all the previous precipitations. Magnesium readily forms a number of slightly soluble compounds, but sodium, potassium, and ammonium ions form very few slightly soluble substances. In view of the fact that ammonium ion is added many times during the analysis, it is necessary to *test the originial solution* for that ion.

Ammonium ion gives practically all the precipitates that it is possible to get with potassium ion. It is therefore necessary to destroy all the ammonium ion before testing for potassium. This is done by oxidizing the ammonium ion with aqua regia and igniting the residue to drive off the last traces of ammonium compounds. Since the other ions do not offer any great interference with each other in these tests, it is not necessary to do any separation other than this.

GROUP V ANALYSIS

Group unknown (or filtrate from Group IV). Use for the following tests.

To 2 drops of the solution add 1 drop of 6*N* NH_4Cl, 1 drop of 6*N* NH_4OH, and 1 drop of NaH_2PO_4. Rub the inside wall of the beaker with a stirring rod, and let stand 10 or 15 min. (see Note 1).

WHITE PPT.
indicates Mg^{++} present.

To 2 or 3 drops of the unknown add 2 drops of water and 1 drop of *p*-nitrobenzeneazoresorcinol reagent Finally add 6*N* NaOH, drop by drop with stirring, until the mixture turns blue or violet (see Note 2). Centrifuge.

BLUE LAKE or PRECIPITATE
confirms presence of Mg^{++}.

Place the remaining unknown in a crucible, and evaporate to dryness. Add 15 drops of freshly prepared aqua regia, and evaporate again to dryness. Ignite the residue (heat the crucible almost to redness) until no more white fumes escape (Question 5) Cool, then dissolve the residue in 5 or 6 drops of water Use this solution for the following tests.

To 1 drop of this solution on a watch glass add 1 drop of sodium cobaltinitrite soln (see Notes 3 and 4). Let stand

PALE YELLOW PPT.
indicates K^+ present

Confirm by heating on the steam bath until the precipitate redissolves, cooling and then adding more reagent Reappearance of the precipitate is excellent confirmation for K^+

To another drop of the prepared solution apply the flame test, using the platinum wire and looking at the flame with and without the blue glass

LAVENDER FLAME visible through BLUE GLASS
confirms presence of K^+ (see Note 5)

BRIGHT YELLOW LASTING FLAME
indicates Na^+ (see Note 7).

To a third drop of this solution on a spot plate or watch glass (black background) add 8 drops of zinc uranyl acetate soln Rub the inside of the container with a stirring rod, and let stand at least 5 min. (see Note 6).

YELLOW PPT.
confirms Na^+.

The test for NH_4^+ must be made on the *original* general or group unknown *before any reagents are added* to it The test should be performed as described in Preliminary Experiment 2*e*.

BLUE COLORATION
on litmus indicates NH_4^+ (see Note 9).

NOTES

1. The precipitate does not form rapidly unless an unusually large concentration of Mg^{++} is present The procedure described is used to overcome supersaturation.

2. The blue precipitate or lake does not form in solutions of Mg^{++} in which large concentrations of ammonium salts are present, unless enough NaOH

is added to destroy these salts completely. The dye itself is an excellent indicator for the quantity of NaOH needed, the solution changing from a yellow color to a violet or blue. It will be recalled that any unknown that has been taken through the Group III and IV precipitations must, of necessity, contain large quantities of NH_4^+ When the test is performed as described, however, this reagent gives highly dependable results.

3. This reagent is prepared by the student just before using. Make a saturated solution of sodium cobaltinitrite by shaking a couple small crystals of the solid with 3 drops of water Dilute with an equal volume of water, and filter Use at once, as the reagent decomposes sufficiently in a comparatively short time to give poor results

4. All the slightly soluble salts of potassium, ammonium, and sodium readily form supersaturated solutions Consequently, when trying to precipitate compounds of these ions, use all the precautions possible against supersaturation.

5. The light from the lavender potassium flame will penetrate a piece of blue glass while the yellow light of the sodium flame will not This makes it possible to see the potassium flame even if sodium is present Occasionally, however, a double thickness of glass is required.

6. Due to the saturated condition of the zinc uranyl acetate reagent and the long period of standing, needle-like crystals of the *reagent* sometimes form around the edge of the mixture being tested for Na^+. The *sodium* precipitate is very grainy and is a nontransparent yellow If any doubt exists, add 4 or 5 drops of water and stir The *reagent* will dissolve readily.

7. Owing to the extreme sensitivity of the sodium flame test and the common occurrence of sodium, fleeting flame tests should not be trusted. The coloration should last at least 10 sec and should be confirmed by the precipitation test Care must be exercised to avoid getting the fingers into the mixture, as the sodium compounds in the perspiration will give this test readily.

8. Overheating will cause loss of the ammonium salts present, as most ammonium salts decompose or volatilize on heating

9. If the paper does not become uniformly blue, it indicates that any blue spots present are due to spattering of the sodium hydroxide If spattering is noticed, the test must be tried with a fresh sample of unknown.

QUESTIONS

1. Explain, using ionic equations, the effect produced on the OH^- concentration of NH_4OH by the addition of NH_4Cl.

Using this information then explain why $Mg(OH)_2$ is not precipitated from solutions of Mg^{++} and ammonium salts by addition of NH_4OH.

2. If the precipitation of Group IV was incomplete, would the phosphate test for Mg^{++} on the filtrate be dependable? Explain.

3. How could you distinguish between K^+ and NH_4^+ by the use of sodium cobaltinitrite reagent? Why would your method work?

4. What are the *common* name of and a commercial use for the product of the reaction between K^+ and $H_2C_4H_4O_6$?

5. What is the reason for treating the unknown with aqua regia, evaporating, and igniting the residue before testing for K^+?

What role does the aqua regia play?

6. Which of the cations of Group V give characteristic flame colorations? Describe these colorations.

7. Why are the members of Group V placed together in this group?

8. Write equations for the reactions each of the cations of this group undergoes during the analysis

9. Which of the metals of this group would probably *not* be present in any of the common *alloys*?

Auxiliary Tests

Silver. 1. If 1 drop of a 0.03 per cent solution of 5-(*p*-dimethylaminobenzal) rhodanine in acetone is added to the ammoniacal solution obtained with the AgCl in Group I, this being followed by the addition of 1 drop of $6N$ HNO_3, a purple-red precipitate will form. The test will detect as little as 0.001 mg of Ag^+.

2. Diphenylthiocarbazone (dithizon) reagent with silver ion in slightly alkaline solutions gives a fine violet precipitate (see also lead, zinc, cadmium, and cobalt).

Mercury. 1. One drop of the solution obtained by dissolving in aqua regia the precipitate of Hg and $HgNH_2Cl$ in Group I or the HgS in Group II, if treated with 1 drop of $1N$ $HC_2H_3O_2$, 1 drop of saturated $NaC_2H_3O_2$, and 1 drop of a *freshly prepared* alcoholic solution of gallic acid, will give a yellow or orange precipitate if mercury is present. Of the Group I and II metals, only Ag^+ interferes.

2. If the mercury solution obtained from the aqua regia treatment in Group I or Group II is treated with diphenylcarbazide reagent, a deep blue color will form. The reagent is made by saturating 50 per cent acetone with diphenylcarbazide, saturating this with KSCN, and adding 1 g. of KI for each 100 ml. of solution.

3. A drop of solution containing mercurous ion placed on a piece of filter paper and treated with a drop of $NaNO_2$ solution gives a dark stain of metallic mercury. Silver interferes, but the colored products of copper, iron, nickel, cobalt, and chromium can be washed off.

4. If a drop of a solution containing mercurous ions and a drop of aniline are added to a drop of $SnCl_2$ solution on filter paper, a black stain of metallic mercury will result.

Lead. 1. A drop of a solution containing lead ion, on filter paper, converted to PbO_2 by treatment with H_2O_2 and NH_4OH and heated in a jet of steam to decompose the unused H_2O_2, will give a blue spot with a 0.1 per cent solution of tetramethyldiaminodiphenylmethane in 10 per cent acetic acid. Bismuth does not interfere.

2. In a slightly alkaline solution containing KCN, lead ion will give a red-violet coloration with diphenylthiocarbazone reagent. Under these conditions silver, copper, cadmium, nickel, zinc, and antimony do not interfere.

3. A trace of bismuth, followed by a drop of sodium stannite solution, added to an alkaline solution containing lead ions will produce a dark stain of metallic lead in a short time. The bismuth alone gives the test if added in sufficient quantities, so a blank should be run at the same time.

Copper. 1. When 1 drop of the ammoniacal solution obtained by the precipitation of $Bi(OH)_3$ in Group II is placed on a piece of filter paper and 1 drop of a 5 per cent solution of α-benzoinoxime in ethyl alcohol is added, a green spot will form if copper is present.

2. If to a faintly acid solution containing cupric ion, an excess of zinc ion and a drop of $(NH_4)_2Hg(SCN)_4$ solution are added, a colored precipitate will be obtained. The color will range from lavender for minute traces of copper to a purple-black for greater concentrations of copper. If copper is present in greater concentration than zinc, an apple-green precipitate will form.

3. If a solution of cupric ion is sufficiently concentrated, the addition of KI solution will produce free iodine and a white precipitate of cuprous iodide. Many metallic ions interfere with this test, the reaction serving better as a test for moderate concentrations of iodide ion.

Bismuth. 1. When 1 drop of the solution obtained by dissolving the $Bi(OH)_3$ from Group II in HCl is treated with 1 drop of cinchonine reagent (see reagent list), an orange precipitate will form if as much as 0.00014 mg. of Bi^{+++} is present.

2. When a solution of $BiCl_3$ or $Bi(NO_3)_3$ is treated with a 1 per cent solution of dimethylglyoxime and made strongly ammoniacal, a voluminous yellow precipitate will form. If $Bi_2(SO_4)_3$ is used in place of the chloride or nitrate, a white precipitate will result.

3. If a drop of a solution containing even a trace of bismuth ion is put on filter paper and is treated with a solution containing lead ion, a drop of 6*N* NaOH, and a drop or two of sodium stannite solution, a black deposit of metallic lead will form. The bismuth acts as a catalyst for the reduction of the lead, and this reaction serves as a very sensitive test for bismuth. A blank should be run at the same time, however, as the lead will be reduced, in time, whether bismuth is present or not. Easily reduced ions, such as silver and mercury, interfere.

4. A drop of bismuth ion in 10 per cent HNO_3, placed on a filter paper and treated with a dilute solution of KI, will give a black stain of BiI_3. The stain should be washed with distilled water to remove iodine set free by ferric or cupric ions. Excess KI converts it to a solution of yellow BiI_4^- which readily hydrolyzes to orange BiOI. Mercury interferes.

Cadmium. 1. If a drop of a solution containing Cd^{++} is placed on a piece of filter paper, a crystal of thiosinamine (allylthiourea) added to the spot, 6*N* NaOH added to make it alkaline, and the spot finally heated for 1 or 2 minutes in a jet of steam, the spot around the crystal will turn bright yellow. The test can be used on the solution obtained by dissolving the CdS from Group II in dilute H_2SO_4.

2 When an ammoniacal solution of cadmium ion containing excess KCN is treated with formaldehyde and heated, a precipitate of $Cd(OH)_2$ will form. If the precipitation is performed in the presence of dinitrodiphenylcarbazide, the precipitate will be blue. The precipitate of $Cd(OH)_2$ may be dissolved in dilute HCl, and other confirmatory tests applied.

3. A solution containing cadmium ion, treated with a mixture of solid Na_2CO_3 and finely powdered charcoal in a test tube, evaporated to dryness, then heated strongly, will give in the cooler portions of the test tube a mirror of cadmium metal edged with brown. If sulfur is added to the test tube and distilled over the mirror, a layer of CdS will be formed which will be orange while hot but yellow when cool.

Tin. 1. A saturated solution of cacotheline in water, added to the solution prepared as described in the analytical procedure for the gold test for tin, will give a violet coloration.

2. If a drop of a solution containing tin (Sn^{++} or Sn^{++++}) is mixed with a drop of 0.05*N* KI solution and a drop of this mixture

is brought into contact with a drop of concentrated H_2SO_4 on a glass slide, a fine yellow precipitate of SnI_2 or SnI_4 will form at the interface between the two liquids, gradually spreading into a broader band. Antimony and arsenic interfere somewhat, giving iodine and a yellow-orange precipitate. This, however, usually appears only as a *narrow line* at the interface *without spreading*. Controls should be run in case of doubt.

3. A borax bead tinted blue by dipping in strong $Cu(NO_3)_2$ solution and heating will give with tin (even in traces and in any type of compound) a red or reddish-violet bead. The color is best developed by heating in a reducing flame. The bead is colorless while hot, the color appearing rather suddenly while cooling. As the test requires experience for dependability, beginners should consider only positive tests as significant.

Antimony. 1. An excellent confirmation test for Sb^{+++} can be made using sodium thiosulfate, $Na_2S_2O_3$. With saturated $NaHCO_3$ solution almost neutralize 2 or 3 drops of the HCl solution obtained in separating arsenic from antimony and tin. Finally, add one-fifth the volume of the solution of 6*N* HCl; stir; and heat almost to boiling. At once add a volume of solid $Na_2S_2O_3$ the size of a large match head, and heat quickly. If Sb^{+++} is present, a red-orange precipitate will form. A yellow precipitate may be due to tin, or it may be only some sulfur formed by decomposition of the $S_2O_3^{--}$ by the acid.

2. A strongly acid (HCl) solution containing antimony ion, treated with a drop of 0.05*N* KNO_2 and heated to decompose excess HNO_2, will give a violet color on addition of a drop of a 0.1 per cent solution of rhodamine B (tetraethylrhodamine) in water. Tungsten and oxidizing agents interfere. As little as 0.0005 mg. of antimony can be detected in the presence of 12,400 times as much tin by this test.

3. By boiling the slightly acid solution with excess chlorine water, antimony can be precipitated as Sb_2O_5 (separation from tin). The resulting precipitate dissolved in HCl may be tested by any of the usual methods.

Aluminum. 1. A drop of a solution of aluminum ion containing a trace of cobalt on a filter paper that was previously treated with saturated $KClO_3$ solution and dried will, on treatment with NH_3 fumes and burning, leave an ash that varies in color from an olive green to a light blue. In the absence of aluminum ion, the ash is black.

2. If solutions of ammonium chloride and KCNO are added to a solution containing aluminum ion and the mixture is heated, a granular precipitate of $Al(OH)_3$ will form. Prolonged heating reduces the effectiveness of this precipitation.

Chromium. 1. A solution containing CrO_4^{--} gives a blue coloration with benzidine reagent. The test may be used on the HNO_3-K_2SO_4 extract from the precipitate of $BaCrO_4$ as obtained in Group III.

