Qualitative Testing and Inorganic Chemistry

PREFACE

There is a trend today to abandon the second-semester freshman course in qualitative analysis in favor of a year's general chemistry which includes a few weeks of analysis and chemical equilibrium. I think that some excellent chemistry, particularly in the laboratory, is lost that way, and in this book I use the opposite approach to curriculum revision by emphasizing the best of the "qual" and adding related general chemistry to that. Modernization of the stereotyped "qual" program is desirable, because it has always seemed to admit its laboratory procedures have little value outside the classroom and palmed off the theoretical sections as chemical major preparation for advanced study. I never became enthusiastic over that, neither did the nonmajors who constitute the large majority of most classes, since they were not getting anything they could use. As this is the last chemistry required of most people, one should not feel obligated to fit time-honored material into a narrow, half-century old outline. I therefore try to develop the subject in both lecture and laboratory as something alive with applications for any physical science student by presenting it not as an isolated factual body but as a relative of many scientific areas. This makes for a rather large volume although not necessarily one written down to a descriptive level. The text probably cannot be completely covered in a semester, but the instructor can vary the course within it, and extra reading and laboratory work are available as needed.

This book assumes a reader's sound background of at least one semester or two quarters of general college chemistry which considered such topics as properties of matter, chemical symbolism, nomenclature and equations, structure of atoms and molecules and their weight relationships, the periodic system, the gas laws, types of solutions, introductory redox and equilibrium, and descriptive chemistry of important nonmetals. The second course may then be free to use its own text, such as this one, for the chemistry of the metals, some topics in "modern" inorganic chemistry, the elaboration of equilibrium systems, and the qualitative testing of selected cations and anions. To tie these topics together I use examples and problems from the laboratory work and industry and explain how our knowledge developed historically through experimentation. The emphasis is on the broad view of inorganic chemistry.

After a review of equation writing and calculations on solution concentration (Chapters 1 and 2), atomic structure and bonding are reviewed and extended for use in explaining the constitution of Werner ions and, together with conductance studies, in formulating the acid–base theories (Chapters 3, 4, and 5). The next six chapters develop chemical equilibrium with reference to substances handled in the laboratory, and many experimental methods for determining equilibrium constants are explained to give the reader more feeling for the abstractions. Chapter 12 classifies some organic qualitative reagents. The next chapter briefly treats process metallurgy and the crystalline structure of metals. Chapter 14 outlines general laboratory procedures, and the following five chapters cover the usual five cation groups. These include a factual description of the chemistry of each metal, an explanation and flowsheet of group analysis, preliminary laboratory study of the ions, detailed procedure for sample analysis, and all reaction equations. The preliminaries are almost entirely alternate tests for ions rather than a duplication of descriptive material. It is believed this will allow more analytical time on samples, yet many of the preliminaries will be done conscientiously in the course of "unknown" investigation, since the checking of the sample using blanks, "knowns," and confirmatory examinations has added meaning and incentive.

Chapter 20 describes eight "new" metals, Li, Be, Ti, Zr, V, Mo, W, and U, and contains enough laboratory direction for their identification in the usual alloys and matrixes. They are not included in the next chapter on the general cation unknown, however, although two of industry's procedures are reprinted for identifying some commercial alloys. Chapter 22 concerns the chemistry and analysis of 18 anions, mainly by spot testing so any or all can be included without changing laboratory directions. The last chapter is a collection of 13 so-called special experiments which can be employed as class demonstrations or assigned to individuals in place of more complex samples. A few of them illustrate the basis for theoretical principles, and the rest hold human and applied interest and demonstrate such qualitative testing techniques as microscopy, chromatography, fluorescence, electrography, etc.

Most chapters end with a set of problems, some with answers, and recent references to *J. Chem. Educ.* and *Anal. Chem.* The latter are only meant to be a literature introduction which interested students can read with benefit, and they are not meant to be research-type source material.

The class-room instruction of qualitative analysis and inorganic chemistry inherently includes the well-known problem of laboratory and lecture coordination. In the past, I used the lecture hours at the semester's beginning to rapidly review solution concentrations, equation writing, and chemical bonding (Chapters 1, 2, and 3) and used the quiz hours to give laboratory orientation and directions for group 1 and 2 cations (Chapters 14, 15, and 16). After that I took up Werner compounds, acid–base theories and reaction rates (Chapters 4, 5, and 6) and then started equilibrium (Chapters 7, 8, 9, 10, and 11). Other years I have varied this by beginning the equilibrium sections right after a review of the first two chapters so they coincide with the current laboratory work: sulfide solubilities, *p*H control, etc. I then alternated descriptive chapters with those on calculations, for the sake of variety. The chapter on metallurgy is appropriate when a metal or mineral sample is analyzed, and the section on organic reagents can follow anion analysis or precede a general unknown. The special experiments can be used individually or as class demonstrations and interwoven wherever they seem indicated, for instance, flame and bead tests with cation groups 4 and 5. I usually finished the semester with several lectures on a topic of special interest, such as electrochemical corrosion, physical metallurgy, crystallography, or refractory metals and had fun with related industrial samples possessing analytical aspects, or on field trips to plants using metals and quality control.

Whatever the instructor's preference for topics, presentation order, or his group's training and ability, I hope the material is here for a beneficial and interesting time.

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Van Nuys, California
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1

CHEMICAL EQUATIONS

Few chemistry courses contain so many reactions of compounds of different elements as does qualitative analysis, and indeed one purpose of teaching this subject is to acquaint students with inorganic reactions. It becomes necessary, therefore, that one be able to write and balance chemical equations, which are the shorthand statements of reactions.

It is assumed the student can write formulas and give names for simple compounds and that some of this chapter will be review material. Tables A24 and A25, giving *valence numbers*, *symbols for elements*, and *formulas for radicals*, will be helpful.

Information That Equations Can impart

1. *Can give a simple description of reaction and the ratio of substances present.*

$$4Fe + 3O_2 = 2Fe_2O_3$$

This means that reaction between iron and oxygen produces ferric oxide. Each *symbol* like Fe and O represents one *atom* of a particular element, or *Avogadro's number* (*N*) of atoms, 6.02×10^{23}, which is also called a *mole* of particles. Each *formula* like Fe_2O_3 stands for a *molecule* of a *compound* (whose composition is known by chemical analysis) or Avogadro's number of molecules, 6.02×10^{23}. The *coefficients* 4, 3, and 2 indicate that 4 atoms of iron and 3 molecules of oxygen combine to form 2 molecules of ferric oxide. The *subscripts* 2, 2, and 3 indicate, respectively, that the oxygen molecule is composed of 2 atoms of oxygen and that the Fe_2O_3 molecule is made of 2 atoms of iron and 3 of oxygen. A coefficient multiplies each atom and subscript in the entire term it precedes; a subscript multiplies only the atom or radical that precedes it.

The principal *reaction* is conventionally the one pictured going from left to right. The left-side terms are called *reactants* or *starting materials*, and the terms on the right side are *products* or *resultants.*

2. *Can give the weight ratios (and volume ratios for gases) of substances present.* Since each term may stand for N particles, and since N atoms comprise a *gram atomic weight* and N molecules a *gram molecular weight*, one may use the properly written equation to make calculations in what are known as weight-weight, weight-volume, volume-volume, and *material-balance problems.* A mole of oxygen molecules occupies 22.4 liters, a volume known as a gram molecular or *molar volume*, at *standard conditions* (*s.c.*) *of temperature* (0 C = 273 A) *and pressure* (760 *mm Hg* = 13.7 *lb/in.*^{2} = 1.00 *atm*). The equation therefore gives the information that (4)(55.85) g Fe + (3)(32.00) g O_2 or (3)(22.4) liters O_2 react to produce (2)[(2)(55.85) + (3)(32.00)] g of Fe_2O_3 if the process is 100% complete. This maximum quantity is called the *theoretical yield* of the chemical process. Grams and liters are the laboratory units most used. Engineering units are usually pounds and cubic feet. A pound molecular gas volume at standard conditions is 359 cubic feet. The total weights of reactants must equal the total weights of products in ordinary (non-nuclear energy) reactions.

3. *Can show the physical states of the substances.* It will be the convention for equations in this book to represent solids in bold face, gases in italic, and dissolved substances and liquids in ordinary type. For the student writing equations, solids may be underlined and precipitates (Solubility Table, back cover) may be accompanied by a downward pointing arrow, as $\underline{AgCl}\downarrow$; gases may have a line over them and/or an upward arrow, as $\overline{NO_2}\uparrow$. Alternately, the symbols (g), (l), (s) indicating gas, liquid, solid are also used. For example $H_2O(g)$ means steam or water vapor. Strong acids, strong bases, and most salts dissociate to yield *ions* in aqueous solution, whereas weak acids (Table A20), weak bases (Table A21), and a few heavy metal salts are weakly ionized and accordingly represented as molecules. *Oxidation states of elements* and *valences of radicals* will be shown in equations as needed (see the sections on balancing redox reactions). Water will be shown if it is a reactant or is necessary to clarify the mechanism, but it is otherwise omitted as most reactions in this course are understood to be in aqueous solution. The equation

$$H^+ + HSO_4^- + \mathbf{Pb} = \mathit{H}_2 + \mathbf{PbSO_4}$$

accordingly means that sulfuric acid dissociates in steps (the first of which is complete) and reacts with metallic lead to produce hydrogen gas and a precipitate of lead sulfate.

4. *Can indicate reversibility.* For many purposes one may say that *a reaction is essentially complete in the direction in which a gas is formed (and escapes), a precipitate comes down, or a slightly ionized compound is produced* (H_2O, weak acids, weak bases, some heavy metal salts). Since even these processes are not 100% conversions, an *equals sign* or *double arrows* is used to show a state of reversibility or *equilibrium* in which at least minute amounts of each substance are present, and a heavier or longer arrow may be used to show the direction in which most of the material is displaced.

$$Ag^+ + Cl^- \rightleftharpoons AgCl$$

This is interpreted to mean that the silver ion and chloride ion react in water to precipitate silver chloride, but AgCl, not being completely insoluble, is in equilibrium with a low concentration of its ions. The compounds listed in tables in Chapters 15–20 are some common ones with low aqueous solubility. If the condition of reversibility of a reaction is not known, the equals sign may be used. A single arrow will mean the reaction is for all purposes complete as

$$C + O_2 \rightarrow CO_2$$

5. *Can describe special features of the reaction.* An *exothermic reaction* evolves heat and an *endothermic reaction* absorbs heat. *Heat of reaction* will be designated accordingly H_r or $-H_r$. If the actual value of H_r is known or is of importance it is given in kilocalories per mole of product. If heat is externally applied to a system to cause it to proceed, a *triangle*, or actual temperature, will be put with the arrow or equals sign. If one is discussing the *rates or speeds of the reaction* to the right or left, the symbols s_r and s_l or s_1 and s_2 may be used with their respective arrows, and *rate constants* k_1 and k_2 will be handled the same way (see Chapter 6). If no reaction takes place, the letters *N.R.* or the words "no reaction," will be used where products would appear. *Catalysts* will also be indicated with the equals sign.

Some reactions are *photochemical processes,* that is they are dependent upon energy from light for initiation, and the symbol used for a quantum of light will be *hν* (Chapter 3). Mathematical symbols referred to in problem solving will often be written under the corresponding terms in the chemical equation to insure clear understanding of the substitutions.

$$2H_2O_2 \xrightarrow[Fe_2O_3]{\Delta} 2H_2O + O_2$$

This symbolism is interpreted to mean that liquid hydrogen peroxide is decomposed by heating with a solid ferric oxide catalyst, yielding steam and oxygen gas.

$$H_2O + CO \underset{s_l}{\overset{s_r}{\rightleftharpoons}} H_2 + CO_2 - H_r$$

This means that steam and carbon monoxide react at rate s_r to form hydrogen and carbon dioxide which themselves react at rate s_l to return the original reactants. In going to the right, heat is absorbed. H_r is the heat of reaction.

6. *Can give colors of substances.* The system of abbreviations of colors to be used throughout the book is given in Table A27. Colors of precipitates and of ions in solution are helpful in identifying samples. Combinations of these abbreviations may be made as

$$4\mathrm{Fe}^{+3}_{Y\text{-}Or} + 3\mathrm{Fe(CN)}^{-4}_{6\,Y} = \mathbf{Fe_4[Fe(CN)_6]_3}_{D\text{-}Bu}$$

meaning 4 moles of yellow–orange ferric ions react with 3 moles of yellow ferrocyanide ions to precipitate a mole of dark-blue ferric ferrocyanide molecules.

7. *Can show structures and bonding.* Sometimes it is important to know how many electrons are available for reaction and how radicals and molecules are bonded together. Accurate representation of structural features often enables chemists to predict the course of reactions and the constitution of the products. Quite a number of examples of this are given in later chapters, particularly those on bond types, complex ions, and organic chemistry.

Balancing Simpler Equations

The first step in equation writing is to give correct symbols and/or formulas for all reactants and products. The next step is to establish by means of coefficients the same number of like atoms on both sides, and, if charged particles are shown, equivalent total charge on both sides. For example, aluminum metal will react with silver ions to give aluminum ions plus silver metal. If one ignores a balance with respect to electrical neutrality, then the equation

$$\mathbf{Al + Ag^{+} = Al^{+3} + Ag}$$

is incorrect, although correct symbols for all substances are shown and the numbers of atoms balance. Noting that the left side must have 3 positive charges to balance the 3 on the right side, one puts the coefficient

3 in front of Ag^+; this means that 3 will be used as a coefficient for Ag on the right side for material balance:

$$Al + 3Ag^+ = Al^{+3} + 3Ag$$

Predicting the Course of Simpler Reactions

In order to write equations one must have firsthand knowledge of the chemical characteristics of the reactants or be able to predict them by the aid of some generalizations. Equations should not only be balanced but should also have the possibility of actually proceeding as written. This guarantee of reaction cannot always be given, of course, so research work often calls for analysis of reaction mixtures to see what happened.

In general, reactions go essentially "to completion" if (*a*) *a gas is formed* (*b*) *an insoluble compound precipitates* (see Table A22 and the table inside the back cover) (*c*) *a weakly ionized substance forms* (Tables A20, A21, A22, and a few heavy metal salts mentioned in the descriptive sections on the ions), and (*d*) *the emf of a redox reaction is positive* (Tables A18, A19, and discussions in this chapter and Chapter 11). These four principles will always be useful to remember, though they do not always aid in predicting what the reaction products will be. For this more specific information is needed.

Chemically similar substances are expected to react alike, and the following summary of **type reactions** is derived from such comparisons. With this aid, plus the periodic table (Chapter 3), the chemical activity series (this chapter), and the tables mentioned above, one can correctly predict the outcome of many of the simpler reactions.

Example 1–1. In the group 1 cation reactions (Chapter 15) one mixes solns.* of potassium chromate and lead nitrate and a yellow ppt. is observed to form. What is the equation?

Following the type reactions summary, one recognizes the reactants as two salts and expects, according to reaction (3) under IV, (the numbering is purely arbitrary), two other salts to form. Each can only form from combination of a + to a − ion, so there is only one other combination of the four ions possible. The correct formulas for reactants and products are

$$K_2CrO_4 + Pb(NO_3)_2 = KNO_3 + PbCrO_4$$

The left side has 2 K's and 2 NO_3's which must be accounted for by putting the coefficient 2 in front of KNO_3. This balances the *molecular equation*:

$$K_2CrO_4 + Pb(NO_3)_2 = 2KNO_3 + PbCrO_4$$

Inspection of the solubility table shows that of these, only lead chromate is insoluble, so the other ions are merely present as spectators in soln. and do not

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* Abbreviations are given in the Appendix, Table A26.

participate in the essential reaction. Stripped of them, the *ionic equation* is simply

$$Pb^{+2} + CrO_4^{-2} = PbCrO_{4Y}$$

Example 1–2. What happens when a strip of silver and a strip of zinc are put in a cupric sulfate soln.?