2. Tetramethyldiaminodiphenylmethane gives a bluish-purple coloration if added to a buffered acetic acid solution of chromate ion. To test for chromic ion, it is best to add the reagent (a 0.1 per cent solution in acetic acid) to the solution, make the latter alkaline with NaOH, and add a few grains of Na_2O_2. Warm on the steam bath until bubbling has practically ceased; cool; and make acid with acetic acid. A bluish-violet color appears, becoming more intense and more reddish on standing. Carried out in this manner on a portion of the Group III*A* solution [see Group III (Option I) procedure], this serves as an unusually certain, moderately sensitive test for chromium. In very dilute solutions the test is faint and fleeting, especially if too great excess of Na_2O_2 is used.

Zinc. 1. A portion of the solution being tested in Group III for Zn^{++} may be tested by adding 1 drop of NH_4SCN solution and 1 drop of pyridine to the solution. A white precipitate of $Zn(C_5H_5N)_4(SCN)_2$ confirms the presence of zinc.

2. Diphenylthiocarbazone forms with acetic acid-acetate or neutral or slightly basic solutions of zinc ion a red-purple precipitate soluble in the $CHCl_3$ or CCl_4 of the reagent solution. The change is startling, the color going from the rich green of the reagent to a pink or red. Moderate quantites of manganese, cobalt, and nickel will not interfere if the solution is made ammoniacal and agitated for a minute or two before adding the reagent. Interference by silver, copper, mercury, gold, bismuth, cadmium, and lead is masked by a preliminary treatment of the solution with $Na_2S_2O_3$. With $Na_2S_2O_3$ and KCN (in *faintly acid* solution to mask nickel, cobalt, and palladium) the reagent is specific for zinc.

3. A test developed by Benedetti-Pichler makes use of ashless filter paper soaked in a solution of 4 g. of $K_3Co(CN)_6$ and 1 g. of $KClO_3$ per 100 ml. of water and carefully dried. A drop of zinc solution in the center of a 1-in. square of such paper, dried

to a brown spot and burned, will leave a green ash if zinc is present to a concentration of 1 mg. per milliliter. Special methods of using this test will detect as little as 0.0006 mg. of zinc. The ash is best observed if caught on white porcelain.

Nickel. 1. If to a neutral or slightly alkaline solution containing nickel ion a little ethylenediamine and $Na_2S_2O_3$ are added, a violet crystalline precipitate will form. Although this test is not so sensitive as the test using dimethylglyoxime, it is specific in the presence of large concentrations of iron, cobalt, copper, and chromium.

2. In the absence of cobalt, the borax bead test (see Preliminary Experiments) gives a reddish-brown color if used on the nickel filtrate in Group III.

Manganese. 1. A solution of manganous ion in concentrated nitric acid gives, on boiling with solid PbO_2, a pink or violet solution of $HMnO_4$ (very specific).

2. A drop of a solution of manganese ion made alkaline with NaOH and evaporated to dryness will, on treatment with a 1 per cent solution of strychnine in concentrated H_2SO_4, give a blue-violet color, slowly turning red. Cobalt interferes, but its interference is removed by preliminary treatment with KCN. Oxidizing agents interfere.

Ammonium. 1. The tests described under the title Potassium may be used for ammonium ion in the absence of the former. The best way to use them if K^+ is present is to make the solution alkaline with NaOH and distill into a drop or two of distilled water containing a little HCl. As NH_3 is readily volatile, it will distill over and the tests can be applied to the resulting solution. An alternative is to hold a drop of the reagent (*e.g.*, H_2PtCl_6) in the tip of a glass tube over the solution made alkaline with NaOH and to warm the latter, observing the appearance of cloudiness in the reagent.

2. Nessler's solution, an alkaline solution of K_2HgI_4, turns brownish if added to solutions containing ammonium ion. Since the depth of color is roughly proportional to the concentration of ammonium ion, this reaction is often used in the colorimetric estimation of low concentrations of NH_4^+.

ANION ANALYSIS

Introduction. In the qualitative analysis for cations, use is made of precipitations, dissolutions, and color-change reactions, each performed under carefully controlled conditions of hydrogen ion concentration and each making use of certain reagents each at a definite point in the procedure. The reagents used in these analyses are chosen chiefly for the anions that they provide; consequently, in most cases, it could be said that *solutions of certain anions* are used as reagents.

On the other hand, in the analysis of unknowns to determine which *anions* are present, it is only natural that *cations* should be used as the reagents to produce recognizable precipitates. In addition, however, many *anions* are used in the identification tests for other anions; for owing to the fact that the nonmetals in the anions are capable of existing in several valence states, most anions are capable of undergoing numerous reactions not only with cations but also with other anions. For this reason, too, there are many anions that cannot exist together in the same solution—or that although capable of existing together under some conditions, react with one another to form other substances under changed conditions, such as changes in pH. As a result the analysis for the anions in complex mixtures is by no means simple, for the analytical procedure itself requires many changes in condition.

There are many ways in which the common anions may be classified for analytical purposes. Most of those commonly used, however, are based upon the following characteristics: (1) if they form volatile products on being acidified and warmed; (2) if their barium or calcium salts are insoluble (*a*) in acid or (*b*) in neutral solutions; and (3) if their silver salts are insoluble in (*a*) neutral or (*b*) dilute nitric acid solutions.

Many of the anions fall in two or more of these classes; consequently, their grouping in the analytical procedure will depend upon which reagent is added first. For example, $CO_3^{=}$ forms CO_2 when it is acidified and warmed; also, its barium and silver

salts are insoluble in neutral solutions. For this reason, different analytical procedures may place $CO_3^=$ in quite different groups even when the reagents used are the same, if only the order of use of these reagents is different for the two procedures.

The analytical procedure used here works well when applied to the limited group of anions considered in this text and may be extended to include others as well. In this procedure, the anions are divided into the following groups:

Anion Group I: The Volatile Group. This group consists of those anions which, on acidification with a dilute, nonoxidizing acid, yield readily volatile products. These anions and their volatilization products are $S^=$ (H_2S), NO_2^- (N_2O_3), $SO_3^=$ (SO_2), $CO_3^=$ (CO_2), ClO^- (Cl_2), and CN^- (HCN).

Anion Group II: The Silver Nitrate Group. The anions in this group are those anions which are not in Group I and whose silver salts are insoluble in dilute nitric acid. These inclued I^-, Br^-, Cl^-, SCN^-, $Fe(CN)_6^=$, and $Fe(CN)_6^{\equiv}$.

Anion Group III: The Barium-calcium Group. In this group are those anions which do not have characteristics of those in Group I or II and whose barium or calcium salts are insoluble in neutral or weakly alkaline solutions. Those considered in this work are $CrO_4^=$, $PO_4^{\equiv}$, $AsO_3^{\equiv}$, $AsO_4^{\equiv}$, $B_4O_7^=$ or $BO_3^{\equiv}$, F^-, $SO_4^=$, and $SiO_3^=$. Of these, both the barium and the calcium salts of $AsO_3^{\equiv}$ are somewhat soluble. For this reason, very small quantities of $AsO_3^{\equiv}$ may be missed in this group and the anion must therefore be sought in Group IV. This is similar to the behavior of lead among the cations, lead appearing in the procedures for both Group I and Group II of the cations.

Anion Group IV: The Soluble Group. The anions in this group include ClO_3^-, MnO_4^-, $C_2H_3O_2^-$, NO_3^-, and $AsO_3^{\equiv}$. These anions do not form readily volatile compounds with dilute acids; and under the conditions used in this procedure, their silver, barium, and calcium salts are soluble. In truth it may be stated that the anions of this group, with the exception of $AsO_3^{\equiv}$, form soluble salts with practically all metals, the solubilities of only a few basic salts being really low.

In general the procedure of analysis used in this course will follow the four groupings outlined above. From the standpoint of simplification, however, as well as for the purpose of understanding more fully the properties of the anions, the oxidizing

and reducing properties of many of the anions must also be considered.

Oxidation-reduction Reactions of Anions. Of the common anions some are reducing agents, some are oxidizing agents, and some are neither oxidizing nor reducing. Such a classification must not be considered clean-cut, however, for it must be remembered that the behavior of any chemical individual depends upon the substances present with which it has an opportunity to react. The chemical properties of any substance are always described in terms of *what it will do if brought in contact with certain other substances or classes of substances* under specified conditions. A notable example of this is involved in the reactions of NO_2^-. If a solution of nitrite is mixed with a strong oxidizing agent such as $KMnO_4$ or $NaClO$, the NO_2^- acts as a *reducing agent*, itself being oxidized to NO_3^-. On the other hand if acidified and mixed with I^- the NO_2^- acts as an *oxidizing agent*, oxidizing the I^- to I_2, the NO_2^- itself being reduced to NO. For this reason it is impossible to classify NO_2^- as being strictly oxidizing or strictly reducing in character. This dual nature is due to the fact that the nitrogen in NO_2^-, which has a valence that lies between the maximum and minimum valences exhibited by nitrogen in its various compounds, is capable of being oxidized to higher valences (as in NO_2 or NO_3^-), or of being reduced to lower valences (*e.g.*, as in NO, N_2, and NH_3). It should be evident, therefore, that any other anions that contain elements capable of exhibiting both higher and lower valences may, if conditions and reagents are properly chosen, display either oxidizing or reducing properties. Examples of such anions are $SO_3^=$, $AsO_3^=$, and ClO^-. It is fortunate for our purposes, therefore, that most ions of this type show stronger tendencies to act one way than to act the other. For example, $SO_3^=$ usually acts as a reducing agent; only in the presence of very powerful reducing agents such as H_2S does it act as an oxidizing agent. On the other hand, ClO^- acts almost exclusively as an oxidizing agent, rarely exhibiting its reducing properties.

Both Br^- and I^- are strictly reducing in action; but of the two, the I^- is by far the more powerful in most reactions. Thus I^- is capable of reducing Fe^{+++} to Fe^{++} and Cu^{++} to Cu_2^{++}; whereas Br^- does not reduce either of these ions.

The activity of any group of ions as oxidizing or reducing agents (see Chap. X) cannot be accurately compared without first carefully defining conditions as well as reactants. As an illustration suppose that one considers first the effect of *acidity* on a typical pair of reactions. If a solution of free iodine is added to a neutral solution of $AsO_3^{\equiv}$ or of $SO_3^{=}$, the iodine will be quickly reduced to I^-, the $AsO_3^{\equiv}$ forming $AsO_4^{\equiv}$ and the $SO_3^{=}$ being oxidized to $SO_4^{=}$. If the same reactions are attempted in moderately acid solutions, the $SO_3^{=}$ will again reduce the I_2, yielding the same products as before, but the $AsO_3^{\equiv}$ will not reduce the I_2. Thus a change in pH may make an ion change completely its type of behavior; and while an acidic unknown may contain both $AsO_3^{\equiv}$ and free iodine, neutralization of such a mixture would immediately bring about reaction.

The effect of changes in pH on the course of a reaction may often be predicted by applying the law of mass action to the equilibrium involved. Thus the behavior of I_2 and $AsO_3^{\equiv}$ described above might have been anticipated from a consideration of the equation for the reaction:

$$AsO_3^{\equiv} + I_2 + H_2O \rightleftharpoons AsO_4^{\equiv} + 2H^+ + 2I^-$$

A study of this reaction shows that a high concentration of H^+ favors the reduction of $AsO_4^{\equiv}$ by I^- whereas a low H^+ concentration favors the oxidation of $AsO_3^{\equiv}$ to $AsO_4^{\equiv}$ by I_2. In Cation Group II, therefore, where $AsO_4^{\equiv}$ is reduced by I^- to $AsO_3^{\equiv}$, the reduction proceeds normally, since the solution is acid. Similarly, in testing anion solutions with I_2 it is found that acidic solutions of $AsO_3^{\equiv}$ will not reduce I_2; but if the solution containing $AsO_3^{\equiv}$ is made either very faintly acid, very slightly basic, or neutral, the $AsO_3^{\equiv}$ will react with I_2 to form $AsO_4^{\equiv}$, the lower the H^+ concentration the more complete being the reaction.*

The effect of the H^+ concentration on oxidation-reduction reactions is also well illustrated by the reactions of ClO_3^-.

* The same might be said of the reaction between $SO_3^=$ and I_2

$$SO_3^= + H_2O + I_2 \rightarrow SO_4^= + 2H^+ + 2I^-$$

One essential difference is, however, that $AsO_3^{\equiv}$ is potentially (see Chap. X) a much weaker reducing agent than is $SO_3^=$ under similar conditions, consequently, the $SO_3^=$ is sufficiently active to reduce I_2 even in acid solutions, whereas $AsO_3^{\equiv}$ is not.

When ClO_3^- reacts with a reducing agent such as I^-, the reduction of the ClO_3^- and the oxidizing action of the ClO_3 are favored by a high H^+ concentration:

$$ClO_3^- + 6H^+ + 6I^- \rightleftharpoons Cl^- + 3H_2O + 3I_2$$

In fact, ClO_3^- has no apparent effect on cold, alkaline or neutral solutions of I^-.

Analytical Classification. From the standpoint of their most commonly displayed oxidizing and reducing characteristics, the anions that are considered in this course may be divided roughly into three classes.

1. *Reducing Ions.* Of these, $S^=$, $SO_3^=$, NO_2^-, and I^- are strong reducing agents, especially in acid solutions. All of them may be oxidized, slowly by the oxygen in air and quickly by more active oxidizing agents. In addition, SCN^-, Br^-, $Fe(CN)_6^{4-}$, and AsO_3^{3-} are moderately active reducing agents; while in strongly acid solutions, Cl^- can be oxidized by such strong oxidizing agents as MnO_4^- or MnO_2. CN^-, especially in neutral or alkaline solutions, can, with strong oxidizing agents, act as a reducing agent.

2. *Oxidizing Ions.* Of these ClO^-, $Fe(CN)_6^{3-}$, MnO_4^-, and $CrO_4^=$ are the most active, the first three being active even in alkaline solutions. Acid solutions of ClO_3^- are quite strongly oxidizing but its basic or neutral solutions are relatively inactive. Similarly, AsO_4^{3-} and NO_3^- are moderately active oxidizing agents in acid solution.

In addition to these, $SO_3^=$, though normally a reducing agent, is capable of oxidizing $S^=$ to S° in acid solution. In other respects, however, both of these ions behave as strong reducing agents.

3. *Nonoxidizing and Nonreducing Ions.* The anions, $CO_3^=$, $SO_4^=$, PO_4^{3-}, $B_4O_7^=$, $SiO_3^=$, F^-, and $C_2H_3O_2^-$, are neither reducing nor oxidizing. Cl^-, though weakly reducing in nature when in strongly acid solutions, usually acts as if it were in this class except when in unusually high concentrations or in the presence of powerful oxidizing agents. Even then, heat is usually required to make its oxidation proceed rapidly.