Under (1) of III in the type reactions, one expects a single replacement reaction because the reactants are a metal and a salt. Checking the positions of Ag, Cu, and Zn in Table 1–1 shows Ag to be less easily oxidized than Cu, so Ag will not react with Cu^{+2}, but Zn which is above Cu and more readily oxidized will react. The salt formed will be zinc sulfate, but since it is ionic and sol., the essentials of the reaction mixt. are,

$$Zn + Cu^{+2} = Zn^{+2} + Cu$$

Example 1–3. A sodium thiosulfate soln. is acidified with hydrochloric acid. The mixt. bubbles, a sharp smelling gas is evolved, and the soln. turns milky. Explain.

This is an example of type (4) under IV. It is noted there that as thiosulfuric acid is displaced by a strong acid, it decomp. to give sulfur dioxide (the gas) and sulfur (the milky precipitate). If the soln. is evaporated, NaCl would be found, but in soln., Na^+ and Cl^- do not affect the reaction course so the process is

$$2H^+ + S_2O_3^{-2} = (H_2S_2O_3) = H_2O + SO_2 + S$$

The *parenthesis* is used to denote an *unstable intermediate*.

The following reaction types are a useful starting point for predicting reaction products, but the student must realize that there are some exceptions to these simple rules.

SOME SIMPLE TYPE REACTIONS

I. Simple Syntheses

A. Two Elements = Compound

*(1) $$\text{Metal} + O_2 = \text{Metal oxide}$$

Exceptions: Au and Pt give no reaction; Na, K, Ba give peroxides. Higher oxidation states of metal are usually formed.

*(2) $$\text{Nonmetal} + O_2 = \text{Nonmetal oxide}$$

Exceptions: Periodic table group O (rare gases) give no reaction.

*(3) $$\text{Metal} + S = \text{Metal sulfide}$$

Lower reaction temperatures favor lower oxidation states of metal.

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* More important types among qualitative analysis reactions.

*(4) Metal + X_2 = Metal halide (X_2 = halogen, periodic group VIIA)

Higher oxidation states of metal expected with light halogens. I_2 often gives low yields.

(5) Very active metals + H_2 = Metal hydride (H is the anion)

Very active metals are the first 8 in Table 1-1.

TABLE 1-1. ELECTROCHEMICAL SERIES FOR SOME METALLIC ELEMENTS*

React with cold water	Decreasing reactivity ↓	Li	Ease of reduction increases ↓	Not reduced by hydrogen	Not reduced by carbon	Electrolysis of molten salt	Only compounds occur in nature
		Cs					
		Rb					
		K					
		Ba					
		Sr					
		Ca					
		Na					
React with steam		La					
		Mg					
		Be					
		Al			Reduced by carbon	Electrolysis of water solutions	
		Mn					
		Zn					
		Cr					
		Fe		Reduced by hydrogen			
React with acids		Cd					
		Co					
		Ni					
		Sn					
		Pb					Native and combined
React directly with oxygen to form oxides		H					
		Cu					
		Sb					
		As					
		Bi		Reduced by heat		Electrolysis or heat	
		Ag					
		Hg					
Oxides are prepared indirectly		Pt					Native
		Au					

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* Related tables are A18 and A19.

(6) Active nonmetals + H_2 = Nonmetal hydride

A catalyst may be needed, as in NH_3 synthesis; others, like HF or HCl formation, may be explosive at low temperature.

B. Element + Compound = More Complex Compound

(1) Sulfite + O_2 = Sulfate

(2) Nitrite + O_2 = Nitrate

C. Compound A + Compound B = More Complex Compound

*(1) Acidic oxide + H_2O = Acid

($CO_2 \rightarrow H_2CO_3$, $SO_2 \rightarrow H_2SO_3$, $SO_3 \rightarrow H_2SO_4$, $N_2O_3 \rightarrow HNO_2$, $N_2O_5 \rightarrow HNO_3$, $P_4O_6 \rightarrow H_3PO_3$, $P_4O_{10} \rightarrow H_3PO_4$, $Cl_2O_5 \rightarrow HClO_3$, etc.)

*(2) Basic oxide + H_2O = Base (some are hydrated oxides)

*(3) Salt + NH_3 = Ammoniate (ammine)

(See Chapter 4. Generally the *coordination number* is twice the metal oxidation number. Transition metal salts are common examples.)

(4) Salt + H_2O = Hydrate (One needs to learn specific examples.)

(5) Basic oxide + Acidic oxide = Salt

Metal oxides, except those of some high oxidation states like Mn_2O_7, are basic; nonmetal oxides including SiO_2 are acidic.

II. Simple Decompositions

These generally infer the reverse of the preceding syntheses. Decomposition may be effected by supplying heat, light, and/or electrical energy.

Exceptions: Carbonates of periodic group IA (alkali metals) and of barium are not appreciably decomposed by heat. Chlorates give chlorides, not chlorites, upon heating. Only oxides and sulfides of metals quite low in the Electrochemical Series for Some Metallic Elements, Table 1–1, are easily decomposed by heat. The sulfur is oxidized in hot air to SO_2 gas.

III. Single Replacements

A. Element A + Compound A = Element B + Compound B

*(1) Metal + salt = Metal′ + salt′

Reacting metal is above displaced metal (ion) in electrochemical series. Note which can be chemically displaced from solution (without electrolysis).

*(2) Metal + acid = H_2 + salt

See electrochemical series. Metals below H may react with acids giving H_2O, a salt, and acid reduction products, but not H_2 gas.

*(3) Halogen + halide = Halogen′ + halide′

Reacting elemental halogen has a smaller atomic number than the displaced halogen or reaction doesn't occur.

(4) Metal + H_2O = H_2 + oxide or hydroxide

See electrochemical series; from Mg up, hydroxides are the products. Note the temperatures needed.

(5) Metal oxides + C or $H_2 \overset{\Delta}{=}$ Metal + CO, CO_2, or H_2O

See electrochemical series. Metals easiest to reduce are at the bottom.

(6) Active metals + base = H_2 + salt

Metal is part of complex anion in products like $Zn(OH)_4^{-2}$ and $Al(OH)_4^-$.

IV. Double Replacements

A. Compound A + Compound B = Two or More Other Compounds

*(1) Acid + base = Salt + H_2O

Acid of type HX, base of type MOH = Salt MX + H_2O.

*(2) Salt + H_2O = (Weak) acid + (weak) base

Either or both products must be weakly dissociated for this *hydrolysis* to take place; see Chapter 10.

*(3) Salt A + salt B = Salt C + salt D

This proceeds if one or both products precipitates or is weakly ionized. See solubility data, back cover.

*(4) Salt of weak acid + strong acid = Salt of strong acid + weak acid

See Table A20 for list of weak acids. Some weak acids are unstable and decompose as formed. See tests 22–1, 22–9, 22–12, and 22–15.

*(5) Salt of weak base + strong base = Salt of strong base + weak base

See Table A21 for list of weak bases.

*(6) Metal oxide + acid = Salt + H_2O

*(7) Metal sulfide + nonoxidizing acid = Salt + H_2S

Some sulfides with very low solubility react slowly or not at all; see Table A22.

Balancing Redox Equations

Reactions considered in this section are more complicated types in which oxidation and reduction (*redox*) take place. *Oxidation of an element is defined as a real or apparent loss of electron(s) resulting in a change from a lower to a higher (more positive) oxidation state. Reduction is the real or apparent gain in electron(s) resulting in a change from a higher to a lower (less positive) oxidation state.* Equations in which redox occurs are balanced by use of coefficients to equalize the electron loss and gain and simultaneously give an atomic balance.

Oxidation numbers must be learned for some elements and others can be deduced as needed. Elements that are uncombined or are present as polyatomic molecules have zero oxidation states. Elements in periodic group IA are +1 (H may be −1 as in NaH), and in IIA are +2. Halogens not in combination with oxygen are −1. Oxygen is −2 except in peroxides where it is −1. Aluminum is (III). With these in mind one can find the oxidation numbers of elements combined with them since the sum of the numbers with their signs algebraically added is zero for a given compound. Considering HNO_3 for example, H is +1, the oxygen total is (3)(−2) = −6, so N must have an oxidation number of (V). This does not mean, however, that N^{+5} is capable of independent existence but it is only a notational convenience to be used in relating actual or assigned electron transfer in equation balancing, as will be illustrated later. Oxidation states are indicated by Roman numerals as N^{V}, Mn^{VII}, etc., or as nitrogen (V), manganese (VII), etc. The actual charge an ion has due to electron loss or gain, as Na^{+}, K^{+}, Ca^{+2}, Mg^{+2}, Sr^{+2}, Ba^{+2}, Cl^{-}, Br^{-}, and I^{-}, is the *valence* or *valence number*. Since few other cases are so definitely electrovalent as these, the more general term oxidation state (or number) will often be used along with Roman numeral notation. See also Chapter 3. Of the metals to be analyzed in the laboratory the following exist in solution in combined forms other than simple hydrated ions and Roman numerals are used for their oxidation states: Bi^{III}, As^{III}, Sb^{III}, Sn^{II}, and Sn^{IV}. Trivalent ions like Cr^{+3}, Fe^{+3}, and Al^{+3} are also frequently found in complexes (Chapter 4), and where there is doubt, the Roman symbols can be used.

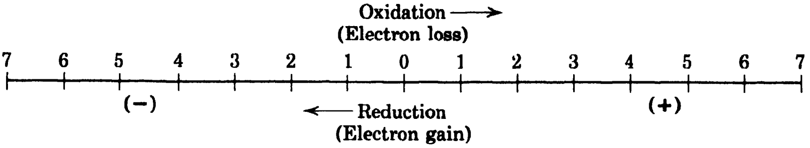

FIG. 1-1. A representation of redox.

The Change in Oxidation State Method. Redox equations can be balanced merely by first equating the changes in oxidation number (electron transfer) and then balancing all other terms. The method involves these steps: (*a*) write the correct formulas for all substances. (*b*) Determine which elements change oxidation states, and balance the changes with coefficients. The elements may be connected with lines to follow the process. If an element directly concerned with the redox has a subscript, make that number a coefficient on the other side of the equation (since at least that multiple will be needed there), and then balance the total oxidation number change. (*c*) After the electron change is balanced, balance all other elements starting with those that occur the least number of times. If ions are represented, the total charges on each side must also balance.

Example 1-4. Potassium dichromate in acid soln. will oxidize oxalic acid, and the products will be chromic sulfate, potassium sulfate, carbon dioxide and water. The *molecular equation* is

$$+12 \qquad (6e^- \text{ gain} = \text{reduction}) \qquad +6$$
$$K_2Cr_2O_7 + H_2SO_4 + H_2C_2O_4 = Cr_2(SO_4)_3 + K_2SO_4 + 2CO_2 + H_2O$$
$$+6 \qquad (2e^- \text{ loss} = \text{oxidation}) \qquad +8$$

The elements changing oxidation numbers are chromium (being reduced) and carbon (being oxidized). Cr has a subscript 2 on each side so one is ready to balance the total change in 2 Cr's which is 6 electrons. C has the subscript 2 on the left side and none on the right so 2 is made a coeff. before CO_2, since at least that many carbons will be needed there. The total change of 2 electrons lost by the 2 C's must now be balanced against the 6 electrons gained by the 2 Cr's. This balance is made by deducing that 6 is the least common multiple of electron loss and gain, so both are made equal to 6 by multiplication of coeffs. as needed. These will be 1 for each end of the Cr bracket and 3 for the compds. at each end of the C bracket. CO_2, which was multiplied previously by 2, is now multiplied by 3, giving CO_2 a final coeff. of 6. The oxidation number changes are now balanced:

$$K_2Cr_2O_7 + H_2SO_4 + 3H_2C_2O_4 = Cr_2(SO_4)_3 + K_2SO_4 + 6\mathit{CO}_2 + H_2O$$

Next, the other atoms are balanced. One notices that there are 2 K's on each side and that they check already. Since Cr and K are balanced on the right side, then no further change in right side SO_4 is expected; a total of 4 SO_4's are needed from H_2SO_4 on the left. This gives 8 H's from $4H_2SO_4$ and 6 H's from $3H_2C_2O_4$, enough to combine with the oxygen from $K_2Cr_2O_7$ to make $7H_2O$ on the right side. Twelve O's from 3 $H_2C_2O_4$'s balance the O in 6 CO_2. The final molecular equation reads

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2C_2O_4 = Cr_2(SO_4)_3 + K_2SO_4 + 6\mathit{CO}_2 + 7H_2O$$

Inspection of this shows that K^+ and SO_4^{-2} were not altered in any way during reaction. Of the remaining substances, dichromate, hydrogen, and chromic ions will exist as such in soln., while oxalic acid (a weak acid), carbon dioxide, and water will remain largely in the molecular form. The correct *ionic equation* consequently is

$$Cr_2O_7^{-2} + 8H^+ + 3H_2C_2O_4 = 2Cr^{+3} + 6\mathit{CO}_2 + 7H_2O$$

Had this equation (without coeff.) been originally given for balancing, the process would have been the same. As a final check one sees that the ionic charge is +6 on both sides.

Example 1–5. Balance:

$$HNO_3 + CdS = Cd(NO_3)_2 + \mathit{NO} + H_2O + S$$

The oxidation state of N in NO_3 is (V), so, in going to NO in which it is (II), $3e^-$ were gained. Nitric acid is therefore the oxidizing agent and N^V is red. The oxidation number of sulfide sulfur is −2 and it is oxidized to zero as free sulfur, so sulfide is the red. agent and electron donor, and its electron change is 2. By multiplying the electron gain by 2 and the loss by 3, a balance of 6 electrons for each is obtained giving

$$2HNO_3 + 3CdS = Cd(NO_3)_2 + 2\mathit{NO} + H_2O + 3S$$

Now a variation from the previous example is noticed. With 3 Cd's on the left, the correct coeff. for cadmium nitrate is 3, meaning 6 more NO_3^-'s are needed than provided for when only the red. of N was taken into account. These 6 must come from HNO_3, so 6 are *added* to the 2 already shown, accounting for 2 N's, which change oxidation number and 6 that do not. The 8 H's now available will produce 4 H_2O's and a check on O balance shows 24 on both sides:

$$8HNO_3 + 3CdS = 3Cd(NO_3)_2 + 2\mathit{NO} + 4H_2O + 3S$$

The Half-Cell Method. (*a*) This method is explained in Chapter 11 along with the use of Appendix Tables A18 and A19 which list reactions of oxidizing and reducing agents in acidic and basic solution. For purposes here, Tables 1–2 and 1–3 (which are adaptations of the more advanced information) may be used. In general, any substance listed among the oxidizing agents will oxidize any substance among the reducing agents.