A study of the properties of these ions enables one to make several simplifications in the analysis of anion unknowns. For example, if an *active reducing* ion is found to be present in the

solution of an unknown, obviously the most active of the oxidizing agents cannot be there.* On the other hand, the ions of Type III can exist in solution with either oxidizing or reducing ions.

On the basis of their oxidizing and reducing characteristics, the analysis of any mixture of anions may be greatly simplified by elimination tests. These are based on the reactions of the anions, in *acid* solution, with very *dilute* $KMnO_4$ *solution* (test for reducing ions), with a *blue solution of* I_2 *in starch*-KI *mixture* (test for *strong* reducing agents), and with a *colorless starch*-KI *mixture* (test for oxidizing agents).

Preliminary Examination and Treatment of Solid Unknowns. Although the methods of analysis necessary to fit all cases wherein solid unknowns must be handled are far too complex to be studied in a limited course such as this,† simpler solid unknowns can be dissolved and analyzed quite readily. Before the dissolution or analysis can be attempted, however, a few simple preliminary tests should be performed and the knowledge obtained in the cation analysis of the unknown should be carefully considered.

If the original unknown is water soluble, much can often be deduced concerning the nature of the anions present. For example, a water-soluble solid that contained any of the members of the Group I or II cations obviously could not contain $S^=$—for the sulfides of these metals are not soluble in water. Similarly, in a water-soluble unknown if Ba^{++} were present, $SO_4^=$ and $CrO_4^=$ must be absent; and if Ag^+ were present, all the members of Anion Group II must be absent! By noting whether the aqueous solution of the water-soluble solid is acidic, basic, or neutral and by considering solubility relationships, a knowledge of the cations can be used to eliminate many anions.

If the solid is not water soluble but is soluble in dilute HCl or in dilute HNO_3, a careful study of the characteristics of the compounds of those cations known to be present will give much information of this same type.

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* This rule has exceptions. For example, $AsO_3^=$ and $AsO_4^=$ can exist together; for if $AsO_3^=$ reduced $AsO_4^=$, it would reduce the $AsO_4^=$ to $AsO_3^=$ and would itself be oxidized to $AsO_4^=$. A similar situation exists in regard to $Fe(CN)_6^{\equiv}$ and $Fe(CN)_6^{\equiv}$ mixtures.

† For such cases see the much more comprehensive work, "Analytical Chemistry," Vol. I, "Qualitative Analysis," by Treadwell and Hall, John Wiley & Sons, Inc., New York, 1937.

When a solid unknown is obtained, therefore, test its solubility in (1) water, (2) dilute HCl or dilute HNO_3,* and (3) aqua regia. It is not necessary to use all these; try them in the order mentioned, and stop as soon as one is found that will dissolve all the solid. Remember that if some of the solid dissolves in a given reagent, perhaps a second or third treatment with the same reagent will complete the task. Use the information gained as follows:

1. If the solid is soluble in water, use the aqueous solution for the analysis as described in the following pages.

2. If the unknown was insoluble in water but was soluble in HCl or HNO_3, place a 0.1-g. portion of the untreated solid in a test tube, add 2 or 3 ml. of saturated Na_2CO_3 solution, and heat on the steam bath 10 or 15 min, replacing with distilled water any liquid lost by evaporation. Filter the mixture, and use the filtrate for the analysis for all anions *except* $CO_3^{=}$.† Save the precipitate; for if tests for PO_4^{-} in Anion Group III prove negative, this precipitate should be dissolved in HNO_3 and the resulting solution tested for that anion.

3. If the precipitate was insoluble in water, in HCl, and in HNO_3 but was soluble in aqua regia, a complete analysis is probably beyond the scope of this text. Most of the possible components, however, can be detected by digesting a sample of the unknown with Na_2CO_3 solution and running the analysis on this solution as described in case 2.

Treat the precipitate with dilute HNO_3; filter if any solid fails to dissolve; and save the filtrate to use in testing for $PO_4^{=}$.

There are many unknowns that cannot be analyzed satisfactorily by this means, *e.g.*, the halides of silver, which are so insoluble that they are not dissolved by any of these reagents. For the treatment of these more difficult substances, refer to more comprehensive works on the subject.

* If all but a gummy dark or yellow mass dissolves, this mass tending to float in the solution, the undissolved residue may be sulfur. If this seems probable, remove and wash the residue, and try burning it on a crucible lid. Burning, accompanied by the characteristic odor of SO_2, confirms sulfur and indicates the presence of sulfides in the unknown.

† It should be obvious that if Na_2CO_3 has been added to the unknown, tests for $CO_3^{=}$ on this solution would be uninformative. In Anion Group I, however, a procedure is described by means of which tests for $CO_3^{=}$ can be run on the original solid.

Preliminary Oxidation—reduction Tests. Before proceeding with the analysis of any unknown, tests should be made for oxidizing and reducing properties; for by this means many ions usually may be shown absent These tests and the interpretation thereof are described in the following paragraphs.

To 6 or 8 drops of the unknown solution* add dilute H_2SO_4 or NaOH until the solution is neutral or only *faintly* acid; then at once use for the following tests:†

Test I. To 2 drops of the neutral unknown add 1 drop of 6*N* H_2SO_4 and 1 drop of 0 5 per cent $KMnO_4$, and *stir*.

A positive test is obtained if the *purple or pink color* disappears within 5 sec ‡

Test II. (To be performed only if Test I is positive, *i e*, if the color bleaches in 5 sec) To 2 drops of the neutral unknown add 1 drop of 6*N* H_2SO_4 and 1 drop of a dark blue solution of I_2 in starch-KI solution.

A positive test consists of the blue disappearing within 5 sec

Test III. To 2 drops of the neutral unknown add 1 drop of 6*N* H_2SO_4 and 1 or 2 drops of a *colorless* mixture of equal volumes of fresh starch solution and 1*N* KI solution.

A *positive* test consists of the solution turning blue§ within 10 sec ||

The interpretation of these tests is based upon the following facts:

1. If NO_2^-, $S^=$, $SO_3^=$, SCN^-, I^-, $Fe(CN)_6^{\equiv}$, $AsO_4^{\equiv}$, or a high concentration of Br^- is present, the *color of the* MnO_4^- *will disappear* instantly. Even low concentrations of Br^- will cause bleaching within 5 sec. This test being positive indicates that with few exceptions active oxidizing agents cannot be present.

2 If $S^=$, $SO_3^=$, or $Fe(CN)_6^{\equiv}$ is present, the blue color of the solution of *iodine in starch*-KI will *fade* within 5 sec

3. If NO_2^-, ClO^-, $Fe(CN)_6^{\equiv}$, $CrO_4^=$, $AsO_4^{\equiv}$, MnO_4^-, or ClO_3^- is present, the starch-KI solution will react within 10 sec to *produce free iodine.*

Fe^{+++} or Cu^{++} will also give this test.

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* If the unknown is a water-insoluble solid, use the Na_2CO_3 solution described earlier for such cases.

† Speed is essential, as otherwise the volatile members of Anion Group I may be lost.

‡ If I^- or Br^- is present, the solution will turn yellow or brown; consequently, a positive test is obtained if the color of the MnO_4^- disappears, even though a brown or yellow is obtained.

§ If large concentrations of oxidizing agents are present, or if the starch is not good, the solution may turn yellow, brown, or almost black instead of blue. Such colors are due to an excessive amount of I_2 being formed. In all such cases shake the mixture with a few drops of CCl_4. If the CCl_4 layer assumes the violet color characteristic of free iodine, consider the test positive.

|| On standing, the solution will turn blue even in the absence of oxidizing agents, unless reducing agents are present. This is due to air oxidation of the acidic I^- solution. The reaction usually takes several minutes,

To simplify the elimination of different ions by means of these oxidation and reduction tests, use the following suggestions. To do so, make a list of all the ions that might possibly be present in your unknown; then cross off, one by one, the ions that your tests and this list suggest as having been eliminated. *These tests do not eliminate any of the Type* III *anions.*

1. Test I is positive.* Eliminate ClO^-, $CrO_4^=$, MnO_4^-, and ClO_3^-
2. Test I *is negative.* Eliminate NO_2^-, $S^=$, $SO_3^=$, SCN^-, $Fe(CN)_6^{\equiv}$, I^-, Br^-, and $AsO_3^{\equiv}$.
3. *Test* II *is positive.* Eliminate NO_2^-, ClO^-, $CrO_4^=$, $AsO_4^{\equiv}$, MnO_4^-, and ClO_3^-.
4. *Test* II *is negative.* Eliminate $S^=$, $SO_3^=$, and [unless $Fe(CN)_6^{\equiv}$ is present] $Fe(CN)_6^{\equiv}$.
5. *Test* III *is positive.* Eliminate $S^=$, $SO_3^=$, and SCN^-.
6. *Test* III *is negative* Eliminate NO_2^-, ClO^-, $Fe(CN)_6^{\equiv}$, $CrO_4^=$, MnO_4^-, and ClO_3^-.

Not only can certain anions be eliminated on the basis of these tests, but also certain positive information can be gained. For example, if Tests I and III are both positive, one (but *only one*) of the following will be responsible: (1) NO_2^- alone; (2) $Fe(CN)_6^=$ and $Fe(CN)_6^{\equiv}$ together; or (3) $AsO_3^=$ and $AsO_4^{\equiv}$ together. If all three tests are positive, $Fe(CN)_6^{\equiv}$ and $Fe(CN)_6^{\equiv}$ are responsible, the others mentioned being absent.

QUESTIONS

1. The oxidation tests on a general anion unknown show Test I positive and Tests II and III negative. What ions are eliminated? For which must tests be run?
2. Answer Question 1, assuming Test III positive and Tests I and II negative.
3. Answer Question 1, assuming all tests are negative
4. Answer Question 1, assuming Tests I and II positive but Test III negative
5. If the unknown in Question 2 contained only the members of Anion Group I, what information would this give you?

ANION GROUP I ANALYSIS

By means of the preliminary oxidation-reduction tests determine which of the ions, $S^=$, $SO_3^=$, NO_2^-, or ClO^- can be present (see Note 1), then test individually for the different anions using the following procedures:

1. Sulfides (see Note 2). Assemble the apparatus illustrated in Fig 27. On one of the nichrome wire supports hang a bit of filter paper moistened

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however; and if the solution is not disturbed, it will be seen that when the change is due to the air, the blue appears first at the *surface* of the mixture instead of within it.

* If organic compounds are present, too great dependence cannot be placed on the test with $KMnO_4$, as many organic compounds are capable of reducing MnO_4^- in acid solutions.

with $Pb(C_2H_3O_2)_2$ soln.; on the other, a bit of filter paper moistened with Sb^{+++} test solution. In the flask place 4 or 5 drops of unknown, an equal volume of water, and 4 or 5 drops of $NaHCO_3$ soln.; then acidify the mixture with dil. $HC_2H_3O_2$; and quickly put the cork and its test papers into the mouth of the flask. Be sure that the vent functions properly to prevent the formation of pressure within the flask. Let stand on top the steam bath for 2 or 3 min, if necessary, then observe the colors of the test papers.

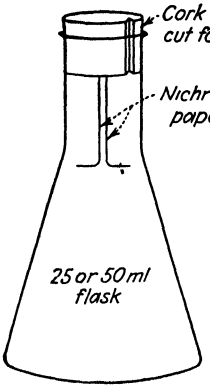


FIG. 27.—Vapor-testing apparatus

BROWN or BLACK

lead acetate paper and

ORANGE

antimony test paper show $S^=$ present.

2. Sulfites, Nitrites, and Hypochlorites (see Note 1) Use the apparatus described for $S^=$, only use as one test paper a bit of moist starch-KI and as the other a bit of filter paper moistened with a mixture of equal volumes of fresh starch soln. and 0.05*M* HIO_3 soln (*Caution.* Do not let these test papers come into contact with each other, as they will immediately react with each other. Also avoid H_2S in the air, as it also will give a test with the starch-HIO_3 paper.)

In the flask place 5 or 6 drops of the unknown, an equal volume of water, and 4 or 5 drops of $NaHCO_3$ soln. Add enough dilute $HC_2H_3O_2$ to make the solution strongly acid; then *at once* put the stopper with the test papers into the flask. Be sure that a vent is provided in the cork for the escape of vapors; then place the whole on the steam bath. Observe occasionally for 1 or 2 min. Finally, remove the strips of paper, and observe them a few seconds.

STARCH-HIO_3 PAPER TURNS BLUE or BROWN but the starch-KI remains colorless. $SO_3^=$ is present. (*Caution:* See Note 3.)

STARCH-KI PAPER TURNS BLUE or BROWN

(the starch-HIO_3 paper turns only slowly or not at all). NO_2^- or ClO^- is present (see Note 4).

As a further check for $SO_3^=$ add 3 drops of the unknown to 3 or 4 drops of water, then acidify with HCl *Keeping the solution cold*, add $BaCl_2$ soln. until precipitation is complete; then filter. To the filtrate (which should contain excess $BaCl_2$) add 2 or 3 drops of *yellow* bromine water. A white precipitate or turbidity confirms $SO_3^=$. The bromine oxidizes the $SO_3^=$ to $SO_4^=$ to give the test.

Confirm a NO_2^- test by adding 2 drops of ferrous ammonium sulfate soln. to 2 drops of the unknown and acidifying with dilute H_2SO_4. A

dark brown solution which loses color with the production of a yellowish gas on warming confirms NO_2^-.

Confirm ClO^- by adding 1 drop of $Pb(C_2H_3O_2)_2$ soln. to 1 drop of the unknown, making the solution basic with 1*N* NaOH, and warming. A brownish-yellow precipitate whose color forms only on standing or warming (see Note 5) confirms ClO^-.

3. Carbonate Ion, $CO_3^=$. In a 100-mm. test tube fitted with a stopper and glass delivery tube (see Fig. 28) place 3 or 4 drops of the unknown (if $SO_3^=$ is present, add also 1 drop of K_2CrO_4 soln.). Acidify the solution with dil. H_2SO_4; add a tiny pinch of powdered carborundum (see Note 6); then

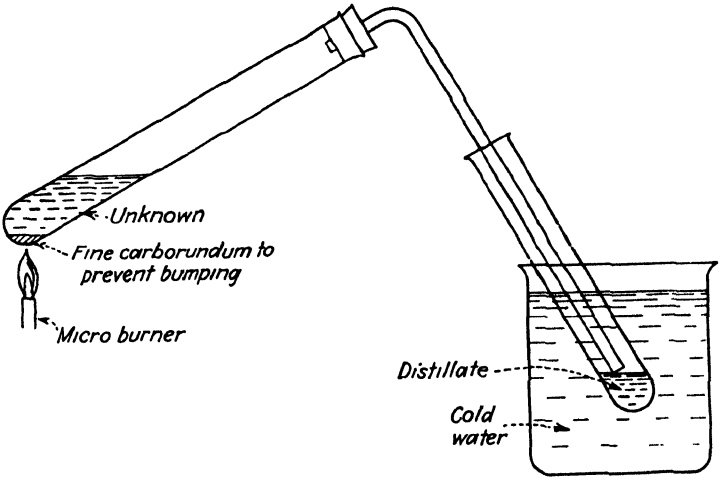


FIG. 28.—Micro distilling apparatus.

put the stopper and delivery tube in place. Adjust the apparatus so the end of the delivery tube is within 1 mm. of the surface of 10 or 12 drops of *clear* limewater in a second test tube (see Note 7). Carefully warm the generator test tube until 4 or 5 drops of liquid have distilled over, watching the limewater during this time.

WHITE PPT. or TURBIDITY

in the limewater shows $CO_3^=$ present (see Note 8).

4. Cyanides. Acidify 1 drop of the unknown with dil. HCl, and add 1 drop of $FeCl_3$ soln. If no deep red, blue, or green coloration is produced, the solution may be used in the tests described below. If the solution assumes one of these colors, put 5 drops of the solution, 6 or 8 drops of $NaHCO_3$, and 5 drops of water in the apparatus in Fig. 28. Acidify with dil. $HC_2H_3O_2$; add a small pinch of powdered carborundum; and distill half the liquid in the generator into a test tube containing 5 or 6 drops of dil. NH_4OH, cooling the receiver by allowing it to dip into cold water. Use this distillate in the following tests.

To about 2 drops of the distillate or unknown add 8 or 10 drops of ammonium polysulfide, $(NH_4)_2S_x$, soln. Transfer to a crucible, and boil gently until the liquid becomes dark red and then milky in appearance. Cool, acidify with 1*N* HCl, then add 3 or 4 drops of $FeCl_3$ soln.

RED COLORATION

of $Fe(SCN)_6^{-3}$ shows CN^- present (Note 9).

Confirm by adding to a clean crucible 2 drops of the distillate or unknown, 1 drop of ferrous ammonium sulfate, and 1 drop of 6*N* NaOH Heat on the steam bath 10 to 15 min.; then acidify the mixture with 6*N* HCl

GREEN or BLUE

coloration or precipitate of Prussian blue confirms CN^- (Note 10).

NOTES

1. It will be recalled from the early discussion of the anions that certain combinations of anions cannot be present in the same solution owing to the fact that they would react with each other if such a mixture were prepared Thus ClO^- is a powerful oxidizing agent, S^- is an active reducing agent, SO_4^- is usually reducing but in acid solution is capable of oxidizing S^- to form S^0, while NO_2^- is both oxidizing and reducing in action, being capable of oxidizing S^- or SO_3^- but of reducing ClO^-

For this reason, it will be seen that of the four anions, S^-, SO_3^-, NO_2^-, and ClO^-, only one should be expected in any one unknown. It is possible to keep solutions containing both SO_3^- and NO_2^- for several hours, but such combinations will not be common

2. Many of the less soluble sulfides such as HgS are not attacked by Na_2CO_3 and are, of course, insoluble in water If the unknown is an insoluble solid, therefore, the failure to obtain a test for S^- by this method does not necessarily mean S^- is absent

Such insoluble sulfides may often be tested by the acid method described on page 281. It is also frequently possible to identify the sulfide by burning a small portion of the solid unknown on the tip of a metal spatula in an oxidizing flame and noting the odor of SO_2 formed

3. The blue coloration with the starch-HIO_3 is produced by the reduction of IO_3^- to I^-, followed by the action of more of the IO_3^- on the I^- to form I_2. As SO_2 is capable of reducing the I_2 to I^- more rapidly than it can be formed by the other reactions, if much SO_4^- is present, it is frequently necessary to remove the paper from the flask and expose it to air (*avoid* H_2S-contaminated air, however) or moisten it with more HIO_3 to get the test.

Sulfides give this same test; but if the test for S^- was positive, it is unnecessary to test for either SO_3^- or NO_2^-.

NO_2^- will also give the starch-HIO_3 test, but the reaction is much slower than that with SO_3^-. The NO_2^- can be recognized, however, owing to the fact that it reacts with both starch-KI and starch-HIO_3.

4. If ClO^- is present, the blue color of the starch-iodine complex may appear, then disappear, owing to the further reaction of the iodine with the Cl_2 or Cl_2O to form IO_3^-. It is well, therefore, to watch the starch-KI paper closely while making this test.

NO_2^- will also produce the blue coloration with starch-KI, but since the two, ClO^- and NO_2^-, cannot be together, the preliminary tests will indicate which one is giving the test.

5. The reaction used here to confirm ClO^- depends upon the fact that ClO^- will oxidize $Pb(OH)_2$ to PbO_2 If peroxides are present, it is necessary to perform the lead test in an acetic acid solution buffered with ammonium acetate. The same results are obtained with ClO^-, but the peroxides will not give the test in such an acid solution

6. When solutions are being boiled they often superheat, *i.e.*, short intervals occur when boiling ceases and the solution heats above its boiling point, then suddenly a large bubble of steam forms, escaping with sufficient violence to throw a lot of the liquid upward. This forms spray which is carried over during a distillation and contaminates the distillate with the nonvolatile components of the original solution This so-called "bumping" can be reduced or even stopped entirely by the addition of a little fine carborundum, pieces of porous clay, finely broken glass, etc. Sharp edges or the capillary openings of these substances provide surfaces at which vapor forms readily and thus prevents superheating by facilitating the boiling action.

Carborundum is used here because it is not attacked by any of the ordinary reagents used and because it is one of the most effective substances used to prevent bumping

7. Limewater readily absorbs CO_2 from the air and in doing so loses strength rapidly Before this test is tried, therefore, 2 or 3 drops of the limewater should be tested by adding to it 1 drop of CO_3^- test solution. If a definite white precipitate is obtained, the reagent is all right

8 In testing for CO_3^- it must be remembered that the air in the laboratory usually contains much CO_2 Consequently, precautions must be taken to minimize contact between the air and any reagents used in this test. Weak tests should always be checked by every possible means, doubtful cases being checked by running the same tests, under identical conditions, on a blank consisting of distilled water and comparing results with those obtained with the unknown.

In the presence of SO_3^-, it is necessary to remove the SO_3^- before making the test for CO_3^-, as both give white precipitates with alkaline solutions of Ca^{++}. The procedure described provides for this by the oxidation of SO_3^- by K_2CrO_4 and H_2SO_4 to form the nonvolatile SO_4^-

9. Sometimes when the $FeCl_3$ is added to this mixture, a red coloration forms but quickly fades. In such cases, add more $FeCl_3$

The phenomenon is due to the fact that any S^- that may yet remain quickly reduces the Fe^{+++} to Fe^{++}. Since Fe^{++} gives no coloration with SCN^-, the color of $Fe(SCN)_6^{=}$ produced at first quickly fades.

10. The test described here depends upon the presence of traces of Fe^{+++} in the ferrous ammonium sulfate. The reaction at first involves $Fe(OH)_2$ and the CN^-.

$$Fe(OH)_2 + CN^- \rightarrow Fe(CN)_2 + 2(OH)^-$$
$$Fe(CN)_2 + 4CN^- \rightarrow Fe(CN)_6^{=}$$

Then the Fe^{+++} reacts with the $Fe(CN)_6^{=}$ to form Prussian blue, $Fe_4(Fe(CN)_6)_3$. When the test obtained is weak, it is best to add a drop of diluted $FeCl_3$ solution so as to furnish more Fe^{+++}.

It will be noted that an excess of CN^- is needed for the formation of the $Fe(CN)_6^{\equiv}$; consequently, a too large excess of ferrous ammonium sulfate should be avoided, and the $FeCl_3$ should be added only after the mixture is acidified.

ANION GROUP II ANALYSIS

To 1 ml. of the original unknown add an equal volume of water; then acidify with 6*N* $HC_2H_3O_2$. Add 10 drops more of the $HC_2H_3O_2$; then evaporate the solution to half its volume to remove members of Anion Group I. *Cool;* then place half of the solution in a separate container. Treat both portions in the following manner (see Note 1).

Add to each solution half its volume of 6*N* HNO_3; stir; then add 5% $AgNO_3$ drop by drop with stirring until precipitation is complete. Filter, *combining the filtrates* from the two portions. Wash the separate precipitates each twice with 3*N* HNO_3, combining the first wash liquids with the filtrates. Finally, wash each precipitate with water.

Filtrates. (combined). Save for Anion Groups III and IV.

Precipitates. May contain AgSCN (white), $Ag_3Fe(CN)_6$ (orange-red), $Ag_4Fe(CN)_6$ (white), AgCl (white), AgBr (pale yellow), and AgI (yellow).
Use one precipitate for Part *A* below; save the second for Part *B*.

PART *A*

Add 3 or 4 drops water and an equal volume of sat NaCl. Let the mixture stand at least 3 min, shaking occasionally, then filter. Wash the precipitate with water, discarding the wash liquid.

Filtrate. Test for SCN^- and $Fe(CN)_6^{\equiv}$.
To 1 drop of filtrate add 1 drop of $FeCl_3$ soln.

DARK RED

color shows SCN^- present (Note 2).

To 3 drops of filtrate add 1 drop of $HgCl_2$ soln, 1 drop of Co^{++} soln., and 1 drop of Zn^{++} soln. *in that order.* Stir vigorously, and let stand.

BLUE PRECIPITATE

confirms SCN^-.

Precipitate. Test for $Fe(CN)_6^{\equiv}$.
Wash the precipitate twice, using 10-drop portions of *cold* 6*N* NH_4OH and discarding the wash liquid. Finally, wash with two portions of cold water.
To the precipitate, add 2 or 3 drops of $FeCl_3$ soln., and shake.

DARK BLUE

color appearing at once shows $Fe(CN)_6^{\equiv}$ present (Note 3).

To 1 drop of filtrate add 1 drop of freshly prepared ferrous ammonium sulfate soln.

DARK BLUE

color shows $Fe(CN)_6^{\equiv}$ present (Note 3).

PART *B*

To this portion of precipitate add 10 drops of conc. NH_4OH and 1 drop of 6*M* NH_4NO_3. Filter, saving both precipitate and filtrate. To the filtrate add $(NH_4)_2S$ until precipitation is complete. Similarly add 8 or 10 drops of $(NH_4)_2S$ to the precipitate from the NH_4OH-NH_4NO_3 treatment. Thoroughly crush the masses of precipitate with the tip of a stirring rod (see Note 4); then combine this mixture with the other. Filter, discarding the precipitate of Ag_2S. To the filtrate add 4 or 5 drops of sat. $NaHCO_3$ soln., then evaporate almost to dryness. Add 15 or 20 drops of water; stir; then add $Ni(NO_3)_2$ soln. until precipitation is complete. Filter, discarding the precipitate. Acidify slightly with 6*N* $HC_2H_3O_2$. (*Caution.* Foaming may occur.) Then add $Ni(NO_3)_2$ soln. until precipitation again is complete. Filter, discarding any precipitate (see Note 5). Use the filtrate as follows.

Iodide. To the filtrate add 2 or 3 drops of 6*N* HNO_3, then add 3 or 4 drops of NO_2^- test solution. Let stand about 1 min; then shake the mixture with a few drops of CCl_4.

PINK or VIOLET

layer of CCl_4 shows I^- present (see Note 6). Save the water layer for the next test.

Bromide. Boil the solution until no more violet vapors of I_2 form (or until about one-fourth of the liquid is gone) (see Note 7). If I^- was present, cool the mixture, then add 1 drop of NO_2^- test solution and more CCl_4 to see if all the I^- has been removed. If not, add more NO_2^- and a little water, and repeat the boiling.

When all I^- and I_2 have been removed, cool the solution, add an equal volume of 6*N* HNO_3, then add 0.1*N* $KMnO_4$ soln. until a pink color remains. At once shake the mixture with CCl_4.

YELLOW or ORANGE

layer of CCl_4 shows Br^- present (see Note 8). Save the water layer for the next test.

Chloride. Remove the aqueous layer from the Br^- test; and if necessary, add enough 0.5 % $KMnO_4$ soln. to keep the solution pink for about 15 sec. (to make sure that all Br^- has been oxidized). Finally boil the solution in a crucible until about one-third the liquid is done, ignoring any formation of MnO_2. Cool the mixture, and dissolve any MnO_2 by adding several drops of HNO_3 and 1 or 2 drops of H_2O_2. To the mixture add 5% $AgNO_3$

soln. until precipitation is complete. Filter, and wash any precipitate, first with $3N$ HNO_3, then with water

WHITE PPT.

indicates Cl^- present (see Note 9).

Remove the bulb from a medicine dropper, and with a stirring rod push into the tube, from the top, a moderately tight but thin wad of clean cotton. To the precipitate above add 4 or 5 drops of water, stir, and with another dropper transfer the mixture of water and precipitate to the improvised filter. Let the water drain through the cotton. Then attaching a rubber tube to the top of the dropper blow through it to free the cotton and tube of water. Next put 10 drops of dil HNO_3 into a test tube. Place the dropper-filter above it; then fill the dropper with $1N$ NH_4OH. Collect the first 4 drops of NH_4OH in the HNO_3.

WHITE TURBIDITY

confirms Cl^- (see Note 10).

NOTES

1. The solution is divided here so as to make it unnecessary to divide the precipitate later, as the latter process is difficult when only small precipitates are obtained.

2. *If NO_2^- was found present,* or if the test for SCN^- is weak, the original unknown must be tested for SCN^-. To do this add $Pb(C_2H_3O_2)_2$ solution to 3 or 4 drops of the unknown until precipitation is complete Filter; then add the filtrate to a mixture of 5 drops of $6N$ HNO_3 and 5 drops of $FeCl_3$ to obtain a deep red color. The color usually fades in a short time. The excess of $FeCl_3$ is needed, as a number of ions are capable of reducing Fe^{+++} to Fe^{++} and thus interfering with the test for SCN^- The $Pb(C_2H_3O_2)_2$ removes I^- and $S^=$, both of which interfere.

3. In case of doubt, the tests for $Fe(CN)_6^{-4}$ and $Fe(CN)_6^{=}$ should be made on the original unknown. In both cases add dilute HCl, if necessary, to make the solution acid; then add several drops of $FeSO_4$ solution to one portion to test for $Fe(CN)_6^{-4}$; to another portion add several drops of $FeCl_3$ solution to test for $Fe(CN)_6^{=}$.

4. To get efficient conversion of the AgBr, AgI, and $Ag_4Fe(CN)_6$, the solid and liquid must be thoroughly slimed; otherwise, a film of Ag_2S will form on the outside of the solid and prevent the $S^=$ in the $(NH_4)_2S$ solution getting to the silver salts beneath. Since AgCl, AgSCN, and $Ag_3Fe(CN)_6$ are soluble in the NH_4OH, these react readily with the $S^=$ that is added to the filtrate. In the presence of the NH_4NO_3, some of the AgBr is also in the dissolved state.