TABLE 1–2. REACTIONS OF SOME COMMON OXIDIZING AGENTS IN ACID SOLUTION

(In Order of Decreasing Oxidizing Strength)

Oxidizing Mixture	Element	e^- Change	Equivalent Weight of Oxidant	Reduction Products
$F_2 + 2H^+$	F	2	38/2	2HF
F_2	F	2	38/2	$2F^-$
$O_3 + 2H^+$	O	2	48/2	$O_2 + H_2O$
$H_2O_2 + 2H^+$	O	2	34/2	$2H_2O$
$NaBiO_3 + 6H^+$	Bi	2	280/2	$Bi^{III} + 3H_2O + Na^+$
$KMnO_4 + 8H^+$	Mn	5	158/5	$Mn^{+2} + 4H_2O + K^+$
$PbO_2 + 4H^+$	Pb	2	239/2	$Pb^{+2} + 2H_2O$
Cl_2	Cl	2	71/2	$2Cl^-$
$K_2Cr_2O_7 + 14H^+$	Cr	6	294/6	$2Cr^{+3} + 7H_2O + 2K^+$
$MnO_2 + 4H^+$	Mn	2	87/2	$Mn^{+2} + 2H_2O$
$O_2 + 4H^+$	O	4	32/4	$2H_2O$
$KClO_3 + 3H^+$	Cl	2	123/2	$HClO_2 + H_2O + K^+$
Br_2	Br	2	160/2	$2Br^-$
$HNO_3 + 3H^+$ (dil.)	N	3	63/3	$NO + 2H_2O$
Fe^{III}	Fe	1	55.9/1	Fe^{+2}
I_2	I	2	254/2	$2I^-$

Example 1–6. Balance the reaction equation in which bismuthate ion reacts with ferrous ion in acid soln.

From Tables 1–2 and 1–3, the reactants and products are found to be

$$BiO_3^- + H^+ + Fe^{+2} = Fe^{+3} + H_2O + Bi^{III}$$

By further noting that the electron change in iron is one and in bismuth two, the final equation is

$$BiO_3^- + 6H^+ + 2Fe^{+2} = 2Fe^{+3} + 3H_2O + Bi^{III}$$

When a half reaction in question cannot be found in tables, as might be the case in research work, predictions of reaction products can be difficult. Then analogies from periodic table relationships and a knowledge of other reactions of the particular element, its oxidization states, and their interconvertibility are some guide posts in prognostications.

(*b*) As a variation of the method, a given reaction can be divided into two half reactions, and, with the addition of H_2O, H^+, or OH^- (depending on acid or base solutions) to one side or the other of the half reactions, and adjustment of charge with electron additions, one is able to balance quite complex equations.

TABLE 1–3. REACTIONS OF SOME COMMON REDUCING AGENTS IN ACID SOLUTION

(In Order of Decreasing Reducing Strength)

Reducing Mixture	Element	e^- Change	Equivalent Weight of Reductant	Oxidation Products
Alkali metals	M	1	$M/1$	M^+
Alkaline earth metals	M	2	$M/2$	M^{+2}
Al	Al	3	27/3	Al^{+3}
Zn	Zn	2	65.4/2	Zn^{+2}
AsH_3	As	3	78/3	$As + 3H^+$
$H_2C_2O_4$	C	2	90/2	$2CO_2 + 2H^+$
Fe	Fe	2	55.9/2	Fe^{+2}
Cd	Cd	2	112/2	Cd^{+2}
$H_3PO_3 + H_2O$	P	2	82/2	$H_3PO_4 + 2H^+$
H_2	H	2	2.0/2	$2H^+$
H_2S	S	2	34/2	$2H^+ + S$
Sn^{II}	Sn	2	119/2	Sn^{IV}
Cu^+	Cu	1	63.5/1	Cu^{+2}
Cu	Cu	2	63.5/2	Cu^{+2}
$2I^-$	I	2	254/2	I_2
Fe^{+2}	Fe	1	55.9/1	Fe^{+3}

Example 1-7. Balance, as described above:

$$As_2S_3 + HNO_3 = H_3AsO_4 + NO_2 + S + H_2O$$

This looks formidable because both As and S are oxidized and N is reduced. Dividing into two halves, we get

$$As_2S_3 = H_3AsO_4 + S$$

$$HNO_3 = NO_2 + H_2O$$

Division is always made so that one partial or half-reaction contains the oxidation and the other the reduction. The arsenic partial requires H_2O on the left to supply hydrogen and oxygen. This balances with respect to atoms as

$$8H_2O + As_2S_3 = 2H_3AsO_4 + 3S + 10H^+$$

The nitric acid partial requires H^+ on the left:

$$H^+ + HNO_3 = \mathit{NO}_2 + H_2O$$

For balance of charge, the As half reaction needs $10e^-$ on the right side, and the HNO_3 half reaction needs $1e$ on the left. The two partials are balanced with each other by multiplying the HNO_3 reaction by 10, thus attaining over-all electronic balance. The whole reaction is obtained by adding the half reactions and canceling $10e^-$, $10H^+$, and $8H_2O$ from both sides:

$$\begin{array}{r} 8H_2O + As_2S_3 = 2H_3AsO_4 + 3S + 10H^+ + 10e^- \\ 10e^- + 10HNO_3 + 10H^+ = 10\mathit{NO}_2 + 10H_2O \\ \hline As_2S_3 + 10HNO_3 = 2H_3AsO_4 + 3S + 10\mathit{NO}_2 + 2H_2O \end{array}$$

Note in this variation we were not concerned with oxidation states.

PROBLEMS

1. Name the following substances. Refer to Tables A24 and A25 for nomenclature aid: $KClO_3$, $NaClO$, $Ca(ClO_4)_2$, $Mg(ClO_2)_2$, $Bi(NO_3)_3$, MnI_2, CrF_3, $Pb_3(PO_4)_2$, $LiHCO_3$, TiO_2, $CuSO_4 \cdot 5H_2O$, $Mg(BO_2)_2$, $SnCO_3$, $Ni(OH)_2$, $CuBr$, Al_2O_3, $Fe(C_2H_3O_2)_3$, $AgCN$, Hg_2Cl_2, $Fe(CNS)_2$, $Co(NO_2)_2$, CdS, $As_2(SO_3)_3$, $Sb_2(C_2O_4)_3$, $Sn(HS)_4$, $BaCrO_4$, $PbCr_2O_7$, $Hg(HSO_3)_2$, $Zn_2P_2O_7$, $(NH_4)_3PO_3$, $Na_2B_4O_7 \cdot 10H_2O$, $(BiO)BiO_3$, SF_6, $CaMnO_4$.

2. Give formulas for: silver iodide, lead (plumbous) chlorate, mercurous arsenate, mercuric (ortho)phosphate, bismuth metaphosphate, cadmium tartrate, cuprous sulfide, arsenous oxide, antimonic fluoride, stannous bromide, cobaltous cyanate, nickelic oxide, ferric thiosulfate, zinc metastannate, chromic carbonate, manganous bisulfate, aluminum bromate, calcium formate, magnesium sulfite, strontium hypochlorite, ammonium acetate, sodium peroxydisulfate, potassium permanganate, lithium hyponitrite.

3. Write balanced equations showing formation of the following acids, using part I, C(3) of the type reactions compilation: H_2CO_3, HNO_2, H_2SO_4, $H_4P_2O_7$, H_3PO_4, HNO_3, H_2SO_3, $HClO_2$, $HClO_3$, $HClO_4$. Match the names to the acids: chloric, sulfurous, sulfuric, chlorous, nitric, pyrophosphoric, nitrous, perchloric, carbonic, orthophosphoric.

4. Predict the products (include indication of ions, molecules, gases, and solids) and balance: (*a*) $CaO + H_2O = ?$ (*b*) $Mg + O_2 \overset{\Delta}{=} ?$ (*c*) $Mg + N_2 \overset{\Delta}{=} ?$ (*d*) $Na + H_2O = ?$ (*e*) $Al(OH)_3 + HBr = ?$ (*f*) potassium carbonate + sulfuric acid = ? (*g*) sulfite ion + hydrogen ion = ? (*h*) copper metal + chlorine = ? (*i*) barium nitrite + oxygen = ? (*j*) sodium carbonate decahydrate is heated = ? (*k*) $CoO + C \overset{\Delta}{=} ?$ (*l*) Li + hydrogen = ? (*m*) sodium ferrocyanide + cupric nitrate = ? (*n*) ammonium chloride + barium hydroxide = ? (*o*) hydriodic acid + silver nitrate = ? (*p*) ferric acetate

+ sodium orthophosphate = ? (*q*) ethyl alcohol is burned = ? (*r*) zinc sulfide + HCl = ? (*s*) aluminium + bismuth chloride = ? (*t*) bromine + NaCl = ? (*u*) zinc + potassium hydroxide = ? (*v*) arsenic + magnesium sulfate = ? (*w*) mercuric oxide is heated = ? (*x*) manganese + acetic acid = ? (*y*) sulfuric acid + aluminium cyanide = ? (*z*) lead + AuCl = ?

5. Predict the products and balance: (*a*) $Cl_2 + H_2S = ?$ (*b*) $Sn^{II} + H^+ + PbO_2 = ?$ (*c*) $KClO_3 + H^+ + Cu^+ = ?$ (*d*) $KMnO_4 + H^+ + Fe = ?$ (*e*) dichromate ion + hydrogen sulfide in acid solution = ? (*f*) $I^- + H_2O_2 + H^+ = ?$ (*g*) ozone + arsine in acid solution = ? (*h*) $BiO_3^- + H_2C_2O_4 + H^+ = ?$ (*i*) manganese dioxide + stannous ion in acid solution = ? (*j*) H_3PO_3 + permanganate in acid solution = ?

6. Indicate insoluble solids and gases, and balance by the change of oxidation state number method:

(*a*) $KI + PbCrO_4 + HCl = PbCl_2 + KCl + CrCl_3 + I_2 + H_2O$
(*b*) $KMnO_4 + HNO_2 + H_2SO_4 = MnSO_4 + K_2SO_4 + H_2O + HNO_3$
(*c*) $Mn(OH)_3 + HCl + H_2O_2 = MnCl_2 + H_2O + O_2$
(*d*) $KI + NaBrO_3 + HCl = KCl + NaBr + H_2O + I_2$
(*e*) $Na_2C_2O_4 + NaMnO_4 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2 + MnSO_1$
(*f*) $MnSO_4 + PbO_2 + HNO_3 = HMnO_4 + PbSO_4 + Pb(NO_3)_2 + H_2O$
(*g*) $NaBiO_3 + H_2SO_4 + NaAsO_2 = H_3AsO_4 + H_2O + Na_2SO_4 + Bi_2(SO_4)_3$
(*h*) $HNO_3 + Bi_2S_3 = Bi(NO_3)_3 + H_2O + NO + S$
(*i*) $CuSO_4 + KI = K_2SO_4 + CuI + I_2$
(*j*) $CrI_3 + KOH + Cl_2 = K_2CrO_4 + KIO_4 + KCl + H_2O$

7. Divide each of the reactions of problem 6 into two half reactions containing only the essential ions and molecules and balance them using the half cell method.

8. Show reaction between bases of Li^+, Mg^{+2}, and Al^{+3} and acids of Br^-, NO_3^-, SO_4^{-2}, and PO_4^{-3}. Name each salt formed.

9. (*a*) In problem 6, point out which substance is the oxidizing agent and which the reducing agent for each reaction. (*b*) Name each substance in each equation.

10. Reactions tend toward completion in the direction in which a precipitate forms. Which of these compounds are essentially water-insoluble: NaOH, HNO_3, $Cr(OH)_3$, AgI, $Cd(NO_3)_2$, SnS_2, CaC_2O_4, $BaCrO_4$, $K_4Fe(CN)_6$, $MgCl_2$, $MnSO_1$, $CaCO_3$, $HgCl_2$, $CuSO_4$.

11. From the table of salt solubilities (back cover) one may draw the generalization that almost all Na^+, K^+ and NH_4^+ compounds are water soluble as are most salts containing $C_2H_3O_2^-$, ClO_3^-, NO_2^- and NO_3^-. What generalizations can one make on the water solubilities of (*a*) chlorides, bromides, iodides (*b*) phosphates (*c*) carbonates (*d*) sulfides, and (*e*) sulfates?

12. *Complete* and balance the following half reactions, including electrons:

(*a*) $e^- + CeO_2 + H^+ = Ce^{+3}$
(*b*) $CuS = Cu^{+2} + SO_4^{-2} + 8H^+$
(*c*) $Na = Na^+$

(*d*) $5e^- + MnO_4^- = H_2O + Mn^{+2}$
(*e*) $IO_3^- = H_3IO_6^{-2} + 2e^-$
(*f*) $Br^- + 6OH^- = BrO_3^-$
(*g*) $AsO_2^- + 2H_2O = As + OH^-$
(*h*) $Hg_2^{+2} = 2Hg^{+2}$
(*i*) $BiOCl + H^+ = Bi + Cl^-$
(*j*) $I_2 + H_2O = IO_3 + H^+ + e$

13. What is the oxidation state of each element: HNO_3, $HMnO_4$, $NaAl(OH)_4$ SbH_3, $Hg_2Cr_2O_7$, $Hg(NH_2)Cl$, Na_2O_2, $BaCO_3$, $KCr(OH)_4$, $Fe_3[Fe(CN)_6]_4$?

14. How does one interpret the following:

(*a*) $MnO_{4_{Pu}} + H_2S + Cl^- = Cl_{2_{L\text{-}Y}} + S_s + H_2O + Mn_P^{+2}$
(*b*) $H^+ + OH^- \rightleftharpoons H_2O + H_,$
(*c*) $Cu_{Bu}^+ + Cd^{+2} + 8NH_3 = Cu(NH_3)_{4_{D\text{-}Bu}}^{+2} + Cd(NH_3)_{4_{Cl}}^{+2}$

15. Jackson P. Slipshod is a student capable of forming a snap opinion on any subject. He glances at one reaction equation and announces the Slipshod rule: "The number of compounds in a given molecular redox equation is the same as the number of elements involved." Inspect several more examples than J.P.S. inspected and modify his rule if you reach a different conclusion. How does the rule help balance equations when only the reactants are given?

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2

EXPRESSING THE CONCENTRATION OF SOLUTIONS

A *solution* is a homogeneous mixture whose composition can be varied and whose *components* are not easily interconverted. The component in largest amount is the *solvent*, the other components are *solutes*. Solutions are classified in various ways: as *dilute* (ratio of solute(s) to solvent is small), *concentrated* (ratio of solute(s) to solvent is larger), or *saturated* (a maximum amount of solute is in solution in equilibrium with excess solid solute at a specified temperature). Another classification is according to the original physical states of solvent and solute. Of the nine possibilities, three will be illustrated many times in the laboratory: a gas dissolved in a liquid (H_2S in H_2O), a liquid in a liquid (H_2SO_4 in H_2O), and a solid in a liquid ($AgNO_3$ in H_2O). Water will be understood as the solvent unless otherwise stated. The solving of problems dealing with solutions depends upon exact expression of solution concentration, and the following sections explain the most often used terms and methods.

Weight Ratio

Some handbook solubility data are given in *grams of solute per* 100 *g of solvent.* Determination of solubility and its expression are illustrated.

Example 2–1. 20.00 ml of satd. $KClO_3$ soln. at 20 C weighs 21.000 g, and after low temp. vacuum evap. of the water (to prevent decompn. of $KClO_3$ by heating), the residue of $KClO_3$ weighs 1.450 g. Calculate the soly. in g/100 g H_2O.