5. The $Ni(NO_3)_2$ is added here to remove any $S^=$ [from the $(NH_4)_2S$], CN^-, or $Fe(CN)_6^{=}$ present. The last may have been in the original unknown,

or it may have been formed by reduction of any $Fe(CN)_6^{=}$, as the latter is easily reduced by $(NH_4)_2S$ or even by NH_3 in alkaline solution.

6. If NO_2^- was present and no I^- or Br^- is found, it will be necessary to test for I^- and Br^- on the original unknown, as in removing Anion Group I both I^- and Br^- may be oxidized to the free element and vaporized. In such cases use 5 or 6 drops of the original unknown and perform the tests exactly as described in the paragraphs under Iodides and Bromides in the procedure.

7. Do not boil too long, as if the solution becomes too concentrated, the NO_2^- and HNO_3 may oxidize the Br^- to Br_2 and cause loss or weakening of the later tests for Br^-.

8. Sometimes traces of MnO_2 cling to the interface between the water and the CCl_4, making it look yellowish. If this occurs, add 1 drop of dilute HNO_3 and 1 drop of 3 per cent H_2O_2 to the mixture and shake it. This will remove the MnO_2. The color of the bromine should be observed at once, however, as it frequently fades within a short time.

9. If any Br^- slips through to this point, a very pale yellow (almost white) precipitate of AgBr will form and will give a weak test similar to that for Cl^-. If Br^- was present and the tests obtained for Cl^- are not conclusive, they should be checked before any Cl^- is reported.

10. The test here depends upon the greater rate at which AgCl dissolves in 1*N* NH_4OH as contrasted to the rate of dissolution of AgBr in this reagent.

Unless the turbidity is strong or a white precipitate forms, a test obtained here should not be trusted. Bromide frequently slips through and gives a test similar to that for Cl^-, even yielding a weak confirmation test. Also, Cl^- is frequently an impurity in reagents and weak tests may come from that source.

ANION GROUP III ANALYSIS

To the filtrate from Anion Group II add 1*N* HCl until precipitation of the excess Ag^+ is complete. Filter, discarding the precipitate, then make the filtrate *faintly* basic with NaOH. To this add $Ba(NO_3)_2$-$Ca(NO_4)_2$ reagent until precipitation is complete. Let stand several minutes to insure completeness of the precipitation; then filter. Wash the precipitate with water.

Filtrate. Test for Group IV.	**Precipitate.** To the precipitate add 10 or 15 drops of 6*N* HNO_3; stir, and warm on the steam bath 1 min. Filter. If any precipitate remains, repeat the treatment with HNO_3, combining the filtrates. Wash the precipitate with cold water, discarding the wash water.

Filtrate. Contains $CrO_4^=$, $BO_3^=$, $AsO_3^=$, $AsO_4^=$, and $PO_4^{\equiv}$. Test as described under Subgroup III*A*.	**Precipitate.** Contains $BaSO_4$, $BaSiO_3$, CaF_2, and $CaSiO_3$. Test as described under Subgroup III*B* (see Note 8).

Anion Group IIIA Analysis

To the filtrate containing this subgroup add 6*N* NaOH, drop by drop with thorough stirring, until the solution is very slightly basic to litmus; then to the mixture add one-third its volume of 6*N* $HC_2H_3O_2$. Stir; let stand 3 or 4 min.; and filter.

Filtrate. Contains $BO_3^{\equiv}$, $AsO_3^{\equiv}$, $AsO_4^{\equiv}$, and $PO_4^{\equiv}$. Evaporate to half its volume, then to the mixture add one-fourth its volume of 6*N* HCl. Use the solution as follows.

On an inverted crucible lid place 2 drops of the solution; add 8 or 10 drops of alcoholic tumeric soln.; and evaporate to dryness on the steam bath.

RED-BROWN SPOT turning BLUISH-BLACK

on adding 1*N* NaOH shows $BO_3^{\equiv}$ (or $B_4O_7^{=}$) present (see Note 1).

To 2 or 3 drops of the solution add 1 drop of Cu^{++} test solution; then add 2 drops of 6*N* NaOH.

Stir, then heat to boiling.

YELLOW or REDDISH PPT.

indicates $AsO_3^{\equiv}$ (see Note 2).

Pass H_2S into the remainder of the solution until precipitation is complete. Filter.

Precipitate. $BaCrO_4$.

YELLOW PPT.

indicates $CrO_4^{=}$.

To the precipitate add 5 or 6 drops of 1*N* HNO_3, stir, and warm for 1 or 2 min. Add 1 drop of K_2SO_4 soln., stir, and filter.

To 1 drop of the filtrate add 1 drop of 2*N* $NH_4C_2H_3O_2$ and 2 drops of 5% $AgNO_3$, and stir.

PURPLISH-BROWN PPT.

confirms $CrO_4^{=}$.

To the remainder of the filtrate in a 75-mm. test tube add a 1-cm. layer of diethyl ether and 1 drop of 3% H_2O_2. Shake quickly and observe *at once*.

BLUE ETHER LAYER

confirms $CrO_4^{=}$.

Filtrate. Add 2 or 3 small crystals of NH_4I, and heat almost to boiling. Pass in H_2S until precipitation is complete. Filter (see Note 5).

Precipitate.

BRIGHT YELLOW PPT.

of As_2S_3 confirms $AsO_3^{\equiv}$ present (see Notes 3 and 4).

Filtrate. Evaporate to dryness; add 5 or 6 drops of conc. HNO_3; and evaporate again to dryness. Dissolve the residue in 10 or 15 drops of 6*N* HNO_3, warming and stirring. Divide the solution into two equal portions.

Precipitate.

LIGHT YELLOW PPT.

shows $AsO_4^{\equiv}$ present (see Note 4).

To one portion, add half its volume of ammonium molybdate reagent; stir; and let stand on the steam bath 10 or 15 min.

FINE CRYSTALLINE YELLOW PPT.

indicates $PO_4^{\equiv}$ (see Note 6).

To the second portion add conc. NH_4OH until it is basic, then add 3 or 4 drops of $MgCl_2$ soln. Place on the steam bath 10 to 15 min., stirring to overcome supersaturation.

FINE CRYSTALLINE WHITE PPT.

confirms $PO_4^{\equiv}$ (see Note 7)

Anion Group IIIB Analysis

Divide the precipitate into two equal parts, and use these portions to test for sulfate and silicate, respectively. Use the *original unknown* to test for fluorides (see Note 8).

Sulfates. To one portion of the precipitate add an equal volume of finely powdered wood charcoal and twice its volume of powdered Na_2CO_3. Mix thoroughly; then add 1 or 2 drops of water to make a paste. Transfer this paste to a small depression scraped in a *clean* charcoal block, then with the *reducing* flame from a blowpipe heat the mixture *as strongly as possible* for 3 or 4 min. Let cool; then transfer half the mixture to a freshly polished silver coin, and add 1 drop water. Set aside 10 or 15 min in an H_2S-free portion of the room. Finally, wash and examine the coin.

YELLOWISH or BROWN STAIN

on the coin indicates $SO_4^=$ (Note 9).

Confirm by dissolving the remainder of the heated mixture in 10 drops of water, filtering, and treating the filtrate with $Pb(C_2H_3O_2)_2$ soln and $HC_2H_3O_2$ to get a brown or black precipitate of PbS.

Silicates. Prepare a bead of microcosmic salt, $NaNH_4HPO_4$, in a loop of platinum wire, using the procedure described in Cation Group III for the preparation of borax beads. Heat the bead until it is a transparent glass; then touch the hot bead to a little of the second portion of precipitate. Heat strongly, cool; and examine the bead; then heat again; and again let the bead cool, and examine it.

PERMANENT TURBIDITY or SKELETON-LIKE STRUCTURE

in the bead indicates $SiO_3^=$ present (see Note 10).

A confirmation test may be performed as follows: Place 8 or 10 drops of the original unknown solution in a clean lead dish and evaporate to dryness on the water bath. (If the unknown is solid, use a volume the size of a match head.) Prepare a loop in a platinum wire; and inserting the glass handle attached to the wire through a cork, mount the wire on a ring stand. Place a drop of distilled water in the loop of the wire; then adjust the loop so it is about 5 mm. above the material in the lead dish on the steam bath. Add a little Na_2F_2 and 2 or 3 drops of conc H_2SO_4 to the material in the dish; stir; and let stand 10 or 15 minutes, occasionally examining the water droplet very carefully.

TURBIDITY

in the water droplet confirms silicate or SiO_2 (Note 11).

Confirm by transferring the droplet to a *paraffin-coated* slide, adding 1 drop of conc HNO_3 and 1 drop of ammonium molybdate soln. Let stand 2 or 3 min., then add 1 drop of benzidine soln.

BLUE COLORATION

confirms SiO_2 or silicates.

Fluorides. In a lead dish place 8 or 10 drops of the original unknown solution (see Note 8). (If the unknown is a solid, use a volume the size of a match head.) Heat on the steam bath until *all water* is removed. In the meantime, warm a piece of a glass slide by holding it high over a flame, and rub it with paraffin until a thin but uniform coating of wax covers one side of the glass. Let the slide cool; then using a knife tip or file tip scratch a small design through the wax. *Be sure to expose the glass* under the lines of the design, but *do not scratch* the glass itself. When all is ready, let the lead dish cool; then add just enough conc. H_2SO_4 to moisten the solid sample. Mix with a matchstick, then place the glass, design side down, firmly over the lead dish Set aside *overnight* (see Note 12). Finally, scrape and wipe off the paraffin, and examine the glass.

ETCHED DESIGN

on the glass shows fluorides present.

Notes

1. An excellent check for the presence of borates may be made on this same solution. To do this, place 3 or 4 drops of the *cold* unknown solution in a crucible, add an equal volume of saturated $KHSO_4$ or $NaHSO_4$ solution and 10 or 15 drops of methyl alcohol. Ignite the mixture and note the color of the flame. A pale greenish coloration in the edges of the flame indicates borates.

It should be remembered, however, that compounds of copper and of barium also give a green coloration to a flame, consequently, the test is not useful in the presence of these metals.

2. The reactions occurring here between the Cu^{++}, the OH^-, and the $AsO_3^{\equiv}$ are as illustrated by the following:

$$Cu^{++} + 2(OH^-) \rightarrow Cu(OH)_2$$
$$Cu(OH)_2 + AsO_3^{\equiv} \rightarrow Cu_2O + AsO_4 + H_2O$$

3. As the precipitation of $AsO_3^{\equiv}$ is incomplete at the beginning of Group III, if $AsO_3^{\equiv}$ seems absent, it should be checked in Group IV.

4. The precipitate obtained here may be checked for *arsenic* as further confirmation if desired. To do this, use the same procedure as was described in Cation Group II*B*, dissolving the precipitate in NH_4OH and H_2O_2 and applying the magnesia mixture and the molybdate tests.

5. The function of the NH_4I here is as in Cation Group II, to reduce any $AsO_4^{\equiv}$ to $AsO_3^{\equiv}$. A full discussion of this is given in a footnote on page 222 and in the discussion on page 215.

6. A dirty white precipitate of molybdic acid sometimes forms here instead of the yellow precipitate. If this happens, two things may be assumed: (*a*) The HNO_3 concentration is lower than it should be, and (*b*) phosphate is probably absent.

As $AsO_4^{\equiv}$ gives the same kind of precipitate as does $PO_4^{\equiv}$, it is essential that all $AsO_4^{\equiv}$ have been removed by H_2S in the preceding test.

7 If the precipitate obtained with the $MgCl_2$ is not fine and gramy, add several drops of NH_4Cl to the mixture, stir, and let stand If a gramy precipitate *remains*, $PO_4^{\equiv}$ is present; but if all the precipitate dissolves, it probably was $Mg(OH)_2$ and $PO_4^{\equiv}$ is absent.

8 Even if no precipitate is formed in this subgroup, fluoride may be present The precipitation of fluorides in Group III is often incomplete, expecially in the presence of ammonium salts or in the absence of sulfates; consequently, since the other ions will not interfere, the fluoride test should be performed on the original unknown.

9 The silver coin test is really a test for the presence of *sulfur*, as the test may be obtained from most sulfur compounds. Used as described and at this point in the procedure, it constitutes a test for $SO_4^{=}$ merely because other sulfur compounds are eliminated.

10 It must be remembered that if the original unknown were a solid that was treated with Na_2CO_3, the Na_2CO_3 usually will have dissolved small quantities of glass from the apparatus Also, the NaOH used earlier usually contains silicates from its action on the glass of the reagent bottle. Only definite tests should be accepted, therefore, as indicating the presence of $SiO_3^{=}$ in the original unknown.

11. The water turbidity test for silicates and silicon dioxide depends upon the following reactions:

$$SiO_2 + 2H_2F_2 \rightarrow SiF_4(\uparrow) + 2H_2O$$
$$SiF_4 + 4H_2O \rightarrow H_4SiO_4(\downarrow) + 2H_2F_2$$

The turbidity is caused by the insoluble gelatinous H_4SiO_4.

The drop of water must be watched carefully, as the precipitate may disappear if too much H_2F_2 vaporizes and dissolves in the water.

12 If a large amount of fluoride is present in the unknown, the test may be obtained in a few minutes. It is safest, however, to let the test proceed overnight.

ANION GROUP IV ANALYSIS

Though the filtrate from the Group III precipitation may be used to test for ClO_3^- and for $AsO_3^{\equiv}$ (see Note 1), it is obvious that since acetic and nitric acids were used earlier in the separation, the tests for $C_2H_3O_2^-$ and NO_3^- must be performed on an especially prepared solution of the original unknown. Owing to the fact that MnO_4^- is usually decomposed during the group separations, it is best identified by tests applied to the original unknown.

Arsenites. Apply the two tests described for $AsO_3^{\equiv}$ in Anion Group III*A* to the filtrate from Anion Group III.

Chlorate. To 3 drops of the filtrate from Anion Group III add 2 drops of $4N$ HNO_3, and then add 5% $AgNO_3$ until precipitation of chloride is complete and a slight excess of $AgNO_3$ remains. Filter, discarding the precipitate. To the filtrate add 2 or 3 drops of $NaHSO_3$ soln., and warm.

WHITE PRECIPITATE

of AgCl indicates ClO_3^- (Note 2).

If MnO_4^- is absent, test as follows: To 2 or 3 drops of filtrate add 1 drop of $6N$ H_2SO_4 and a mixture of 1 drop of *fresh* starch soln. and 1 drop of *colorless* $1N$ KI soln. Stir the mixture.