The data shows that the wt ratio of solute/solvent at 20 C is 1.450/(21.000 − 1.450). Solving for that wt of solute which is equiv. to 100 g of solvent gives

$$? \text{ g } KClO_3 = 100 \text{ g } H_2O \text{ } (1.450 \text{ g } KClO_3/19.550 \text{ g } H_2O)$$
$$= 7.425 \text{ g } KClO_3/100 \text{ g } H_2O. \quad (\textit{Ans.})$$

Solution concentration in these terms is generally reserved for the discussion of *saturated solutions* and is an expression of the maximum equilibrium solubility.

Weight Percent

The *weight per cent* of a solution refers to per cent solute and implies that when the solution is to be used, its *weight* and not its *volume* will be measured.

Example 2-2. Calculate the wt % $KClO_3$ in the soln. of Example 2-1. The calcn. infers the statement:

$$\text{Wt } \% = (\text{wt solute/wt solute} + \text{wt solvent}) \ 100\,\% \qquad ((2\text{–}1)$$
$$= 100 \text{ (wt solute/wt solution)}$$

Substitution gives 6.90 wt % $KClO_3$. (*Ans.*)

The student should observe in these two examples that no molecular weights entered the definitions or calculations.

Weight ratio and weight per cent are two methods of solution concentration expression in *physical* units. The methods following are in chemical units.

Formality (F)

The *formality* of a solution is the number of gram formula weights (form. wt) of solute dissolved in a liter of the solution:

$$F = \text{g solute per liter of solution/formula wt solute} \qquad (2\text{–}2)$$
$$= \text{Formula wts of solute per liter of solution}$$

Thus a measured *volume* of solution contains a known weight of solute.

Molarity (M)

The *molarity* of a solution is the number of gram molecular weights (*moles*) of solute dissolved in a liter of the solution:

$$M = \text{g solute per liter of solution/mol. wt solute} \qquad (2\text{–}3)$$
$$= \text{Moles of solute per liter of solution}$$

Example 2–3. One dissolves 39.215 g of Mohr's salt, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (392.15)* in enough H_2O to make 10 liters of soln. Calculate F and M with respect to the solute and M with respect to each ion.

The soln. contains 3.9215 g of solute per liter, and since the mol. wt and form. wt are identical, then with regard to the entire solute,

$$F = M = 3.9215\ \text{g}/392.15 = 0.0100 \quad (\textit{Ans.})$$

The compd., as a typical salt, will be considered to dissoc. completely, each molecule giving $Fe^{+2} + 2SO_4^{-2} + 2NH_4^+$. Therefore with regard to the ions, the soln. is 0.0100 M in Fe^{+2}, 0.0200 M in SO_4^{-2}, and 0.0200 M in NH_4^+. (*Ans.*)

Because ionic compounds are composed of ions both in the solid state and in solution, the term formality rather than molarity is generally used to describe concentrations with respect to the entire solute. A *square bracket* around the abbreviation for a substance like $[Fe^{+2}]$ signifies a molar concentration. Molarities will be used more often in this text.

For small quantities of solutions, mg instead of g, and ml instead of l (liter) are employed. One then defines a millimole (mmole) as a milligram molecular weight, and a molar solution will contain a mg mol. wt per ml of solution.

Example 2–4. A soln. is 1.50 M in $FeSO_4$. Calculate the mg and mmole of Fe^{+2} in 1 ml.

If the soln. is 1.50 M in $FeSO_4$, it is 1.50 M in Fe^{+2}, and the ionic wt of Fe^{+2} (55.85) can be used in place of mol. wt in equation 2–3):

$$\begin{aligned}[Fe^{+2}](55.85) &= \text{g } Fe^{+2} \text{ per liter of soln.} = 83.8 \text{ g } Fe^{+2} \text{ per liter}\\ &= 83.8 \text{ mg } Fe^{+2} \text{ per ml} \qquad (\textit{Ans.})\end{aligned}$$

Since $[Fe^{+2}] = 1.50\ M$, there are 1.50 moles of Fe^{+2} per liter = 1.50 mmoles Fe^{+2} per ml. (*Ans.*)

Molality (m)

The *molality* of a solution is a measure of the number of moles of solute dissolved in a kilogram (1000 g) of solvent. This concentration expression is also known as *weight formality* and *weight molarity*. Solutions concerned with boiling point, freezing point, and osmotic pressure changes are made up using this concentration system. Using a given solvent, one notes the interesting feature that all solutions of the same molality have the same ratio of solute molecules to solvent molecules. One weighs the solution to be used instead of measuring its volume since when one dissolves a weight of solute in a weight of solvent, there is no way to theoretically calculate the final volume, as the volumes (except

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* Appendix tables give mol. wts for use in problem solving. Slide rule accuracy is satisfactory.

those of dilute aqueous solutions) cannot be assumed additive. The final volume may be experimentally observed for an individual mixture but these are not tabulated in reference books.

$$m = \textbf{g solute per 1000 g solvent/mol. wt solute} \qquad (2\text{–}4)$$
$$= \text{Moles of solute per kg of solvent}$$

Example 2–5. Calculate the molality of the soln. from Example 2–1.

As in that example, one first determines that the soln. contains 74.25 g $KClO_3$ (mol. wt 122.5) per 1000 g of H_2O. The molality from equation 2–4 is

$$m = 74.25/122.5 = 0.606 \qquad (\textit{Ans.})$$

Mole Fraction (n) and Mole Per Cent

The *mole fraction* (n) of a solution component is the number of moles of that component in the solution divided by the total moles of solution components present. *Mole per cent* is $100n$. The sum of all mole per cents for a given solution will be 100% and of all mole fractions will be 1.00. Problems concerning Raoult's laws, for example, involve mole fraction computations. For component A in a mixture of A + B + . . . Z,

$$n_A = \textbf{Moles A/(moles A + moles B + . . . moles Z)}$$

Example 2–6. A soln. is made by mixing 100 g of ethylene glycol ($HOCH_2$—CH_2OH = 60.0) and 100 g of H_2O (18.0). Calculate the mole fraction of each component.

Moles H_2O = 100/18.0 = 5.55
Moles glycol = 100/60.0 = 1.67
Total moles = 5.55 + 1.67 = 7.22
n_{H_2O} = moles H_2O/moles soln. = 5.55/7.22 = 0.769 (*Ans.*)
n_{glycol} = moles glycol/moles soln. = 1.67/7.22 = 0.231 (*Ans.*)
$n_{H_2O} + n_{\text{glycol}}$ = 0.769 + 0.231 = 1.000 (Check)

Normality (N)

The *normality* of a solution is an expression of the number of *gram equivalent weights* of solute present in a liter of solution. The gram equivalent weight is also called a gram equivalent or just an *equivalent*.

$$N = \textbf{g solute per liter of solution/equiv. wt solute} \qquad (2\text{–}5)$$
$$= \text{Equivalent of solute per liter of solution}$$

Although this system is very useful in calculations for analytical operations it needs careful definitions, particularly of the equivalent weight. The following brief treatment will be sufficient for our purposes. It is given in more detail in quantitative analysis courses.

A gram equivalent weight of a substance is that gram weight which will react with or is otherwise related to 8.0000 g of oxygen. For instance, in a mole of H_2O weighing 18.0160 g, 2.0160 g of H are combined with 16.0000 g of O, or, by the preceding definition, the gram equivalent weight of H is 1.0080 g. Since this is related to 8.0000 g of O, it may itself be used as an equivalent weight standard; for instance Cl in HCl is found then to have an equivalent weight of 35.457, etc. For substances not entering into redox reactions (considered later in this chapter), the equivalence system is set up on a univalent basis. Though needing later modification, a useful starting point is

$$\text{Equiv. wt} = \text{Form. wt/valence number} \qquad (2\text{–}6)$$

It follows that equal volumes of solutions of like normalities will be chemically related to each other, since they all contain the same number of equivalent weights of solute.

Three cases not concerned with redox are important:

(1) *Equivalent weights of salts* are found by dividing the formula weight by the total valence number (regardless of sign) of the ion for which normality is to be expressed.

(2) *The equivalent weight of an acid* is that weight which furnishes 1.0080 g of H^+ (or reacts with 17.0080 g of OH^-) in a specific reaction.

(3) *The equivalent weight of a base* is that weight which furnishes 17.0080 g of OH^- (or reacts with 1.0080 g of H^+) in a specific reaction.

Thus, for example, $Al_2(SO_4)_3/6$ is the equivalent weight of this salt, $H_3PO_4/2$ is the equivalent weight of this acid if used as $H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O$, and $Ca(OH)_2/2$ is the equivalent weight of this base.

Example 2–7. A bottle of concd. H_2SO_4 has this data on the label: "Sp. gr. 25/4 = 1.840, Assay = 96% H_2SO_4 by wt, Form. wt = 98.08."

Find F and N for this soln. assuming both H^+ will be used in reaction.

The sp. gr. term in the data means that the density of H_2SO_4 at 25 C is compared to the density of H_2O at 4 C, and since the latter is 1.000 g/cc, then 1.840 g/cc is the density of H_2SO_4 at 25 C.* One can therefore find the wt of H_2SO_4 per liter by multiplying the wt per cc by 1000 and multiplying that by 0.96. This establishes the numerator for finding both F and N, using equations 2–2 and 2–5:

$$F = (1.840\ \text{g/cc})(1000\ \text{cc/liter})(0.96)/98.08 = 18.0 \qquad (\textit{Ans.})$$

$$N = (1.840\ \text{g/cc})(1000\ \text{cc/liter})(0.96)/(98.08/2) = 36.0 \qquad (\textit{Ans.})$$

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* Sp. gr. 25/25 would mean the density of the substance in question at 25 C is compared to the density of H_2O at 25 C (0.9971 g/cc). This is *not* numerically equal to the density of the substance at 25 C, though in this problem and this course the distinction is not important. Sp. gr. 25/25 is the usual type measured in the lab.

The milliliter and cubic centimeter will be treated as equal volumes. For accurate calculations, one multiplies the number of ml by 1.000028 to convert to cc.

Normality, Molarity, and Formality Relationships

As anticipated in Example 2–7 a simple relationship exists between M, N, and F for a given solution. It is seen by comparison of formulas 2–2, 2–3, and 2–5 that the terms are related as molecular, equivalent, and formula weights are related. For a given solution component, N will either be the same as M (or F), if mol. wt = equiv. wt, or larger by a multiplying factor that has the value, mol. wt/equiv. wt. In Example 2–7, since the mol. wt or form. wt is twice the equiv. wt, normality could have been found by $N = (98.08/49.04)(F)$.

Working with Equivalents and Milliequivalents

A liter of one normal solution contains one equivalent of reactive component, a half liter of this solution would contain half an equivalent, a tenth liter of half normal solution would contain $(0.1)(0.5) = 0.05$ equivalents of solute, etc. In other words, *for solutions*,

$$\textbf{(liter)}(N) = \textbf{Equivalents} \tag{2–7}$$

and if a *milliequivalent* (meq.) is defined as 0.001 equivalents, then

$$\textbf{(ml)}(N) = \textbf{Milliequivalents} \tag{2–8}$$

The terms can be related to *weights* of reacting materials as well as to solution *volumes*. Considering H_2SO_4 as in Example 2–9, since 49.00 is the equivalent weight, then 49.00 g is one equivalent, 98.00 g = 2 equivalents, etc., or *for weights of pure reactants*

$$\textbf{g equiv. wt} = \textbf{Equivalents} \tag{2–9}$$

and as before

$$\textbf{mg/equiv. wt} = \textbf{Milliequivalents} \tag{2–10}$$

These mathematical definitions of the equivalent and milliequivalent are useful in problem working. If A and B are going to react or be chemically related, then the first statement one may make is, equiv. A = equiv. B or meq. A = meq. B.

Example 2–8. How can one prep. 200 ml of 0.50 N H_2SO_4 from 1.22 M H_2SO_4?

The vol. of more concd. acid used for diln. and the vol. of dild. acid obtained must contain the same number of meq. of H_2SO_4, or meq. concd. acid = meq. dil. acid. In the general case,

$$\textbf{(Ml concd. soln.)}(N \textbf{ concd. soln.}) = \textbf{(ml dil. soln.)}(N \textbf{ dil. soln.}) \tag{2–11}$$

The more concd. acid is 1.22 M or 2.44 N. (Why?) Solving equation 2–11 gives 41.0 ml. This vol. of 1.22 M acid is dil. with water to a total vol. of 200 ml. (*Ans.*)

Example 2-9. Ten ml of a sodium sulfate soln. having a density of 1.10 g/cc 25/4 are mixed with excess barium chloride soln. and the resulting ppt. of barium sulfate weighs 1.000 g. Find the normality of the sulfate soln. and % by wt Na_2SO_4 in it.

In the reaction, meq. Na_2SO_4 = meq. $BaSO_4$. Since Na_2SO_4 is a soln., meq. Na_2SO_4 = (ml)(N), and for the solid, meq. $BaSO_4$ = mg/equiv. wt. The equiv. wt of $BaSO_4$ is half the mol. wt (by equation 2–6), and equating the two definitions for meq. one gets (ml Na_2SO_4)(N Na_2SO_4) = mg $BaSO_4$/equiv. wt $BaSO_4$. Solving for soln. normality gives N = 1000 mg/(10.0 ml)(233/2) = 0.859. (*Ans.*)

The meq. of Na_2SO_4 are now found either by 1000 mg $BaSO_4$/(233/2) or by (10 ml Na_2SO_4)(0.860). Either gives 8.60 meq. From equation 2–10, the mg of Na_2SO_4 can be determined since

$$\text{mg} = (\text{Meq.})(\text{equiv. wt}) = (8.60)(142/2) = 610$$

The % solute in the soln. will be found according to equation 2–1, the soln. density being used to find the soln. wt:

$$\%\ Na_2SO_4 = (610 \text{ mg } Na_2SO_4/11{,}000 \text{ mg soln.})\ 100\% = 5.54\% \quad (\textit{Ans.})$$

Problems like the last one and those in which a substance is determined by titration of a weighed sample are characteristic of *quantitative analysis*. A general formula one can deduce from the stepwise method above for find the % by weight of a reactant X in a mixture is

$$\%\ X = (\text{meq. } X)(\text{equiv. wt } X)(100\%)/\text{mg sample} \qquad (2\text{–}12)$$

Normality and Redox

Equivalent weights of substances undergoing oxidation state changes are calculated in a different way from examples cited thus far. It can be experimentally shown for example that in dilute H_2SO_4 solution, to oxidize 55.85 g of Fe^{+2} to Fe^{+3}, requires 1/5 mole of $KMnO_4$, 1/6 mole of $K_2Cr_2O_7$, or 1 mole of $Ce(SO_4)_2$. These quantities of oxidizing agents must therefore be equivalent to one another, and examination of their oxidizing reactions

$$5e^- + MnO_4^- + 8H^+ = Mn^{+2} + 4H_2O$$

$$6e^- + Cr_2O_7^{-2} + 14H^+ = 2Cr^{+3} + 7H_2O$$

$$e^- + Ce^{+4} = Ce^{+3}$$

shows that the comparison is on the basis of the number of electrons gained per molecule or ion, or their change in oxidation number. Reducing agents are related by the number of electrons donated per molecule or ion, and their corresponding change in oxidation number. The normal system for redox solution concentrations is therefore constituted on a unit change in oxidation number.

Equiv. wt redox agent = Form. wt $/e^-$ change per molecule or ion (12–13)

If one considers a gram mole of reactant, then the equivalent weight is that gram weight which will accept or donate 6.02×10^{23} electrons. The electron change is found in tables of redox half reactions (Tables 1–2, 1–3, A18, and A19) or found when the equation is balanced. Other considerations for problem solving are identical with those already illustrated.