DARK BLUE COLOR

appearing *within 5 sec.* confirms ClO_3^- present (Note 3)

Nitrate and Acetate. If NO_2^- is absent (see Note 4), make 3 drops of the original unknown solution strongly basic with NaOH and heat in a gas evolution tube (with the top removed) until tests with red litmus paper show the vapor to be free of NH_3. Wipe any moisture from the upper inside of the test tube using a cotton swab, and warm the upper part to be sure that no NH_3 is retained. To the mixture of NaOH and NH_3-free unknown add two or three granules of aluminum or a small pinch of zinc dust; then assemble the apparatus, putting a piece of moist red litmus in the upper tube. Heat 5 or 10 min. on the steam bath, observing the paper occasionally.

BLUE COLOR

(see Note 5) *spreading upward* on the litmus paper shows NO_3^- present.

To confirm the presence of nitrates and to test for acetates, make about 6 drops of the original unknown solution slightly acid with dil H_2SO_4, then add sat. Ag_2SO_4 soln. until precipitation is complete (see Note 6). Filter, discarding the precipitate. To the filtrate add $1N$ NaOH until it is *faintly basic;* then add $BaCl_2$-$CaCl_2$ reagent until precipitation is again complete. Filter once more; then add K_2SO_4 soln. to precipitate the excess Ba^{++}, and filter. Evaporate the filtrate to a volume of about 10 drops; filter if necessary; and use this filtrate as the "prepared solution" in the following tests.

To 2 drops of the prepared solution add dil. HCl until the solution is very slightly acid; then add 3 or 4 drops of freshly prepared sat. $FeSO_4$ soln., and stir. Incline the tube at an angle of 45° with the horizontal, and allow conc. H_2SO_4 to flow from the tip of a medicine dropper down the side of the test tube in such a way as to cause it to form a layer of acid under the aqueous layer. Let stand 2 or 3 min., observing occasionally.

BROWN or REDDISH RING

at the interface between the liquids confirms NO_3^-.

In the absence of NO_2^-, ClO_3^-, *and other oxidizing agents*, Lunge's test for nitrates may be used on some of the prepared solution. To perform this, place 1 drop of the solution on a spot plate and beside it place 1 drop of diphenylamine reagent. Draw the drops into contact by means of a stirring rod.

DARK BLUE COLORATION

at the point contact of the two liquids confirms NO_3^-. Note that this is a very sensitive test for NO_3^- but is obtained with almost any good *oxidizing agent.*

To half of the remaining prepared solution in a crucible add a volume of arsenous oxide, As_2O_3, half the size of a small match head. Heat gently with a micro flame to evaporate the liquid; then heat more strongly. Note *cautiously* the odor of any fumes.

GARLIC-LIKE ODOR

of the very poisonous substance, cacodyl oxide, indicates $C_2H_3O_2^-$ present. (NOTE: Several other organic compounds not considered here will give the same test.)

Permanganate. If the original unknown is colorless, MnO_4^- is absent, as this is very intensely colored. If the unknown is purple in color, test as follows:

To 2 or 3 drops of the *original* unknown add H_2SO_4 until it is definitely acid; then add H_2O_2, drop by drop.

RAPID DISAPPEARANCE of VIOLET COLOR of MnO_4^-

accompanied (in high concentrations of MnO_4^-) with evolution of O_2 shows MnO_4^- present. This should be checked against the cation analysis which should show the presence of manganese if MnO_4^- is present.

NOTES

1. Owing to incomplete precipitation of $AsO_3^=$ in Anion Group III, small concentrations of this ion may be missed in that group. In absence of positive tests for $AsO_3^=$ in Anion Group III, therefore, run the identification tests described there, using this solution.

2. This test for ClO_3^- depends upon the following reactions:

$$ClO_3^- + 3SO_3^= \rightarrow Cl^- + 3SO_4^=$$
$$Cl^- + Ag^+ \rightarrow AgCl$$

3. It will be recalled that the reaction of starch-KI to form a blue solution constitutes a test for *oxidizing agents in general.* It is only when other oxidizing agents are absent that a positive test here is indicative of ClO_3^-. The test must be definite and must be used only as a confirmation test, as sometimes weak tests are obtained by the action of excessive quantities of NO_3^- from the HNO_3 used earlier.

If the solution turns brown instead of blue, add a few drops of CCl_4 and shake the mixture. A violet coloration in the CCl_4 is due to free iodine, and such a result constitutes a positive test.

4. If NO_2^- is present, the tests described here for NO_3^- are undependable, as NO_2^- is readily converted to NO_3^- on standing or on being heated:

$$2NO_2^- \rightarrow NO_3^- + NO$$

Any tests made for NO_3^- in the presence of NO_2^- must be made on the original unknown, with as little manipulation as possible. For such tests see more comprehensive textbooks.

5. If the litmus paper shows small blue spots, the coloration is due to spray of the alkaline solution carried upward with the vapor and hydrogen. In such cases the test must be repeated.

6. The Ag_2SO_4 is used to remove any Group II anions. If these anions (with the exception of Cl^-) are absent, this step may be omitted.

For similar reasons, the $BaCl_2$–$CaCl_2$ reagent need not be used if $CrO_4^=$ (in Anion Group III) is absent.

APPENDIX

TABLE VII.—OXIDATION-REDUCTION POTENTIALS*

Electrode Reaction	E.m.f., Volt
$Li^+ + \epsilon \rightarrow Li$	−3.02
$Cs^+ + \epsilon \rightarrow Cs$	−3.02
$Rb^+ + \epsilon \rightarrow Rb$	−2.99
$K^+ + \epsilon \rightarrow K$	−2.922
$Ba^{++} + 2\epsilon \rightarrow Ba$	−2.90
$Sr^{++} + 2\epsilon \rightarrow Sr$	−2.89
$Ca^{++} + 2\epsilon \rightarrow Ca$	−2.87
$Na^+ + \epsilon \rightarrow Na$	−2.712
$Mg^{++} + 2\epsilon \rightarrow Mg$	−2.34
$\frac{1}{2}H_2 + \epsilon \rightarrow H^-$	−2.33
$Ti^{++} + 2\epsilon \rightarrow Ti$	−1.75
$Al^{+++} + 3\epsilon \rightarrow Al$	−1.67
$Mn^{++} + 2\epsilon \rightarrow Mn$	−1.05
$Zn^{++} + 2\epsilon \rightarrow Zn$	−0.7620
$Cr^{+++} + 3\epsilon \rightarrow Cr$	−0.71
$H_3PO_3 + 2H^+ + 2\epsilon \rightarrow H_2O + H_3PO_2$	−0.59
$As + 3H^+ + 3\epsilon \rightarrow AsH_3$	−0.54
$Fe^{++} + 2\epsilon \rightarrow Fe$	−0.446
$2H^+(10^{-7}M) + 2\epsilon \rightarrow H_2$	−0.414
$Cr^{+++} + \epsilon \rightarrow Cr^{++}$	−0.41
$Cd^{++} + 2\epsilon \rightarrow Cd$	−0.40
$Co^{++} + 2\epsilon \rightarrow Co$	−0.277
$PbCl_2 + 2\epsilon \rightarrow 2Cl^- + Pb$	−0.268
$Ni^{++} + 2\epsilon \rightarrow Ni$	−0.250
$H_3PO_4 + 2H^+ + 2\epsilon \rightarrow H_2O + H_3PO_3$	−0.20
$CuI + \epsilon \rightarrow Cu + I^-$	−0.187
$AgI + \epsilon \rightarrow Ag + I^-$	−0.151
$Sn^{++} + 2\epsilon \rightarrow Sn$	−0.136
$Pb^{++} + 2\epsilon \rightarrow Pb$	−0.126
$Hg_2I_2 + 2\epsilon \rightarrow 2I^- + 2Hg$	−0.0405
$HgI_4^- + 2\epsilon \rightarrow 4I^- + Hg$	−0.04
$Fe^{+++} + 3\epsilon \rightarrow Fe$	−0.036
$2H^+ + 2\epsilon \rightarrow H_2$	0.000
$CuBr + \epsilon \rightarrow Br^- + Cu$	+0.033
$AgBr + \epsilon \rightarrow Br^- + Ag$	+0.073
$CuCl + \epsilon \rightarrow Cl^- + Cu$	+0.124

*Adapted from Latimer and Hildebrand "Reference Book of Inorganic Chemistry."

TABLE VII.—OXIDATION-REDUCTION POTENTIALS.*—(*Continued*)

Electrode Reaction	E.m.f., Volts
$S + 2H^+ + 2\epsilon \rightarrow H_2S$	+0.141
$Sn^{++++} + 2\epsilon \rightarrow Sn^{++}$	+0.15
$Cu^{++} + \epsilon \rightarrow Cu^+$	+0.167
$CuCl_2^- + \epsilon \rightarrow 2Cl^- + Cu$	+0.19
$SO_4^{--} + 4H^+ + 2\epsilon \rightarrow H_2O + H_2SO_3$	+0.20
$SbO^+ + 2H^+ + 3\epsilon \rightarrow Sb + H_2O$	+0.212
$AgCl + \epsilon \rightarrow Cl^- + Ag$	+0.2222
$Hg_2Cl_2 + 2\epsilon \rightarrow 2Cl^- + 2Hg$	+0.2676
$BiO^+ + 2H^+ + 3\epsilon \rightarrow H_2O + Bi$	+0.32
$Cu^{++} + 2\epsilon \rightarrow Cu$	+0.344
$Fe(CN)_6^{---} + \epsilon \rightarrow Fe(CN)_6^{----}$	+0.36
$H_2SO_3 + 4H^+ + 4\epsilon \rightarrow 3H_2O + S$	+0.45
$Cu^+ + \epsilon \rightarrow Cu$	+0.522
$I_2 + 2\epsilon \rightarrow 2I^-$	+0.5345
$I_3^- + 2\epsilon \rightarrow 3I^-$	+0.5355
$H_3AsO_4 + 2H^+ + 2\epsilon \rightarrow HAsO_2 + 2H_2O$	+0.559
$Cu^{++} + Cl^- + \epsilon \rightarrow CuCl$	+0.566
$Sb_2O_5 + 6H^+ + 4\epsilon \rightarrow 3H_2O + 2SbO^+$	+0.64
$Cu^{++} + Br^- + \epsilon \rightarrow CuBr$	+0.657
$O_2 + 2H^+ + 2\epsilon \rightarrow H_2O_2$	+0.682
$PtCl_6^{--} + 2\epsilon \rightarrow 2Cl^- + PtCl_4^{--}$	+0.72
$PtCl_4^{--} + 2\epsilon \rightarrow 4Cl^- + Pt$	+0.73
$H_2SeO_3 + 4H^+ + 4\epsilon \rightarrow Se + 3H_2O$	+0.740
$Fe^{+++} + \epsilon \rightarrow Fe^{++}$	+0.771
$Hg_2^{++} + 2\epsilon \rightarrow 2Hg$	+0.7986
$Ag^+ + \epsilon \rightarrow Ag$	+0.797
$2NO_3^- + 4H^+ + 2\epsilon \rightarrow 2H_2O + N_2O_4$	+0.81
$O_2 + 4H^+(10^{-7}M) + 4\epsilon \rightarrow 2H_2O$	+0.815
$Pd^{++} + 2\epsilon \rightarrow Pd$	+0.83
$Hg^{++} + 2\epsilon \rightarrow Hg$	+0.854
$2Hg^{++} + 2\epsilon \rightarrow Hg_2^{++}$	+0.910
$NO_3^- + 3H^+ + 2\epsilon \rightarrow HNO_2 + H_2O$	+0.94
$NO_3^- + 4H^+ + 3\epsilon \rightarrow NO + 2H_2O$	+0.96
$HNO_2 + H^+ + \epsilon \rightarrow NO + H_2O$	+0.99
$AuCl_4^- + 3\epsilon \rightarrow 4Cl^- + Au$	+1.00
$IO_3^- + 6H^+ + 6\epsilon \rightarrow 3H_2O + I^-$	+1.085
$Br_2(aq) + 2\epsilon \rightarrow 2Br^-$	+1.087
$SeO_4^{--} + 4H^+ + 2\epsilon \rightarrow H_2O + H_2SeO_3$	+1.15
$IO_3^- + 6H^+ + 5\epsilon \rightarrow \frac{1}{2}I_2 + 3H_2O$	+1.195
$Pt^{++} + 2\epsilon \rightarrow Pt$	about +1.2
$O_2 + 4H^+ + 4\epsilon \rightarrow 2H_2O$	+1.229
$MnO_2 + 4H^+ + 2\epsilon \rightarrow 2H_2O + Mn^{++}$	+1.28
$8H^+ + ClO_4^- + 7\epsilon \rightarrow \frac{1}{2}Cl_2 + 4H_2O$	+1.34

* Adapted from Latimer and Hildebrand, "Reference Book of Inorganic Chemistry."

TABLE VII —OXIDATION-REDUCTION POTENTIALS.*—(*Continued*)

Electrode Reaction	E.m.f., Volts
$\frac{1}{2}Cl_2 + \epsilon \rightarrow Cl^-$	+1.358
$Cr_2O_7^{--} + 14H^+ + 6\epsilon \rightarrow 7H_2O + 2Cr^{+++}$	+1.36
$Au^{+++} + 3\epsilon \rightarrow Au$	+1.42
$ClO_3^- + 6H^+ + 6\epsilon \rightarrow 3H_2O + Cl^-$	+1.45
$PbO_2 + 4H^+ + 2\epsilon \rightarrow 2H_2O + Pb^{++}$	+1.456
$6H^+ + ClO_3^- + 5\epsilon \rightarrow \frac{1}{2}Cl_2 + 3H_2O$	+1.47
$Mn^{+++} + \epsilon \rightarrow Mn^{++}$	+1.51
$BrO_3^- + 6H^+ + 5\epsilon \rightarrow \frac{1}{2}Br_2 + 3H_2O$	+1.52
$MnO_4^- + 8H^+ + 5\epsilon \rightarrow 4H_2O + Mn^{++}$	+1.52
$Bi_2O_4 + 4H^+ + 2\epsilon \rightarrow 2H_2O + 2BiO^+$	about +1.59
$HBrO + H^+ + \epsilon \rightarrow \frac{1}{2}Br_2 + H_2O$	+1.59
$Ce^{++++} + \epsilon \rightarrow Ce^{+++}$	+1.61
$H^+ + HClO + \epsilon \rightarrow \frac{1}{2}Cl_2 + H_2O$	+1.63
$MnO_4^- + 4H^+ + 3\epsilon \rightarrow 2H_2O + MnO_2$	+1.67
$Au^+ + \epsilon \rightarrow Au$	+1.68
$PbO_2 + SO_4^{--} + 4H^+ + 2\epsilon \rightarrow 2H_2O + PbSO_4$	+1.685
$H_2O_2 + 2H^+ + 2\epsilon \rightarrow 2H_2O$	+1.77
$Co^{+++} + \epsilon \rightarrow Co^{++}$	+1.84
$S_2O_8^{--} + 2\epsilon \rightarrow 2SO_4^{--}$	+2.05
$O_3 + 2H^+ + 2\epsilon \rightarrow O_2 + H_2O$	+2.07
$F_2 + 2\epsilon \rightarrow 2F^-$	+2.85
$F_2 + 2H^+ + 2\epsilon \rightarrow 2HF$	+3.03

* Adapted from Latimer and Hildebrand, "Reference Book of Inorganic Chemistry."

TABLE VIII.—OXIDATION-REDUCTION POTENTIALS—CLASSIFIED BY KEY ELEMENTS

Key element	Electrode reaction	E.M.F., volts
Aluminum	$Al^{+++} + 3\epsilon \rightarrow Al$	−1 67
Antimony	$SbO^+ + 2H^+ + 3\epsilon \rightarrow Sb + H_2O$	+0 212
	$Sb_2O_4 + 6H^+ + 4\epsilon \rightarrow 2SbO^+ + 3H_2O$	+0 64
Arsenic	$As + 3H^+ + 3\epsilon \rightarrow AsH_3$	−0 54
	$H_3AsO_4 + 2H^+ + 2\epsilon \rightarrow HAsO_2 + 2H_2O$	+0 559
Barium	$Ba^{++} + 2\epsilon \rightarrow Ba$	−2 90
Bismuth	$BiO^+ + 2H^+ + 3\epsilon \rightarrow Bi + H_2O$	+0 32
	$Bi_2O_4 + 4H^+ + 2\epsilon \rightarrow 2BiO^+ + 2H_2O$	+1 59
Bromine	Br_2 (aq) $+ 2\epsilon \rightarrow 2Br^-$	+1 087
	$BrO_3^- + 6H^+ + 5\epsilon \rightarrow \frac{1}{2}Br_2 + 3H_2O$	+1 52
	$HBrO + H^+ + \epsilon \rightarrow \frac{1}{2}Br_2 + H_2O$	+1 59
Cadmium	$Cd^{++} + 2\epsilon \rightarrow Cd$	−0 40
Calcium	$Ca^{++} + 2\epsilon \rightarrow Ca$	−2.87
Cerium	$Ce^{++++} + \epsilon \rightarrow Ce^{+++}$	+1 61
Cesium	$Cs^+ + \epsilon \rightarrow Cs$	−3 02
Chlorine	$ClO_4^- + 8H^+ + 7\epsilon \rightarrow \frac{1}{2}Cl_2 + 4H_2O$	+1 34
	$\frac{1}{2}Cl_2 + \epsilon \rightarrow Cl^-$	+1 358
	$ClO_3^- + 6H^+ + 6\epsilon \rightarrow Cl^- + 3H_2O$	+1 45
	$ClO_3^- + 6H^+ + 5\epsilon \rightarrow \frac{1}{2}Cl_2 + 3H_2O$	+1 47
	$HClO + H^+ + \epsilon \rightarrow \frac{1}{2}Cl_2 + H_2O$	+1 63
Chromium	$Cr^{+++} + 3\epsilon \rightarrow Cr$	−0 71
	$Cr^{+++} + \epsilon \rightarrow Cr^{++}$	−0 41
	$Cr_2O_7^{=} + 14H^+ + 6\epsilon \rightarrow 2Cr^{+++} + 7H_2O$	+1 36
Cobalt	$Co^{++} + 2\epsilon \rightarrow Co$	−0 277
	$Co^{+++} + \epsilon \rightarrow Co^{++}$	+1 84
Copper	$CuI + \epsilon \rightarrow Cu + Br^-$	+0 033
	$CuCl + \epsilon \rightarrow Cu + Cl^-$	+0 124
	$Cu^{++} + \epsilon \rightarrow Cu^+$	+0 167
	$CuCl_2^- + \epsilon \rightarrow Cu + 2Cl^-$	+0 19
	$Cu^{++} + 2\epsilon \rightarrow Cu$	+0 344
	$Cu^+ + \epsilon \rightarrow Cu$	+0 522
	$Cu^{++} + Cl^- + \epsilon \rightarrow CuCl$	+0 566
	$Cu^{++} + Br^- + \epsilon \rightarrow CuBr$	+0 657
Fluorine	$F_2 + 2\epsilon \rightarrow 2F^-$	+2 85
	$F_2 + H_2 + 2\epsilon \rightarrow 2HF$	+3 03
Gold	$AuCl_4^- + 3\epsilon \rightarrow Au + 4Cl^-$	+1 00
	$Au^{+++} + 3\epsilon \rightarrow Au$	+1 42
	$Au^+ + \epsilon \rightarrow Au$	+1 68
Hydrogen	$\frac{1}{2}H_2 + \epsilon \rightarrow H^-$	−2 33
	$2H^+(10^{-7}) + 2\epsilon \rightarrow H_2$	−0 414
	$H^+ + \epsilon \rightarrow \frac{1}{2}H_2$	0 000

TABLE VIII.—OXIDATION-REDUCTION POTENTIALS—CLASSIFIED BY KEY ELEMENTS —(*Continued*)

Key element	Electrode reaction	E.M.F., volts
Iodine	$I_2 + 2\epsilon \rightarrow 2I^-$	+0.534
	$I_3^- + 2\epsilon \rightarrow 3I^-$	+0.5355
	$IO_3^- + 6H^+ + 6\epsilon \rightarrow I^- + 3H_2O$	+1.085
	$IO_3^- + 6H^+ + 5\epsilon \rightarrow \frac{1}{2}I_2 + 3H_2O$	+1.195
Iron	$Fe^{++} + 2\epsilon \rightarrow Fe$	−0.44
	$Fe^{+++} + 3\epsilon \rightarrow Fe$	−0.036
	$Fe(CN)_6^{---} + \epsilon \rightarrow Fe(CN)_6^{--}$	+0.36
	$Fe^{+++} + \epsilon \rightarrow Fe^{++}$	+0.771
Lead	$PbCl_2 + 2\epsilon \rightarrow Pb + 2Cl^-$	−0.268
	$Pb^{++} + 2\epsilon \rightarrow Pb$	−0.126
	$PbO_2 + 4H^+ + 2\epsilon \rightarrow Pb^{++} + 2H_2O$	+1.456
	$PbO_2 + SO_4^{--} + 4H^+ + 2\epsilon \rightarrow PbSO_4 + 2H_2O$	+1.685
Lithium	$Li^+ + \epsilon \rightarrow Li$	−3.02
Magnesium	$Mg^{++} + 2\epsilon \rightarrow Mg$	−2.34
Manganese	$Mn^{++} + 2\epsilon \rightarrow Mn$	−1.05
	$MnO_2 + 4H^+ + 2\epsilon \rightarrow Mn^{++} + 2H_2O$	+1.28
	$Mn^{+++} + \epsilon \rightarrow Mn^{++}$	+1.51
	$MnO_4^- + 8H^+ + 5\epsilon \rightarrow Mn^{++} + 4H_2O$	+1.52
	$MnO_4^- + 4H^+ + 3\epsilon \rightarrow MnO_2 + 2H_2O$	+1.67
Mercury	$Hg_2I_2 + 2\epsilon \rightarrow 2Hg + 2I^-$	−0.0405
	$HgI_4^{--} + 2\epsilon \rightarrow Hg + 4I^-$	−0.04
	$Hg_2Cl_2 + 2\epsilon \rightarrow 2Hg + 2Cl^-$	+0.267
	$Hg_2^{++} + 2\epsilon \rightarrow 2Hg$	+0.7986
	$Hg^{++} + 2\epsilon \rightarrow Hg$	+0.854
	$2Hg^{++} + 2\epsilon \rightarrow Hg_2^{++}$	+0.910
Nickel	$Ni^{++} + 2\epsilon \rightarrow Ni$	−0.250
Nitrogen	$2NO_3^- + 4H^+ + 2\epsilon \rightarrow N_2O_4 + 2H_2O$	+0.81
	$NO_3^- + 3H^+ + 2\epsilon \rightarrow HNO_2 + H_2O$	+0.94
	$NO_3^- + 4H^+ + \epsilon \rightarrow NO + 2H_2O$	+0.96
	$HNO_2 + H^+ + \epsilon \rightarrow NO + H_2O$	+0.99
Oxygen	$O_2 + 2H^+ + 2\epsilon \rightarrow H_2O_2$	+0.682
	$O_2 + 4H^+ (10^{-7}M) + 4\epsilon \rightarrow 2H_2O$	+0.815
	$O_2 + 4H^+ + 4\epsilon \rightarrow 2H_2O$	+1.229
	$H_2O_2 + 2H^+ + 2\epsilon \rightarrow 2H_2O$	+1.77
	$O_3 + 2H^+ + 2\epsilon \rightarrow H_2O + O_2$	+2.07
Palladium	$Pd^{++} + 2\epsilon \rightarrow Pd$	+0.83
Phosphorus	$H_3PO_3 + 2H^+ + 2\epsilon \rightarrow H_3PO_2 + H_2O$	−0.59
	$H_3PO_4 + 2H^+ + 2\epsilon \rightarrow H_3PO_3 + H_2O$	−0.20
Platinum	$PtCl_6^{--} + 2\epsilon \rightarrow PtCl_4^{--} + 2Cl^-$	+0.72
	$PtCl_4^{--} + 2\epsilon \rightarrow Pt + 4Cl^-$	+0.73
	$Pt^{++} + 2\epsilon \rightarrow Pt$	+1.2

TABLE VIII.—OXIDATION-REDUCTION POTENTIALS—CLASSIFIED BY KEY ELEMENTS.—(*Continued*)

Key element	Electrode reaction	E.M.F., volts
Potassium	$K^+ + \epsilon \rightarrow K$	−2.92
Rubidium	$Rb^+ + \epsilon \rightarrow Rb$	−2.99
Selenium	$H_2SeO_3 + 4H^+ + 4\epsilon \rightarrow Se + 3H_2O$	+0.74
	$SeO_4^{--} + 4H^+ + 2\epsilon \rightarrow H_2SeO_3 + H_2O$	+1.15
Silver	$Ag^+ + \epsilon \rightarrow Ag$	+0.797
	$AgI + \epsilon \rightarrow Ag + I^-$	−0.151
	$AgBr + \epsilon \rightarrow Ag + Br^-$	+0.073
	$AgCl + \epsilon \rightarrow Ag + Cl^-$	+0.222
Sodium	$Na^+ + \epsilon \rightarrow Na$	−2.712
Strontium	$Sr^{++} + 2\epsilon \rightarrow Sr$	−2.89
Sulfur	$S + 2H^+ + 2\epsilon \rightarrow H_2S$	+0.141
	$SO_4^{--} + 4H^+ + 2\epsilon \rightarrow H_2SO_3 + H_2O$	+0.20
	$H_2SO_3 + 4H^+ + 4\epsilon \rightarrow S + 3H_2O$	+0.45
	$S_2O_8^{--} + 2\epsilon \rightarrow 2SO_4^{--}$	+2.05
Zinc	$Zn^{++} + 2\epsilon \rightarrow Zn$	−0.762

LOGARITHMS

No.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6386	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

LOGARITHMS.—(*Continued*)

No.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7992	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8219	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	1	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	1	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9594	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

List of Apparatus

Individual

2 Beakers, one 250 ml. and one 400 ml.
2 Crucibles.
1 Crucible lid.
1 Cylinder, graduated, 10 ml.
1 Dish, lead (about 2 cm. diameter and 1 cm. deep)
Filter paper (2 doz. sheets, acid-treated).
1 File, triangular.
1 Flask, Erlenmeyer, 25 ml. or 50 ml.
1 Flask, Florence 500 ml. (to be made into a wash bottle See Fig. 25)
6 Glass rods, 2 mm. by 15 cm long.
Litmus paper, blue and red.
12 Medicine droppers.
6 Microscope slides.
1 Microbeaker, 5 ml.
2 Rubber stoppers, one No. 2 (one-hole) and one No. 5 (two-hole).
1 Sponge.
1 Spot plate, Pyrex, nine-depression.
1 Steam bath (see Fig. 21).
6 Test tubes, Pyrex, 100 by 13 mm.
18 Test tubes, Pyrex 75 by 10 mm.
1 Test tube, Pyrex, 150 by 18 mm.
1 Test-tube brush.
1 Test-tube holder.
1 Test-tube rack (with ½-in. holes).
1 Tongs, crucible.
1 Towel.
2 Ft. tubing, glass, 6 mm. O.D.
1 Ft. tubing, rubber.
2 Watch glasses, 40 mm. diameter.
1 Wing top.
1 Wire, platinum or nichrome flame test.
1 Wire gauze.
1 Wire triangle.

General

In addition to the above, blowpipes, ring stands equipped with rings and clamps, Bunsen burners, and centrifuges (one for each 10 or 12 students) should be available. The Bunsen burner may be used as a micro burner by unscrewing the burner tube and lighting the gas at the orifice in the base.

The authors recommend the more sturdy electrically driven centrifuges with the angle-type head, which have been designed for semimicro work. Experience has shown that their greater original cost, as compared with the cheaper hand-driven types, is many times more than offset by their greater durability.

Reagent Blocks

Reagent blocks of the individual type, containing the most frequently used reagents and supplemented by the less common on a side shelf, save much running about the laboratory and decrease loss of time.

The authors have found that a reagent block* made from a wooden block 12 by 18 by 2 in. thick containing 60 holes bored to hold 3-dram vials and 24 holes to hold 1-dram vials can serve four students each period. The block is mounted on blocks in the middle of the table at a point equally convenient for each of two pairs of students. The larger vials are fitted with Barne's type dropper stoppers and are used for solutions. All vials are labeled on both sides, and the vials and their positions are numbered.

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* The block described here and the working arrangement is shown in the illustration in the article, "Advantages of Semimicro Technic in Teaching Qualitative Analysis," by Arthur, Burrows, Smith, and Adams, *J. Chem. Educ.* **18**, 385 (1941).

List of Reagents

(All chemicals are reagent grade)

SOLIDS

Aluminum, granular.
Ammonium iodide.
Ammonium persulfate.
Arsenous oxide.
Borax.
Carborundum, fine granular.
Charcoal, stick.
Copper (pellets or short wires).
Ferrous ammonium sulfate.
Hydrogen sulfide generating materials (see page 194).
Iron filings (or wire).
Lead dioxide.
Microcosmic salt.
Paraffin.
Potassium chlorate.
Sodium carbonate.
Sodium cobaltinitrite.
Sodium peroxide.
Starch-KI paper.
Zinc (granular, and dust).

LIQUIDS AND SOLUTIONS†

Acid, acetic:
  Dilute (6*N*).
  Dilute (exactly 1*N*).
Acid, hydrochloric:
  Concentrated (approximately 12*N*).
  Dilute (6*N*).
Acid, iodic (0.05*M*):
  Dissolve 1.07 g. of KIO_3 in 100 ml. of 0.05*N* H_2SO_4, or dissolve 0.88 g. of HIO_3 in 100 ml. of water.