Example 2–10. One dissolves 25.00 g of $K_2Cr_2O_7$ (form. wt 294.2) to make 1 liter of soln., and 45.5 ml of this will just oxidize the iron ($Fe^{+2} = Fe^{+3}$) in 1780 mg of properly dissolved iron ore. Calculate N of the oxidizing agent, equiv. wt of Fe, and % Fe in the ore.

As noted above and in Tables 1–2 and A18, the change in oxidation number for dichromate is 6, so the equiv. wt is 294.2/6 = 49.0, and since the solution contains the 25.00 g of $K_2Cr_2O_7$ per liter, N = 25.00 g per liter/49.0 = 0.510 N (*Ans.*)

Iron undergoes a one electron change per ion in the oxidation, $Fe^{+2} = Fe^{+3}$, so its ionic and equiv. wts are the same, 55.85/1. (*Ans.*)

The meq. of $K_2Cr_2O_7$ = (ml)(N) = meq. of Fe^{+2}. The problem with this much elucidated then follows the type solution described by equation 2–12:

$$\%\ \text{Fe} = (45.5\ \text{ml}\ K_2Cr_2O_7)(0.510\ N\ K_2Cr_2O_7)(55.8/1\ \text{equiv. wt}\ Fe^{+2})\ (100\%)/1780\ \text{mg sample}$$

Converting the figures to exponential numbers* for ease in approx. the answer gives

$$= (4.55 \times 10)(5.10 \times 10\ ^{1})(5.59 \times 10)(10^2)/1.78 \times 10^3$$

The ten's cancel:

$$= (4.55)(5.10)(5.59)/1.78$$

This is

$$\cong (5)(5)(6)/2 \cong 75\%$$

and using the slide rule gives the correct value, 72.9% Fe. (*Ans.*)

PROBLEMS

1. A solution is made by dissolving 40.0 g of $Ca(NO_3)_2 \cdot 4H_2O$ (form. wt 236.16) in 380 g of H_2O giving a final volume of 400 ml. Calculate (*a*) F (*b*) M

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* See Appendix, mathematics review, Section A1 and A3.

in Ca^{+2} (*c*) *M* in NO_3^- (*d*) *m* in Ca^{+2} (*e*) *m* in NO_3^- (*f*) density (*g*) *N* in Ca^{+2} (*h*) *N* in NO_3^- (*i*) % by wt solute. [*Ans.* (*a*) 0.423 (*b*) 0.423 (*c*) 0.846 (*d*) 0.447 (*e*) 0.894 (*f*) 1.05 g/cc (*g*) 0.846 (*h*) 0.846 (*i*) 9.53%.]

2. How can one prepare the following?

(*a*) 100 ml of 0.100 *M* Na_2SO_4
(*b*) 250 ml of 0.250 *N* NaOH
(*c*) 10.5 liters of 0.0022 *N* H_2SO_4 (use as diprotic acid)
(*d*) 55.0 ml of 0.10 *N* $KMnO_4$ (use as oxidizing agent in acid)
(*e*) 100 ml of 0.20 *N* $FeSO_4$ (use as red. agent in acid)

3. One wishes to oxidize 0.01 *M* H_2S (acidified) solution. List these oxidants in decreasing order of their capacity: (*a*) 4.5 ml of 0.02 *M* $KMnO_4$ (*b*) 6.3 ml of 0.01 *M* $K_2Cr_2O_7$ (*c*) 8.1 ml of 0.10 *N* $Ce(SO_4)_2$ (*d*) 25 mg of $NaBiO_3$ (*e*) 0.020 g of MnO_2.

4. A solution contains 10 mg Cu^{+2} per ml and was prepared by dissolving $CuSO_4 \cdot 5H_2O$ (form. wt 249.7) in water. Find (*a*) g cupric sulfate pentahydrate in a liter of solution, (*b*) *F* (*c*) *N* (*d*) *M* with respect to each ion, and (*e*) the weight of $BaSO_4$ one could obtain by adding excess $BaCl_2$ to 10 ml of the copper solution.

5. One dissolves 18 g $H_2C_2O_4$ to make 500 ml of soln. Calculate *N* based on these reactions:

(*a*) $H_2C_2O_4 + NaOH = NaHC_2O_4 + H_2O$
(*b*) $H_2C_2O_4 + 2KOH = K_2C_2O_4 + 2H_2O$
(*c*) $H_2C_2O_4 + PbO_2 + H^+ = H_2O + CO_2 + Pb^{+2}$ (balance)
(*d*) $H_2C_2O_4 + Ca^{+2} = CaC_2O_4 + 2H^+$

6. Express each in moles, mmoles, equivalents, and meq.:

(*a*) 150 g 20% H_2O_2 (oxidant in acid)
(*b*) 40 mg NaCl
(*c*) 2.79 g Sn^{II} (reductant in acid)
(*d*) 1 liter O_3 gas, 0 C, 1 atm pressure (oxidant in acid)
(*e*) 10 mg Zn.

7. Thirty-five ml of an NaOH soln. will just neutralize 1.32 g of $KHSO_4$. Find (*a*) how many meq. of acid and base are used (*b*) reaction equation (*c*) mg of NaOH used (*d*) *N* of base, and (*e*) mg of H_2O formed.

8. From which of these can one make the largest volume of 0.1 *N* soln.?

(*a*) 12.6 g H_3PO_4 (as a triprotic acid), (*b*) 6.80 g KI (as a reductant in acid), (*c*) 9.20 g $KClO_3$ (as an oxidant in acid), (*d*) 13.3 g $Ba(OH)_2$ (as a dihydroxy base).

9. A solution of H_3PO_4 has a sp. gr. of 1.75 25/4 and is 90% phosphoric acid by weight. Find (*a*) *F* (*b*) *N* as a triprotic acid (*c*) volume needed to furnish 1.00 g H^+ (*d*) volume needed to make 1 liter of 0.20 *N* acid (*e*) volume needed to make 280 ml of 0.14 *F* acid.

10. Balance the equation:

$$As_2S_5 + HNO_3 = H_3AsO_4 + H_2SO_4 + NO_2 + H_2O$$

(*a*) Find the equiv. wts of the redox agents.

(*b*) If the HNO_3 used had a sp. gr. of 1.42 25/4, and was 72% acid by wt, find *N*.

(*c*) What vol. of this acid would theoretically be needed to react with 50 mg of As_2S_5?

11. The solubility of two typical salts is given below in g/100 g H_2O at various °C temperatures. (*a*) Plot °C on the abscissa and put both curves on the same plot. (*b*) What is the solubility of each at 50 C? (*c*) If one cools a saturated solution of each from 90 C to 10 C, what weights of salts crystallize? (*d*) What is the % by wt solute of each solution at 30 C? Can one determine the formality of either solution from this data alone? If not, what other measurements would be needed? (*f*) At what temperature is their solubility the same? (*g*) What is the molality of each saturated solution at 25 C?

Salt	0°	20°	40°	60°	80°	100°
$K_2Cr_2O_7$ (g/100 g H_2O)	5	12	26	43	61	80
NH_4Cl (g/100 g H_2O)	29.4	37.2	45.8	55.2	65.6	77.3

(*Ans.* (*b*) 34.0 and 50.4 (*c*) 63.0 and 38.0 (*d*) 16.7 and 29.3 (*f*) 91 C (*g*) 0.51 and 7.10.)

12. How does one prepare:

(*a*) A liter of $KMnO_4$ solution of such normality that each ml would oxidize 6 mg of Fe^{+2}? (*Ans.* 3.38 g/liter = 0.107 *N*.)

(*b*) A liter of HCl solution of such normality that each ml would be equivalent to 1% $NaHCO_3$ in reacting with a 1.000-g sample of impure $NaHCO_3$? (*Ans.* 4.35 g/liter = 0.119 *N*.)

13. Jackson Slipshod dissolves 50 g of $AgNO_3$ in 50 ml of H_2O giving 100 g of solution. He computes the normality as $N = 500$ g per liter/170 mol.wt = 2.94. Jackson's Uncle Frisbee (who helps Jack with home work) says that a weight of solution and not its volume was used in the calculation so what he actually found was solution molality. What goes on here?

14. What weights of alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, (mol. wt 949) are needed to prepare solutions 1.0 *N* in K^+, in SO_4^{-2}, and in Al^{+3}? (*Ans.* 474 g, 119 g, 158 g).

15. One has a closed piping system for hot water circulation. One lb of potassium dichromate is dissolved in the water and analysis after mixing shows the solution contains 5 mg of Cr^{VI} per liter. Find (*a*) the solution *F* and (*b*) the gal of water in the pipes.

3

ELECTRONS, ATOMS, BONDS, AND MOLECULES

Introduction

The first modern era atomic model was proposed in about 1900 by J. J. Thompson. He visualized atoms as spheres containing plus and minus charges, respectively protons and electrons, scattered uniformly throughout. He supported this conclusion by calculating that in such a model electrons would vibrate approximately at the frequency of visible light, and hence be able to give the familiar flame tests. The Thompson model lasted until 1911 when Ernest Rutherford, Nobel laureate and the father of atomic physics, announced another concept of the atom which is a helpful visualization even today. His model consisted of a very dense nucleus containing positive protons, equal in number to the atomic number, surrounded by a cloud of negative electrons sufficient to make the atom neutral. He was able to show that the radius of the nucleus is in the order of 10^{-12} cm, whereas the radius of the whole atom including the electron shell is about 10^{-8} cm. The experiment that led him to these conclusions was the now classical one involving bombardment of a very thin gold foil with α-particles (helium nucleii from a radioactive source) and observation of the emergent beam as it traversed a Wilson cloud chamber behind the foil. This chamber is a device containing air supersaturated with water vapor in which moving charged particles ionize air molecules and cause water droplets to condense in their wake and render their paths visible. From the fact that the positive nucleii of atoms in the foil scattered so relatively few α-particles, Rutherford concluded that matter is essentially porous and that Thompson's model did not fit the experimental evidence. From the scattering angles and number of α-particles deflected, Rutherford also computed the atomic and nuclear dimensions given above.

In 1913, the Danish physicist Niels Bohr, who later received a Nobel Prize for his work, began studies to extend the atomic concepts to account for more of the known fundamental concepts of electromagnetism than did any of the atomic models of the time. The idea of a cloud of electrons somehow surrounding the nucleus of the atom did not appear satisfactory and consistent with his experience in related physical measurements for several reasons:

(1) It is too vague about an orderly electron arrangement which one instinctively feels is present because all atoms of a given element have the same definite chemical properties.

(2) If the electron vibrates in its orbit, and it does, it should give off some sort of radiation, but this would mean decreasing electron energy and a gradual spiraling of the electron into the nucleus.

(3) If electrons are in the process of dropping toward the nucleus, they should be found at all distances from it, and gaseous elements should give a continuous spectrum corresponding to all energy states for electrons under the influence of an electric discharge. Such is not the actual case, however, because Balmer in 1885, Paschen in 1896, and others since showed that elements give spectra consisting of lines, which can be interpreted best if one assumes that electrons have a limited number of fixed energy states.

Line Spectra and Energy Levels

The experiments on the line spectra of hydrogen are important since they yielded fundamental information on electrons. The experimenters found that no energy was emitted when hydrogen atoms were bombarded in an electric discharge tube by a beam of speeding electrons until the energy of the beam was increased to a certain value, whereupon the process of energy transfer suddenly became efficient. At this point many of the bombarding electrons lost their speed and the energized H atoms which had been struck gave off light of characteristic wavelength. By using increasingly energetic electrons it was found that there are only a limited number of energies that are absorbed and that result in a series of energy emissions from the excited atoms. These energies are manifested as spectral lines that can be sorted out with a spectrometer or spectroscope (special experiment 5). If the lines are in the visible region, they constitute an *optical spectra.* Excited molecules are also capable of electronic disturbances and of giving spectra.

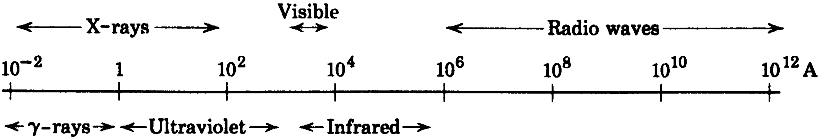

FIG. 3-1. Electromagnetic radiation. Wavelenths are in Angstrom units (1 A = 10^{-8} cm). See Fig. 23-2 for an expansion of the visible region.

Optical spectra come from a disturbance of valence electrons, or, if greater excitation is involved there, *ultraviolet spectra* is the result. A particular type disturbance of the *K* and *L* electrons results in *X-ray spectra*. *Infrared spectra* are associated with internuclear disturbances of vibration and rotational motion. Measurements on these phenomena have proved invaluable in atomic and molecular structure studies. Subsequently all the elements were investigated in this way. All give line spectra.

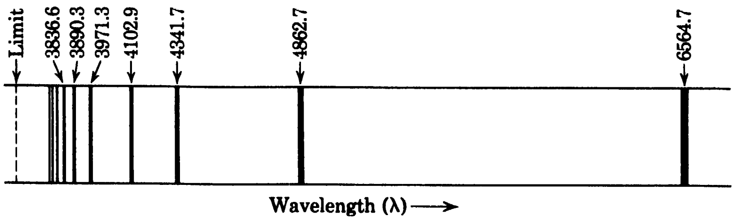

FIG. 3-2. The Balmer series of spectral lines obtained by exciting H atoms.

Up to 1913 no satisfactory correlation was made between the spectral data and the structure of atoms, though it seemed obvious that there should be a connection of fundamental significance. Then Bohr gave his interpretation based upon the *quantum theory* and the great puzzle of electronic structure began to be solved. In 1900 *Max Planck*, and in 1905 *Albert Einstein*, had shown that certain radiation effects could be satisfactorily accounted for if one postulated that light is absorbed and emitted in definite units (called *quanta*) having energy $h\nu$.* Bohr began with the assumption that the hydrogen spectra was due to energy emitted by the electron, which, having been knocked out of its normal position, was returning to that state of lower energy. It followed that the extra-

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* The symbol h is Planck's constant, 6.624×10^{-27} erg sec, and ν is the frequency of radiation in cycles/second. It is defined as c/λ where c is the speed of light, 3×10^{10} cm/sec and λ is the Angstrom wavelength of the radiation being studied.

nuclear electron did not have arbitrary energy but existed in ***definite energy levels*** called ***stationary states***, and a definite amount of energy was needed to displace the electron from a lower energy level (closer to the nucleus) to a higher one (further from the nucleus). Conversely this unit of energy was released when the electron dropped back to its original position.

If E_1 is the energy of a stationary state of higher energy and E_2 the energy of the next state of lower energy, then a quantum of energy is the difference between them, since the electron can exist only in these discrete states and in no intermediate ones, or

$$E_1 - E_2 = h\nu$$

ν is the frequency of radiation needed to cause the electron to jump from E_2 to E_1, or the frequency emitted when it falls from E_1 to E_2. Proceeding with this concept Bohr was able to calculate the wavelengths of

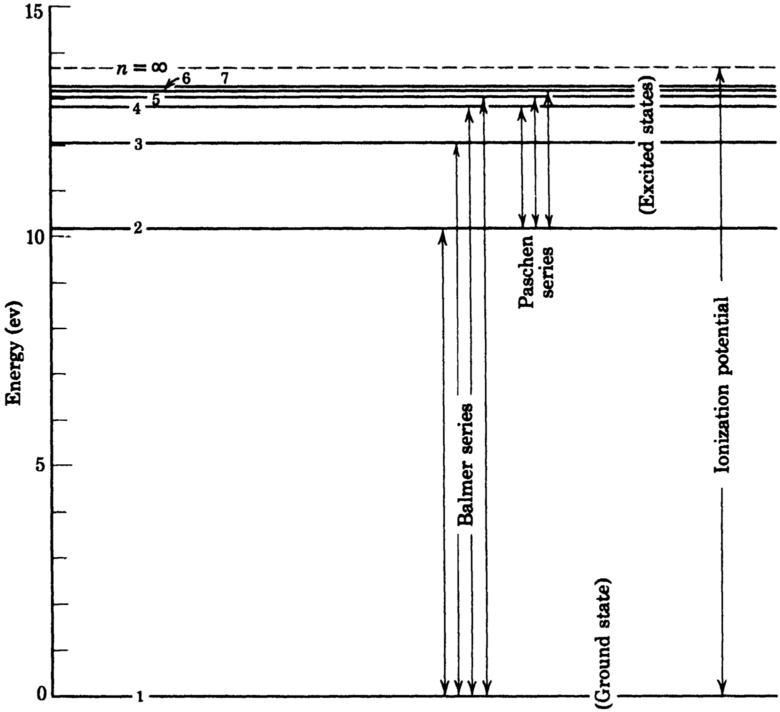


FIG. 3-3. Energy level diagram for hydrogen. To remove the electron from its normal state, $n = 1$, to infinity, $n = \infty$, requires 13.60 electron volts (ev), its ionization potential. One ev is the energy gained by an electron when accelerated by a potential of one volt. One ev is equal to 1.59×10^{-12} ergs and corresponds to an energy of 23.05 kcal/g mole.

hydrogen spectral lines and the radii of electron energy levels from data and physical constants established by earlier investigators by using a variety of different experiments, some not directly related to hydrogen spectra. The concept of *energy quantization* paved the way for the determination of all electronic configurations and chemical bonding as well, two foundations of chemistry.

When the energy levels of an atom are determined from its spectra, an *energy level diagram* can be prepared. One of the most significant values in it is the energy needed to remove the least tightly held electron from the atom to a distance sufficient so that the positive nucleus no longer exerts any attraction on it. This energy is called the *ionization energy or potential.* The energies associated with the removal of successive electrons can also be found experimentally. It is evident that chemical properties are related to these potentials since atoms form chemical bonds according to their abilities to effect a transfer or sharing of electrons. This is considered in a later section in the chapter (see Table 3–5).

Refinement of the Bohr Atom; Quantum Numbers

Study of spectra of elements with instruments of greater resolving power followed Bohr's work, and the new data showed a need for extending the Bohr theories. It was demonstrated, for example, that more spectral lines existed than were originally believed present. This meant that there were more subtle electronic energy changes than formerly proposed; as each of these may be quantized, more quantum numbers were needed to describe the electron. It was then found that certain rules or *selection principles* need be applied to the handling of the numbers for proper accounting of the observations. The reasons behind these will not be developed here, but the rules are summarized below.

(1) The principal quantum number n can have integral values 1, 2, 3 . . . denoting three dimensional shells of energy in which the electron might be found. These are alternately called the K, L, M, N, O, P, and Q shells. The shell closest to the nucleus is described by $n = 1$, the next $n = 2$, etc. If n is large, the electron cloud around the nucleus is large.

(2) For each value of n there are n sublevels within a shell. These are differentiated by the quantum number l, known as the *secondary* or *azimuthal quantum number*. l is linked with the angular momentum of the electron. It may have values 0, 1, 2 . . . $(n - 1)$. Electrons for which $l = 0, 1, 2, 3$ are respectively called s, p, d, f electrons, after spectroscopists' early nomenclature for spectral lines (*s*harp, *p*rincipal, *d*iffuse, *f*undamental). A $1s$ electron is thus an electron in the first shell for which $l = 0$; a $4f$ electron is in the fourth shell with $l = 3$, etc.

TABLE 3–1. VARIATION OF l WITH n

n	Shell	l	Electrons
1	First = K	0	s
2	Second = L	0, 1	s, p
3	Third = M	0, 1, 2	s, p, d
4	Fourth = N	0, 1, 2, 3	s, p, d, f

The l quantum numbers are important in chemical bonding considerations and are considered again under covalence in this chapter. For our purposes, there is no l value greater than 3, so s, p, d, and f electrons will be the only types. l gives the shape of the electron distribution: the simplest is spherical, the next is figure-8 shaped, etc., as explained later.

(3) In 1896, *P. Zeeman* had noted that spectral lines that normally appear singly may appear as doublets under the influence of a magnetic field. To explain this, the quantum number m was introduced. This is related to a part of the total angular momentum of the electron in the direction of the magnetic field. The quantum theory shows mathematically that if this is quantized, it can have all integral values between $-l$ and l including zero, in other words a total of $(2l + 1)$ values. m relates the orientation of the electron clouds to an externally applied magnetic field. For us, the magnetic quantum number will be of minor importance.

TABLE 3–2. VARIATION OF m WITH l

l	Electron	m
0	s	0
1	p	−1, 0, 1
2	d	−2, −1, 0, 1, 2
3	f	−3, −2, −1, 0, 1, 2, 3

(4) Spectral lines under high resolution often appear as multiplets lying close together rather than as single, relatively broad lines. This was not explained until 1925 when *G. Uhlenbeck* and *S. Goudsmit* showed mathematically that the effect could be explained if the electron were considered to be spinning, that the spin contributed to its total angular momentum, and that this contribution might be quantized. The spin quantum number is designated s and can have only the values $\frac{1}{2}$ and $-\frac{1}{2}$

representing opposite spins and corresponding to two levels of nearly equal energy.

(5) *W. Pauli* announced a unifying principle in 1925 that makes it possible to properly assign energy states to the electrons in an atom. One might, for instance, logically suppose that since the first orbit is the one with lowest energy, electrons should be found only in that one. Pauli proposed, however, that it is impossible for two electrons in the same atom to have all four quantum numbers, n, l, m, and s, alike—a statement known as the *Pauli exclusion principle.* This means that a shell may have only as many electrons as the quantum numbers and the Pauli principle permit. The total number of electrons permitted in a shell is found to be $2n^2$ and the number of shells in normal states of atoms is limited as noted in the next table. No atom is known in which the *O*, *P*, and *Q* orbits are completely filled, and no uncombined atom has more than eight electrons in its outer shell.

TABLE 3–3. QUANTUM NUMBER OF ELECTRONS

n	l	m	s	Electrons	Subtotals	Totals
$1 = K$	0	0	$\pm\frac{1}{2}$	1*s*	2	2
$2 = L$	0 1	0 0, ±1	$\pm\frac{1}{2}$ $\pm\frac{1}{2}$	2*s* 2*p*	2 6	8
$3 = M$	0 1 2	0 0, ±1 0, ±1, ±2	$\pm\frac{1}{2}$ $\pm\frac{1}{2}$ $\pm\frac{1}{2}$	3*s* 3*p* 3*d*	2 6 10	18
$4 = N$	0 1 2 3	0 0, ±1 0, ±1, ±2 0, ±1, ±2, ±3	$\pm\frac{1}{2}$ $\pm\frac{1}{2}$ $\pm\frac{1}{2}$ $\pm\frac{1}{2}$	4*s* 4*p* 4*d* 4*f*	2 6 10 14	32
$5 = O$	0 1 2 3	0 0, ±1 0, ±1, ±2 0, ±1, ±2, ±3	$\pm\frac{1}{2}$ $\pm\frac{1}{2}$ $\pm\frac{1}{2}$ $\pm\frac{1}{2}$	5*s* 5*p* 5*d* 5*f*	2 6 10 14	32
$6 = P$	0 1 2	0 0, ±1 0, ±1, ±2	$\pm\frac{1}{2}$ $\pm\frac{1}{2}$ $\pm\frac{1}{2}$	6*s* 6*p* 6*d*	2 6 10	18
$7 = Q$	0	0	$\pm\frac{1}{2}$	7*s*	2	2

Wave Mechanics

Further modifications of the theories of atomic structure followed the suggestion by *L. de Broglie* in 1924 that the electron, like a photon of light, had both corpuscular and wave properties, and that wavelengths could be assigned to electron motion. This was demonstrated experimentally in 1927 by *C. J. Davisson* and *L. H. Germer*, two American physicists, who showed that an electron beam, like X-rays, is diffracted by crystals in which layers of atoms act as a diffraction grating (see Chapter 13). Since the production of a diffraction pattern can only result if the electron beam has wave character, the experiment proved the de Broglie idea. The wavelength λ of the electron can be calculated from the *de Broglie equation*,

$$\lambda = h/mv$$

where h is Planck's constant, m the mass of the electron, and v its velocity. The new theory developed to use the discovery of the electron's wave character and to put the quantum theory on a sounder theoretical basis is called *wave mechanics* or *quantum mechanics*. The mathematical treatment of the new mechanics by the physicists *E. Schrödinger*, *W. Heisenberg*, *A. Sommerfeld*, and *P. A. M. Dirac* is extremely complex.

The electron's motion is pictured in two dimensions and is like that of a shaken rope. In the accompanying figure, the wave patterns are shown as being limited to those which fit the figure, that is, give reinforced waves.

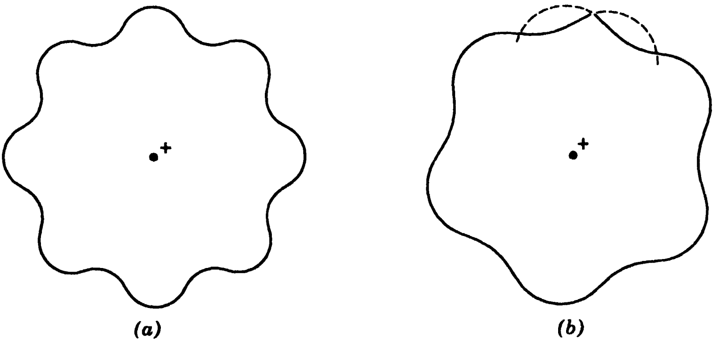


FIG. 3-4. Two dimensional representation of electron wave motion: (*a*) reinforcing and (*b*) nonreinforcing waves. Only (*a*) is permissible.

A three-dimensional picture is not easy to give and from the student's viewpoint the wave concept of electron character suffers because of lack of an atomic model, which was one attractive feature of the Rutherford and Bohr ideas. Wave mechanics treats the electron's position statistically. According to the important *Heisenberg uncertainty principle* (1927), it is impossible experimentally to simultaneously determine the position and speed of the electron. It is also impossible to consider the electron either exclusively as a wave or a particle, but instead one must think of it as having both properties, either of which can become predominant in selected experiments. In wave mechanics an electron is said to be in an *orbital* rather than in an *orbit*. Each orbital can contain a maximum of two electrons. each with a different spin. Orbitals have different shapes and it will be shown later that this results in predictable geometry of molecules and ions whose atoms used certain orbitals in bonding.

s orbitals are spherical and can be thought of as a shell of charge, the density of which is greatest in the center of the shell wall and increasingly diffuse away from the center, as the probability of finding the electron in different parts of the shell is described. The electron's speed is also variable. When both electron motion and speed are treated statistically it is found that the Bohr radius and speed are the average values obtained, however.

p orbitals are mutually at right angles to each other and are pictured as figure-8 shapes; *d and f orbitals* are more complicated. (See Fig. 3–11.)

Electron Configurations

The combined efforts of physicists in spectroscopic investigations and the development of mathematical expressions, and of chemists in relating the physical data to chemical properties, ultimately gave us the probable electronic structures for all the elements. Since the electrons are used in chemical bonding, this information is vital to chemistry.

The filling of orbitals by electrons, in the progression toward heavier elements, can be predicted fairly accurately from two principles. The first is that the most stable (lowest energy) orbitals fill in preference to others. The second is known as the *rule of maximum multiplicity*, which empirically states that for *p*, *d*, and *f* subshells which are capable of holding 6, 10, and 14 electrons, respectively, as many orbitals as possible are singly occupied by electrons before electron pairing (by virtue of opposite spin) takes place. Orbitals will be represented here by circles, and dots inside the circles will represent electrons. Two dots will be a pair of electrons with opposed spins and they are all that can be contained in an orbital. A single dot will mean an unpaired electron. The following figure shows the order in which orbitals are filled.

Examination of Fig. 3–5 brings forth several generalizations to aid in writing ground-state electron configurations.

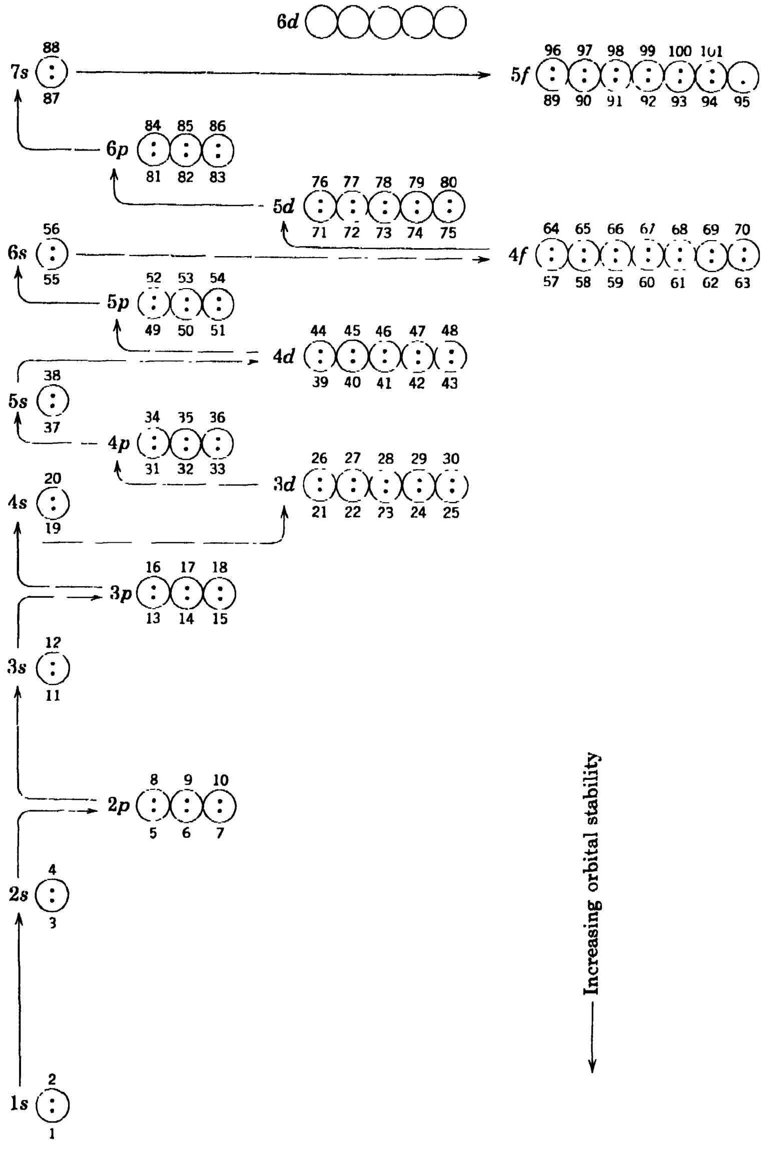


FIG. 3-5. Stabilities of electron orbitals. The small numbers are atomic numbers. Arrows give the order of filling.