---

† Those reagents which are starred (*) are either unstable or volatile. It is recommended that they not be put in individual student reagent blocks but instead be put in larger dropping bottles (about 2 oz.) on the side shelf. In this way the condition of the reagent is more easily checked by the instructor.

Acid, nitric:
  Concentrated (approximately 16*N*).
  Dilute (6*N*).
  Dilute (4*N*).
Acid, sulfuric
  Concentrated (approximately 36*N*).
  Dilute (6*N*).
Acid, tartaric
  Dissolve 10 g in 100 ml of water
Alcohol, ethyl (95 per cent)
Alcohol, methyl.
* Alizarin reagent:
  Dissolve 0.05 g. of alizarin S (blue) in 100 ml of 50 per cent acetone and add 2 drops of glacial acetic acid.
* Aluminon reagent:
  Dissolve 0.1 g of aluminon (the ammonium salt of aurin tricarboxylic acid) in 100 ml of water
Ammonium acetate.
  6*N* solution: Dissolve 46.2 g. in water and dilute to 100 ml.
  2.5*N* solution: Dissolve 18 g in water and dilute to 100 ml.
Ammonium carbonate reagent:
  Dissolve 15 g. of ammonium carbonate and 20 g of ammonium chloride in 100 ml. of 6*N* NH_4OH
Ammonium chloride:
  6*N* solution (approximately): Dissolve 32 g. in 90 ml. of water.
  1*N* solution. Dissolve 5.35 g. in water and dilute to 100 ml.
Ammonium hydroxide:
  Concentrated (approximately 15*N*)
  Dilute (6*N*).
Ammonium mercuric thiocyanate reagent:
  Dissolve 30 g. of ammonium thiocyanate in 100 ml of water, then add 27 g. of mercuric chloride and stir until dissolved
Ammonium molybdate reagent:
  Dissolve 4 g. of MoO_3 in 20 ml. of 6*N* NH_4OH, add 75 ml. of 6*N* HNO_3, and dilute to a volume of 100 ml.
Ammonium nitrate:
  6*N* solution: Dissolve 48 g. in water and dilute to 100 ml
* Ammonium sulfide (mono):
  Saturate 50 ml. of 6*N* NH_4OH with hydrogen sulfide, then add 50 ml. of 6*N* NH_4OH.
* Ammonium sulfide (poly):
  Prepare 100 ml. of the monosulfide as above, then add 1 g. of sulfur and shake the mixture.
Auric chloride (0.05 per cent):
  Dissolve 0.05 g. of auric chloride in 100 ml. of water.
Barium chloride–calcium chloride reagent:
  Dissolve 24 g. of $BaCl_2 \cdot 2H_2O$ and 22 g. of $CaCl_2 \cdot 6H_2O$ in 100 ml. of water.

Barium nitrate:
Dissolve 5.2 g. of $Ba(NO_3)_2$ in 100 ml. of water.

Barium nitrate–calcium nitrate reagent:
Dissolve 5.2 g. of $Ba(NO_3)_2$ and 4.52 g. of $Ca(NO_3)_2 \cdot 4H_2O$ in 100 ml. of water.

* Carbon tetrachloride.

Cupric sulfate (0.1 per cent):
Dissolve 0.1 g. of $CuSO_4 \cdot 5H_2O$ in 100 ml. of water.

Dimethylglyoxime:
Dissolve 1 g. in 100 ml. of ethyl alcohol.

* Ether, diethyl.

Ferric chloride (0.5*M*):
Dissolve 13.5 g. of $FeCl_3 \cdot 6H_2O$ in water and dilute to 100 ml.

Ferrous ammonium sulfate:
Dissolve 2 g. of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ in 80 ml. of water, add 3 ml. of 6*N* H_2SO_4 and dilute to 100 ml.

Hydrogen peroxide:
3 per cent (should be checked occasionally to be sure it has not lost too much strength).

* 8 per cent: Dilute 10 ml. of superoxol with four times its volume of water, add 10 ml. of 6*N* H_2SO_4, then titrate with standard $KMnO_4$ solution to determine exact strength of the superoxol. Dilute according to the results obtained, to make the 8 per cent solution.

* Iodine-starch-KI reagent:
Mix equal volumes of 0.1*N* KI solution and fresh starch solution. Add a solution of iodine in KI solution until the solution is deep blue. Add 1 drop of toluene or chloroform to each bottle as a preservative. Change the solution frequently.

Lead acetate (0.1*N*):
Dissolve 1.9 g. of $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ in 80 ml. of water, add 1 ml. of glacial acetic acid, and dilute to 100 ml.

Magnesium chloride:
Dissolve 10 g. of $MgCl_2 \cdot 6H_2O$ in 100 ml. of water.

Mercuric chloride:
Dissolve 2.7 g. of $HgCl_2$ in 100 ml. of water.

Nickel nitrate (0.5*N*):
Dissolve 14.5 g. of $Ni(NO_3)_2 \cdot 6H_2O$ in water and dilute to 100 ml.

p-Nitrobenzeneazoresorcinol reagent:
Dissolve 0.001 g. in 100 ml. of 0.5 per cent NaOH and filter if necessary.

α-Nitroso-β-naphthol reagent:
Dissolve 1 g. in 50 ml. of glacial acetic acid and add 50 ml. water.

Potassium chromate (1*N*):
Dissolve 9.7 g. in water and dilute to 100 ml.

Potassium cyanide (3 per cent):
Dissolve 3 g. in 100 ml. of water.

Potassium ferricyanide:
Dissolve 6 g. in 100 ml. of water.

Potassium ferrocyanide:
Dissolve 8 g. in 100 ml. of water.
Potassium iodide:
1*N* solution: Dissolve 16.6 g. in water and dilute to 100 ml.
0.1*N* solution. Dissolve 1.7 g. in water to make 100 ml.
Potassium oxalate (1*N*):
Dissolve 8.3 g. in water to make 100 ml.
Potassium permanganate:
0.1*M* solution: Dissolve 1.58 g. in water to make 100 ml.
0.5 per cent solution: Dissolve 0.5 g. in 100 ml. of water.
Potassium sulfate (1*N*):
Dissolve 6.7 g. in water to make 100 ml.
Potassium thiocyanate:
Dissolve 10 g. in 100 ml. of water.
Silver nitrate (5 per cent):
Dissolve 5 g in 100 ml. of water.
Sodium bicarbonate:
Saturated solution.
Sodium bisulfate:
Saturated solution.
Sodium bisulfite:
Dissolve 1 g. in 100 ml. of water.
Sodium carbonate:
Saturated solution.
Sodium chlorate:
Saturated solution.
Sodium chloride:
Saturated solution.
Sodium hydroxide:
6*N* solution: Dissolve 24 g. of NaOH in water to make 100 ml.
Sodium phosphate:
Dissolve 10 g. of $Na_2HPO_4 \cdot 12H_2O$ in 100 ml. of water.
Stannous chloride:
Dissolve 10 g in 50 ml. of concentrated HCl; then add an equal volume of water and two or three pieces of tin.
*** Starch solution.**
Turmeric solution:
Saturated solution in 95 per cent ethyl alcohol.
Zinc uranyl acetate reagent:
Dissolve 10 g. of uranyl acetate and 30 g. of zinc acetate in 100 ml. of 3 per cent acetic acid. Let stand overnight and filter.

RECOMMENDED ORGANIC REAGENTS

(Not included in the regular list)

Benzidine:
Dissolve 0.05 g. of the pure substance in 10 ml. of glacial acetic acid and add 90 ml. of water.

α-Benzoinoxime:
Dissolve 5 g. in 100 ml. of ethyl alcohol.
Cinchonine:
Dissolve 1 g. in 100 ml. of water, add 10 drops of HNO_3, and warm until dissolved. Cool, then add 2 g. of KI.
Diphenylamine:
Dissolve 0.4 g. in 100 ml. of 80 per cent H_2SO_4.
Diphenylthiocarbazone (dithizon):
Dissolve 0.02 g. in 100 ml. of $CHCl_3$ or CCl_4.
Rhodanine (5-*p*-dimethylaminobenzal rhodanine):
Dissolve 0.03 g. in 100 ml. of acetone.
Thiosinamine (allyl thiourea):
Use the solid.

TEST SOLUTIONS AND UNKNOWNS

In making up unknowns and test solutions, some instructors want the solution to contain a definite *weight* of the cation or the anion in a given volume. Others, wishing to emphasize the laws of chemistry rather than the practical aspects of analysis, prefer that the solutions have a standard *molarity*, as most of the calculations in theory are made using the concentrations of solutions in moles per liter.

Semimicro methods do not require any special concentrations for their use. The usual concentrations can be used in semimicroanalysis as well as they could in macroanalysis.

For the instructors convenience, however, the following table is included, giving the weights of the salts of different cations needed to make a solution of the cation for test solutions and unknowns.

It is suggested that these cation stock solutions be diluted 1:9 in actual use.

Anion test solutions should be 0.1*M*, as a rule. Anion unknowns should be made from stock solutions that are 0.5*M* with the sodium or potassium salts of the desired anions.

On an average it will be found that 50 ml. of each test solution and 50 ml. of each stock solution for making unknowns will be more than ample for 40 students, during a one-semester course.

Metal	Formula of salt	Weight of salt per 100 ml. to make	
		0.1*M*, grams	100 mg. per milliliter, grams
Aluminum	$Al(NO_3)_3 \cdot 9H_2O$	3.75	69
Antimony*	$SbCl_3$	2.28	18.7
Arsenic†	As_2O_3	0.98	13
Barium	$Ba(NO_3)_2$	2.61	19
Bismuth‡	$Bi(NO_3)_3 \cdot 5H_2O$	4.85	23.3
Cadmium	$Cd(NO_3)_2 \cdot 4H_2O$	3.08	27.5
Calcium	$Ca(NO_3)_2 \cdot 4H_2O$	2.36	59
Chromium	$Cr(NO_3)_3 \cdot 9H_2O$	4.00	77
Cobalt	$Co(NO_3)_2 \cdot 6H_2O$	2.91	49.5
Copper§	$Cu(NO_3)_2 \cdot 3H_2O$	2.41	38.3
Iron§	$Fe(NO_3)_3 \cdot 9H_2O$	4.04	72.3
	$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	3.92	70.2
Lead§	$Pb(NO_3)_2$	3.31	16
Magnesium	$Mg(NO_3)_2 \cdot 6H_2O$	2.56	106
Manganese	$Mn(NO_3)_2 \cdot 6H_2O$	2.87	52.3
Mercury (Hg^{++})§	$Hg(NO_3)_2$	3.24	15.7
Mercury (Hg_2^{++})‖	$Hg_2(NO_3)_2 \cdot 2H_2O$	2.80	13.6
Nickel	$Ni(NO_3)_2 \cdot 6H_2O$	2.90	49.6
Potassium	KNO_3	1.01	25.6
Silver	$AgNO_3$	1.69	15.8
Sodium	$NaNO_3$	0.85	37
Strontium	$Sr(NO_3)_2 \cdot 4H_2O$	2.83	32.5
Tin (Sn^{++++})†	$SnCl_4 \cdot 3H_2O$	3.14	26.4
Tin (Sn^{++})¶	$SnCl_2 \cdot 2H_2O$	2.25	19
Zinc§	$Zn(NO_3)_2 \cdot 6H_2O$	2.97	45.4

* Use 6*N* HCl as the solvent.

† Dissolve in hot 6*N* HCl.

‡ Dissolve in 3*N* HNO_3.

§ Dissolve in water, then add 1 ml. concentrated HNO_3 to each 100 ml. of solution.

‖ Dissolve in 100 ml. water and add 3 ml. concentrated HNO_3 and a small globule of metallic mercury.

¶ Dissolve in 50 ml. concentrated HCl, dilute to 100 ml., and add a little pure metallic tin.

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PERIODIC CLASSIFICATION OF THE ELEMENTS

The atomic number is given above the symbol of the element; the atomic weight below the name.

GROUP	0 (or VIII b)	I	II	III	IV	V	VI	VII	VIII (or VIII a)
Type of Formula		R_2O a / b	RO a / b	R_2O_3 a / b	RH_4 RO_2 a / b	RH_3 R_2O_5 a / b	RH_2 RO_3 a / b	RH R_2O_7 b	
Period 1		1 H Hydrogen 1.008							
Period 2	2 He Helium 4.00	3 Li Lithium 6.940	4 Be Beryllium 9.02	5 B Boron 10.82	6 C Carbon 12.010	7 N Nitrogen 14.008	8 O Oxygen 16.0000	9 F Fluorine 19.00	
Period 3	10 Ne Neon 20.183	11 Na Sodium 22.997	12 Mg Magnesium 24.32	13 Al Aluminum 26.97	14 Si Silicon 28.06	15 P Phosphorus 31.02	16 S Sulfur 32.06	17 Cl Chlorine 35.457	
Period 4	18 A Argon 39.944	19 K Potassium 39.096 29 Cu Copper 63.57	20 Ca Calcium 40.08 30 Zn Zinc 65 38	21 Sc Scandium 45.10 31 Ga Gallium 69.72	22 Ti Titanium 47.90 32 Ge Germanium 72.60	23 V Vanadium 50.95 33 As Arsenic 74.91	24 Cr Chromium 52.01 34 Se Selenium 78.96	25 Mn Manganese 54.93 35 Br Bromine 79.916	26 Fe Iron 55.84 55.84 27 Co Cobalt 58.94 28 Ni Nickel 58.69
Period 5	36 Kr Krypton 83.7	37 Rb Rubidium 85.48 47 Ag Silver 107.880	38 Sr Strontium 87.63 48 Cd Cadmium 112.41	39 Yt Yttrium 88 92 49 In Indium 114.76	40 Zr Zirconium 91.22 50 Sn Tin 118.70	41 Cb Columbium 92.91 51 Sb Antimony 121.76	42 Mo Molybdenum 95 96 52 Te Tellurium 127.61	43 Ma Masurium 53 I Iodine 126.92	44 Ru Ruthenium 101.7 45 Rh Rhodium 102.91 46 Pd Palladium 106.7
Period 6	54 Xe Xenon 131.3	55 Ca Cesium 132.91 79 Au Gold 197.2	56 Ba Barium 137.36 80 Hg Mercury 200.61	57 La Lanthanum* 138 92 81 Tl Thallium 204.39	72 Hf Hafnium 178.6 82 Pb Lead 207.21	73 Ta Tantalum 180.88 83 Bi Bismuth 209.00	74 W Tungsten 183.92 84 Po Polonium (210)	75 Re Rhenium 186.31 85 ——	76 Os Osmium 190.2 77 Ir Iridium 193.1 78 Pt Platinum 195.23
Period 7	86 Rn Radon 222	87 ——	88 Ra Radium	89 Ac Actinium	90 Th Thorium 232.12	91 Pa	92 U Uranium 238.07		