(1) No electrons enter a *d* subshell until the *s* subshell of the next higher shell has been filled. This is the reason that there are never more than eight electrons in the outermost shell of any atom.

(2) The 4*f* subshell gets no electrons until after the 5*s*, 5*p*, and 6*s* subshells have been filled and the 5*d* subshell has received one electron. The same is true of the 5*f* subshell with respect to prior filling of the 6*s*, 6*p*, 7*s*, and single electron addition to 6*d*. The consequence of this filling order is that there are never more than 18 electrons in the next to outermost shell of any atom.

(3) The electron added in each succeeding element enters the orbital with the lowest $n + l$ value, and when two orbitals have that value, addition is in the orbital with the lower value of *n*.

The student should verify these rules by selecting some examples from the figure.

One may use this diagram to determine the electronic arrangement of atoms or ions derived from them, and as will be seen the number and pairing of electrons and the type orbitals will be matters for attention in predicting such things as the stability, magnetic properties, and geometry of ions and molecules.

Electronic configurations are usually given with a shorthand notation in which each subshell is described by main quantum number, electron type, and a superscript denoting the number of these electrons. For example, element 18, argon, may be described from Fig. 3–5 as having 2 electrons in the 1*s* state, 2 in the 2*s*, and 6 in the 2*p* states; 2 in the 3*s* and 6 in the 3*p* states; or simply, $1s^2$, $2s^22p^6$, $3s^23p^6$. To describe Mn^{+2} in the same way, Fig. 3–5 shows that the *atom* has 25 electrons arranged as $1s^2$, $2s^22p^6$, $3s^23p^6$, $4s^23d^5$. The *dipositive ion* has 2 fewer electrons, but since the 4*s* and 3*d* electrons are approximately equally easy to remove, several structures are possible beyond the filled third shell: $4s^23d^3$ or $4s^13d^4$ or $3d^5$. Magnetic measurements (described later) indicate five unpaired electrons, thus only the last two are possible configurations.

The Periodic Table and Atomic Structure

The periodic arrangement of elements may profitably be reviewed at this point in the light of electron configurations. Figure 3–5 and Fig. 3–6 should be referred to in this discussion.

The first orbital, 1*s*, can only contain two electrons and the *K* shell is completed in helium. The next orbital to begin filling is the 2*s* in lithium. The next electron completes the 2*s* orbital in beryllium. The next three electrons to be added in *B*, *C*, and *N* appear singly in the 2*p* orbitals, and pairing of these occurs in the next three elements, O, *F*, and Ne. As previously explained the *L* shell is complete with two *s* and six *p* electrons,

Group / Period	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1 1*s*	1 H																1 H	2 He
2 2*s*2*p*	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3 3*s*3*p*	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 A
4 4*s*3*d* 4*p*	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5 5*s*4*d* 5*p*	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6 6*s* (4*f*) 5*d* 6*p*	55 Cs	56 Ba	* 57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7 7*s* (5*f*) 6*d*	87 Fr	88 Ra	** 89 Ac															

* Lanthanide Series 4*f*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
** Actinide Series 5*f*	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 E	100 Fm	101 Mv		

FIG. 3–6. The long form of the periodic table.

therefore the next electron to be added in sodium, element 11, is a 3*s* electron. The 3*s* and 3*p* orbitals are built up in the same fashion as the 2*s* and 2*p*, but ten more electrons are needed to complete the 3*d* orbitals and this is not accomplished until Cu. From Fig. 3–5 it is seen that the 4*s* level is of slightly lower energy than the 3*d* so it is filling in K and Ca. As spectroscopic study shows, the next electrons go into the five 3*d* orbitals, between Sc and Cu, rather than the 4*p* positions. The elements in which this takes place constitute the first group of transition elements (see Chapter 17). None have all electrons paired. The 4*s* electrons remain one or two in number while the inner 3*d* orbitals are filling. In Cr and Cu a 4*s* electron has dropped back to the 3*d* state, this being possible since those two levels have about the same energy.

The 3*d* orbitals are filled and the *M* shell is closed with 18 electrons at element 30, zinc. From Ga to Kr the three 4*p* orbitals are filling. The next two electrons go into the 5*s* orbital, as shown in Fig. 3–5. These are elements 37 and 38, rubidium and strontium. Beginning with number 39, yttrium, and extending through number 47, silver, 4*d* orbitals rather than 5*p* are filling and these elements comprise the second transition series. The elements between cadmium and xenon have the 5*p* orbitals filling rather than 4*f*, and this is completed with xenon. Cesium and barium have the xenon core of electrons plus one and two 6*s* electrons, respectively. The next element is lanthanum and its added electron is in a 5*d* orbital. The next fourteen elements are peculiar in this way: electrons are added in the 4*f* orbitals so 4*f*, 5*d*, and 6*p* are all incomplete. These elements are called the *lanthanide series of rare earths* and are grouped separately at the bottom of the main table in Fig. 3–6. By the time element 71, lutecium, is reached, the *N* shell is fully expanded from 18 to 32 electrons.

Following the lanthanide series is another transition group, Hf through Au, in which the 6*s* level holds one or two electrons and filling is in the five 5*d* orbitals. From 81, thallium, to 86, radon, the three 6*p* orbitals are being completed.

The next horizontal row in Fig. 3–6 starts as the preceding one, one electron in an *s* orbital (7*s*) for francium and two for radium. The next added electron in actinium goes into a *d* orbital (6*d*) just as happened with element 57 in the previous row. Beginning with 90, thorium, there are three incomplete orbitals, 5*f*, 6*d*, and 7*s*. Of these, 5*f* is filling while 6*d* contains one, and 7*s* two electrons. The elements 90–103, of which the last two are as yet unknown, constitute a second rare earth group known as the *actinide series*. The elements beyond uranium are not naturally occurring but have been prepared synthetically by nuclear transformations. They are known as the *transuranium elements*.

Atomic Size and Chemical Properties of Elements

One might suppose that atomic size will vary directly with atomic number since the number of electrons increases and electron shells are filling. This is true for a given *vertical group* of elements in the periodic system but not true when considering a *horizontal period.* In the former, a new shell is being filled which results in a somewhat larger radius, but in the latter case the quantum group remains constant as the atomic number (nuclear charge) is increasing. This means that electrons are drawn closer to the nucleus and the size, generally speaking, shrinks. It increases suddenly with the alkali metals of group IA, however, because a new shell is starting (Fig. 3-7).

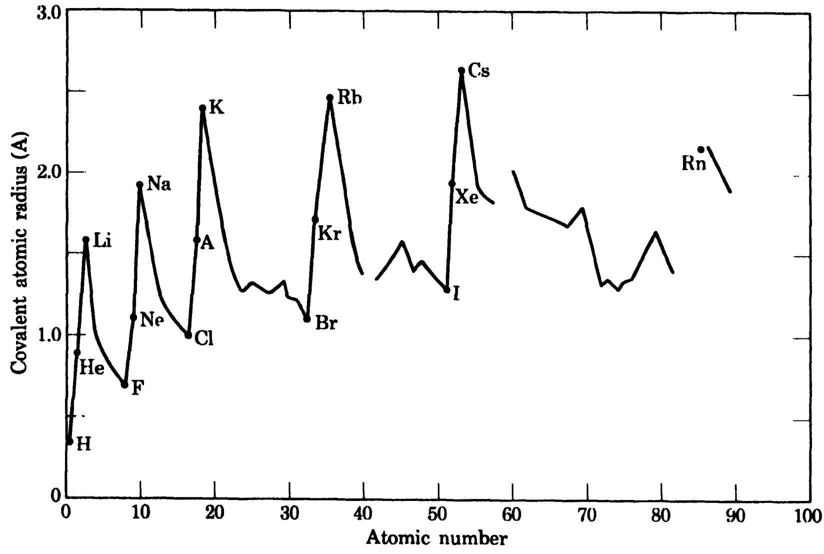


Fig. 3-7. Covalent radii of the elements.

Diffraction studies and quantum mechanical calculations have given approximate radii of elements in compounds in which bonding is by electron sharing (covalence) and radii of ions in compounds in which bonding is electrostatic between the ions (electrovalence). A number of generalizations can be made from a study of these radii, as noted in the next paragraphs.

A postive ion like Na^+ is expected to be smaller than the corresponding atom, because only the *K* and *L* shells are left after the electron is removed from the *M* shell. On the other hand the radius of a negative ion like Cl^- will be slightly larger than the corresponding atom, since the added electron is not accompanied by an added proton in the nucleus. Chloride ion has the same electronic configuration as argon but with one less unit of nuclear charge is more expanded. For a given element, a cation formed from the neutral atom is always smaller than the atom, whereas the corresponding anion is always larger. If several oxidation states are studied, the ionic size is found to vary inversely with the positive oxidation number, as shown in Table 3–4.

TABLE 3–4. RADII OF SOME IONS DERIVED FROM COMMON ELEMENTS

	Group IA			**Group VA**	
No. 3	Li^+	0.60 A	No. 7	N^{+5}	0.11 A
11	Na^+	0.95		N^{-3}	1.71
19	K^+	1.33	33	As^{+5}	0.47
37	Rb^+	1.48		As^{+3}	2.22
55	Cs^+	1.69	51	Sb^{+5}	0.62
				Sb^{-3}	2.45
	Group IIA				
4	Be^{+2}	0.31		**Group VIA**	
12	Mg^{+2}	0.65	8	O^{-2}	1.40
20	Ca^{+2}	0.99	16	S^{+6}	0.29
38	Sr^{+2}	1.13		S^{-2}	1.84
56	Ba^{+2}	1.35			
	First Row Transition			**Group VIIA**	
			9	F^-	1.36
24	Cr^{+3}	0.65	17	Cl^{+7}	0.26
	Cr^{+6}	0.41		Cl^-	1.81
25	Mn^{+2}	0.91	35	Br^{+7}	0.39
	Mn^{+7}	0.46		Br^-	1.95
26	Fe^{+2}	0.83	53	I^{+7}	0.50
	Fe^{+3}	0.67		I^-	2.16

Figure 3–7 shows that changes of atomic size with increasing atomic number are not great in the transition elements. The reason for this is that electrons are not filling the outermost 4*p* orbitals, but 3*d* instead. The two rare earth series at the bottom of the table show decreases in sizes with increasing nuclear charge, since in both series the filling is two orbits in from the outside, and each increase in atomic number merely results in a tighter holding of all electrons. These size changes are known as the *lanthanide* and *actinide contractions.*

Because of the regular decrease in diameter of the +3 lanthanide ions, they have been used in several classical studies to test trends in properties as functions of ionic size. As an example, it has been shown that stability of higher oxidation states increases in the series with increasing atomic number. It is characteristic of the higher states to have electron shared bonds (covalence) rather than ionic bonds, since highly charged ions are not stable. As the size of these ions varies inversely with atomic number, the heavier elements should hold electrons more tightly, show more covalence, and have more compounds containing the metal at higher oxidation numbers. Such trends have been experimentally verified. As another example, one expects the hydroxides, $M(OH)_3$, to become less basic with decreasing ionic size, since the smaller ions will exert greater electron attraction and allow H^+ but not OH^- to dissociate. This increase in acidic character has been observed. $La(OH)_3$ for instance is not only the strongest base in the series but also the strongest trivalent base known.

More quantitatively, if the ionic radius of the metallic element is < 0.5A, its hydroxide is acidic; if slightly > 0.5, the hydroxide is weakly acidic in the higher oxidation states; if $0.5 - 0.9$, the hydroxide is amphoteric; and if the radius is > 0.9, the hydroxide is definitely basic.

Ionic sizes and charges determine the orientation and number of groups (*coordination number*) that are capable of being held about a central element. The first horizontal row of elements has a coordination number of 3 with respect to oxygen, as shown by ions like CO_3^{-2} and NO_3^-. These are planar. Second- and third-row elements, being larger, can coordinate four oxygens giving tetrahedral ions like PO_4^{-3} and ClO_4^-. Heavier ions can coordinate six oxygens in an octahedral arrangement, as in $Sb(OH)_6^-$. Coordination numbers are considered further in the next chapter.

Ionization Potentials

Within a (vertical) family of elements the outer electron levels in the larger atoms are less affected by nuclear attraction than outer electrons in the smaller atoms, since the former are further removed from the nucleus. This effect is manifested in the ionization potentials of the elements (see Fig. 3–3 for H). A plot of atomic number versus ionization potential shows maxima corresponding to the noble gases and minima for the alkali metals, as expected. In addition, the potential varies inversely with atomic size within a family of elements, which is also expected for reasons given before: smaller atoms hold electrons more tightly, since the center of positive charge is closer to them.

In the series Li–Cs, cesium has the lowest ionization potential (removal of a 6*s* electron easier than a 2*s* in the lithium atom), is therefore the best reducing agent, forms a positive ion the easiest and has the greatest metallic character (Chapter 13).

In the series F–I, the electron is expected to be most difficult to remove from the smallest atom, since it must be taken from a shell closer to nuclear attraction than is true for the heavier atoms, and the potentials bear this out. The order of ionization potentials is the same as the trend in electron attracting abilities of the halogens: fluorine is the most electronegative element known and hence an excellent oxidizing agent.

Removal of a second electron from a unipositive ion requires more energy than removal of the atom's first electron, since it must be done against the attraction of a positive ion. Further electron removals become progressively more difficult, precluding the formation of highly charged positive ions in simple chemical reactions. If one electron is readily lost, but not two (Li for example), the valence of the element is +1, if two are detachable with reasonable energy, but not three (Ca for instance), the ion's valence is +2, etc. Table 3–5 helps such speculation.

By examining the ionization potential variations in proceeding horizontally across the periodic table one notices a general increase in value, since the additional electrons in heavier atoms are at about the same distance from the nucleus, thus the increased nuclear charge is capable of holding all electrons more tightly. There are some exceptions. The apparent discrepancy in the aluminum value (5.98) compared to that of the preceding element, Mg (7.64) (Table 3–5) is due to the fact that the added electron in Al is in a $3p$ orbital which is shielded by the just completed $3s$ orbital containing two paired electrons. This *shielding effect* means that the electrons closer to the nucleus absorb a disproportionate share of nuclear attraction, repel outer electrons, and in general allow the latter to be more capable of escape. In a given quantum shell, electron energies increase in the order $s < p < d < f$. It is thus easier to remove an f electron than an s, p, or d electron of the same shell.

In summary, one may state that ionization potential varies with nuclear charge, atomic radius, electron orbital, and screening effect. Generally the ease of electron removal decreases with increasing atomic number in a given horizontal period and increases with increasing atomic number in a given vertical column of the periodic table.

Trends in Families of Elements

Chemical reactions involve electrons in the outermost shells, and so their number, grouping, and energy are important in determining chemical properties. Study of the preceding sections and accompanying tables and figures shows that a repetition of outer electron configuration occurs periodically, and elements having such similarity possess chemical

TABLE 3–5. IONIZATION POTENTIALS OF SOME ELEMENTS

Atomic No.	Element	Group	Ionization Potentials In Electron Volts				
			First	Second	Third	Fourth	Fifth
1	H		13.60				
3	Li	(IA)	5.39	75.62	122.4		
11	Na		5.14	47.29	71.65	98.88	
19	K		4.34	31.81	46	60.9	
37	Rb		4.18	27.36	47?	80?	
55	Cs		3.89	23.4	35?	51?	
4	Be	(IIA)	9.32	18.21	153.9	217.7	
12	Mg		7.64	15.03	80.12	109.3	
20	Ca		6.11	11.87	51.21	67	
38	Sr		5.69	10.98			
56	Ba		5.21	9.95			
24	Cr	(Transition)	6.76	16.6	31?		
25	Mn		7.43	15.70	32?		
26	Fe		7.89	16.16			
27	Co		7.86	17.3			
28	Ni		7.63	18.2			
29	Cu		7.72	20.34	29.5		
30	Zn		9.39	17.89	40.0		
47	Ag		7.57	21.4	35.9		
5	B	(IIIA)	8.29	25.15	37.92	259.3	
13	Al		5.98	18.82	28.44	119.9	
6	C	(IVA)	11.26	24.38	47.86	64.48	392
14	Si		8.15	16.34	33.46	45.13	167
7	N	(VA)	14.54	29.60	47.43	77.45	97.86
15	P		11.0	19.65	30.16		
33	As		10?	20.1	28.0	49.9	62.5
51	Sb		8.64	18?	24.7	44.0	55.5
83	Bi		8?	16.6	25.4	45.1	55.7
8	O	(VIA)	13.61	35.15	54.93		
16	S		10.36	23.4	35.0	47.29	72.5
9	F	(VIIA)	17.42	34.98	62.65		
17	Cl		13.01	23.80	39.90		
35	Br		11.84	19.1	25.7		
53	I		10.44	19.4			
2	He	0	24.58	54.40			
10	Ne		21.56	41.07			
18	A		15.76	27.62			
36	Kr		13.99	26.4			
54	Xe		12.13	21.1?			
86	Rn		10.75				

properties in common. This idea is stated as the *periodic law*, which says that the chemical character of elements is a periodic function of their atomic numbers. The purpose of the following sections is to point out some trends both in horizontal (period) and vertical (family or group) progression through the periodic chart.

Group 0

This group of six "noble" gas elements has almost no chemical properties, and it was this feature that interested chemists. Once the electronic configurations were deduced, theories of chemical bonding followed, using the idea that other elements tend to lose, gain, or share electrons to attain the nearest noble gas (closed) electron arrangement, since that is the one with greatest stability and lowest energy. Table 3–6 shows that except for helium each element has eight electrons in the last shell.

TABLE 3–6. ELECTRON SHELLS OF GROUP 0 ELEMENTS

Atomic No.	Element	Shells and Electrons					
		K	*L*	*M*	*N*	*O*	*P*
2	Helium	2	8				
10	Neon	2	8				
18	Argon	2	8	8			
36	Krypton	2	8	18	8		
54	Xenon	2	8	18	18	8	
86	Radon	2	8	18	32	18	8

Groups IA and IB

Hydrogen is often included in both IA and VIIA, because like IA elements it can lose an *s* electron and become a positive ion or like VIIA elements can gain an electron and become a negative ion (H^- is the hydride ion). The other members of IA are known as the *alkali metals.* All have low first-ionization potentials, hence all give univalent positive ions and act as strong reducing agents. The ions have noble gas electron configurations and form ionic compounds bonded by electrovalences (see p. 51). *As in all periodic groups, the first element of the series is the one which differs most from the rest, whereas the heavier elements are generally the most closely related.* For example, lithium has the highest melting point, boiling point, and hardness and shows some properties characteristic of IIA elements. Other chemistry of these ions is discussed in relation to their qualitative analysis in Chapters 19 and 20.

The elements in group IB, Cu, Ag, Au, are the *subgroup*, whereas the alkali metals are the *main group* of group I elements. Main group elements are characteristically close in electron configuration to noble gas atoms, whereas subgroup elements are not, making for a single valence state in the former and variable valence in the latter. Elements of both groups IA and IB have one electron more readily removable than the rest, although the electron is more difficult to remove from IB members, and they accordingly show some electron sharing (covalent) type bonding which is generally lacking in compounds containing IA elements. The penultimate (next to last) electron shell in IB elements contains 18 electrons, and some of these can be used in bonding, giving the variable valence characteristics. The penultimate shell of IA metals contains two electrons in Li and eight for the rest; these groupings are too stable to be chemically reactive. Further chemistry of copper is given in Chapter 16 and that of silver in Chapter 15.

TABLE 3–7. ELECTRON SHELLS OF THE GROUP IA ELEMENTS

Atomic No.	Element	Shells and Electrons						
		K	*L*	*M*	*N*	*O*	*P*	*Q*
1	Hydrogen	1						
3	Lithium	2	1					
11	Sodium	2	8	1				
19	Potassium	2	8	8	1			
37	Rubidium	2	8	18	8	1		
55	Cesium	2	8	18	18	8	1	
87	Francium	2	8	18	32	18	8	1

Groups IIA and IIB

The elements of IIA, Be, Mg, Ca, Sr, Ba, and Ra, are known as *the alkaline earth metals*. Each has two *s* electrons in the outermost orbital and each exhibits divalency. Due to its small size, Be is the most "different" element of the series. Like other small ions, Be^{+2} is best capable of forming complexes and exhibiting covalence. Be resembles Al of group IIIA in this respect, something other group IIA elements do not. The gradation of properties due to change in ionic size are those expected; lower oxidation potential, etc., with heavier members of the group. Though the penultimate shell contains 18 electrons, none are available for bonding as described for IB metals, since IIA ions are dipositive, and too much energy is required to remove a third electron (Table 3–5).

The group IIB elements, Zn, Cd, and Hg, are also divalent since their electron structures are similar to those of group IIA metals. Mercury is unique among the IIB group. It forms the mercurous ion $^+Hg:Hg^+$, in which one electron from each atom is lost and another is used in a covalent bond. *Covalency is more common in the B group than A group.*

Groups IIIA and IIIB

The IIIA elements are B, Al, Ga, In, and Tl. The last shell of electrons includes a completed *s* orbital and one electron in a *p* orbital. The oxidation states of these elements are (I), (II), and (III), although much of their bonding is covalent. Boron forms no simple ions like B^{+3} and is always covalent. Boron resembles elements adjacent to it, Be and C, almost as much as it does elements below it. The heavier members of the group are more metallic. A glance at the properties of their hydroxides is instructive. $B(OH)_3$ is weakly acidic and is usually written as boric acid, H_3BO_3 (see Chapter 22, part I). $Al(OH)_3$ dissolves to give salts in either acid or base and hence is amphoteric; aluminum chemistry is discussed in Chapter 17. $Tl(OH)_3$ has no acidic properties and Tl(OH), the only stable univalent group III hydroxide, is a fairly strong base. *As a rule, base strength of hydroxides varies inversely with the oxidation state of the metal and varies directly with increasing atomic weight in a family of elements.* All the metals have co-ordination numbers of 4 or 6 in group III.

The group IIIB elements include Sc, Y, La, and Ac, and the two rare earth series as well (see previous discussion). The electronic structure of the latter has been given and it will suffice here to say that the normal oxidation state is (III), and changes in chemical properties are generally in the order expected through the series. Scandium resembles aluminum in that its salts are hydrolyzed and $Sc(OH)_3$ is very weakly basic. Lanthanum salts are less hydrolyzed, its hydroxide is fairly basic, and its chemistry is something like that of Ca. The bonding in these elements is predominantly covalent and they have coordination numbers of 6 and/or 8.

Groups IVA and IVB

All members of these groups have 4 electrons available for bonding and by means of electron sharing can acquire stable octets. The elements of IVA are C, Si, Ge, Sn, and Pb. Again the difference in properties of the first two elements is great, and that of the lower elements much less. Carbon can hold a minimum of 2 and maximum of 4 atoms in covalence, whereas the other elements can bond with 2, 4 or 6 groups. Carbon is unique among all elements in that C—C bonds are strong and long chains and extended rings containing many C atoms are known (Chapter 12). Silicon and germanium also have the properties of nonmetals; they do not give simple ions in solution but are capable of forming covalently bonded compounds, many of great complexity. Lead and tin are metallic; they are discussed in Chapter 16.

The IVB elements, Ti, Zr, and Hf, have 2 electrons in the last level and 10 in the penultimate shell and have oxidation states of (II), (III), and (IV). As expected, covalency decreases with increasing atomic number. None of these is capable of existing as an ion with +4 charge in aqueous solution, however, since the distorting effect of an ion with such a high charge density means it will react with water to form oxygenated ions such as TiO^{+2}. (See Chapter 20.)

Groups VA and VB

The members of group VA are N, P, As, Sb, and Bi and of VB, V, Nb, and Ta. There is not much similarity between the two groups except for some compounds whose oxidation states are (V), as PO_4^{-3} and VO_4^{-3}.

The main group elements form a well-defined series with regularly changing properties due to atomic size variation. The smaller atoms, having greater influence over electrons, can form stronger acids like HNO_3 than can larger central atoms, whose weaker hold on electrons permits the electrons to in turn bond acidic hydrogens more firmly. Multiple bonds and general covalency are more common again in the lighter elements. Sb and Bi are the only metals in group VA and they can form trivalent cations; pentavalent ions have too great a charge to exist and this oxidation state is only known in complex ions like $Sb(OH)_6^-$. See Chapter 16 for further chemistry of As, Sb, and Bi.

The group VB elements are among the transition metals and show the expected gradation of properties. Niobium and tantalum are chemically quite similar, whereas vanadium is the "different" group VB metal. Its chemistry is complex (see Chapter 20) because of the importance of all its oxidation states, (II), (III), (IV), and (V). These, respectively, have 3, 2, 1, and 0 unpaired electrons.

Groups VIA and VIB

The A group elements are O, S, Se, Te, and Po and the B group are Cr, Mo, and W. Except for some compounds in which the oxidation state is (VI), SO_4^{-2}, TeO_4^{-2}, CrO_4^{-2}, WO_4^{-2}, there are few similarities between the groups. *It is a rule that the dissimilarity increases between main and subgroup as elements further toward the right of the periodic chart are considered.*

The group VIA elements need 2 electrons to complete an octet in the last shell and do exist as ions having a valence of −2; the members beyond oxygen also show oxidation numbers of (III), (IV), and (VI). Bonding is covalent in these and none of the elements is markedly metallic. Oxygen has the greatest electronegativity among them (Fig. 3–14), and is different from the others because of this.

Of the group VIB elements, Cr is unique (Chapter 17) and Mo and W more similar. Cr^{III}, Cr^{VI}, Mo^{VI}, and W^{VI} are the important oxidation states and many complex ions containing them are known. *The tendency toward condensation of oxygenated compounds and ions increases with atomic number* (simplest: $2CrO_4^{-2} + 2H^+ = Cr_2O_7^{-2} + H_2O$), which makes the chemistry of Mo, and more especially W, exceedingly complex. *Acid strength decreases with increasing condensation*, a generalization not restricted, however, to these elements. Mo and W are considered further in Chapter 20.

Groups VIIA and VIIB

In group VIIA are the closely related halogens, F, Cl, Br, and I (and At), and in VIIB, Mn, Tc, and Re, whose similarity to the main group is meager.

The halogens are electronegative, since by gaining an electron each attains the next rare gas configuration. Besides a valence of −1, these elements show an increasing number of covalences with increasing atomic number; F having a maximum of 2 as $(HF)_2$; Cl, 4 as $HClO_4$; Br, 5 as BrF_5; and I, 7 as IF_7. F is the "different" halogen. It is a very powerful oxidant, has the highest electronegativity of any element, and because of this and its small size forms compounds the other halogens cannot.

TABLE 3–8. ELECTRON SHELLS OF THE GROUP VIIA ELEMENTS

Atomic No.	Element	Shells and Electrons					
		K	*L*	*M*	*N*	*O*	*P*
9	Fluorine	2	7				
17	Chlorine	2	8	7			
35	Bromine	2	8	18	7		
53	Iodine	2	8	18	18	7	
85	Astatine	2	8	18	32	18	7

Of the group VIIB elements, only Mn is important; Re is rare, and Tc is one of the elements only known through synthesis by nuclear transformation, in this case deuteron bombardment of Mo followed by chemical separation. It resembles Re more closely than Mn. Manganese has all positive oxidation states of (I) through (VII), but the only ion it forms that is related to those of the halogens is MnO_4^-, which like ClO_4^- has the central element in the (VII) state. Manganese chemistry is more fully described in Chapter 17.

Group VIII

This central periodic grouping contains three sets of three elements each. For purposes here the first member of each group will be discussed briefly, namely Fe, Co, and Ni (note their positions, Fig. 3–6), since they are included in the laboratory work. (See Chapter 17.)

With increasing atomic number, the ability to form the tripositive state decreases sharply; Fe^{III} is common, quite a number of Co^{III} complexes have been prepared, but only a few compounds of Ni^{III} are known. Salts of the divalent ions are most common and stability of this oxidation state increases in the same order. Oxidation states beyond (III) are not stable in neutral aqueous solution because of their strong oxidizing power. These typical transition metals have unpaired electrons due to an incomplete penultimate shell containing between 8 and 18 electrons. Solutions of such ions absorb light in the visible region and appear colored. Iron has 8 more electrons than the preceding rare gas, cobalt 9 more, and Ni, 10. The heavier elements below these three show similar trends. In the triad Ru, Rh, Pd, the tendency for formation of higher oxidation states decreases in that order as is the case for the triad Os, Ir, Pt. Thus in the fluorides of the latter, OsF_8 is known but only IrF_6 and PtF_3 have been synthesized.

Chemical Bonding

Now that ideas concerning electronic configurations have been reviewed and extended and some relationships among periodic groupings of elements mentioned, the remainder of this chapter will deal with forces holding atoms together and methods of investigating chemical bonding.

ELECTROVALENCE

The *electrovalent or ionic bond* concept was given by *Kossel* in 1916. He simply suggested that properties of electrolytes could be best explained if it is assumed that salts are composed of ions bonded together by electrostatic attraction between unlike charges. Ions are formed by electron transfer (redox) between atoms such that the resulting configurations have greater stability. Anions formed in this way have rare gas structures, whereas cations may or may not result in such electron arrangement. The simplest cases are those involving elements of the electronegative groups VIA and VIIA and the electropositive groups IA and IIA. Figure 3–8 shows how typical elements of these groups may react to yield noble gas configurations.

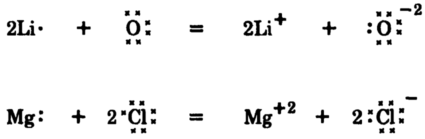


FIG. 3–8. Formation of two compounds by electron transfer. Dots represent electrons from the metals, ×'s those from the nonmetals. The ions are held together by electrostatic (coulombic) forces exerted in three dimensions which result in the building of symmetrical ionic crystals.

Subgroup elements form ions that do not have noble gas arrangements. *Subgroup ions are characterized (a) as possessing 18 electrons in the last shell or (b) as having between 8 and 18 electrons in the last shell, which is called the transition type structure.* Thus Zn, 2, 8, 18, 2, gives Zn^{+2}, 2, 8, 18, and Cu, 2, 8, 18, 1, gives Cu^{+}, 2, 8, 18, while Fe, 2, 8, 14, 2, gives Fe^{+2}, 2, 8, 14, and Fe^{+3}, 2, 8, 13. *The most stable cations are those with the rare gas structure, next are those with the 18 electron group arrangement, and last are those of the transition ion type.* The latter types increase their stabilities, however, through complex formation by addition of groups capable of donating otherwise unshared electron pairs to vacant orbitals in the metal ions (Chapter 4).

From a study on bond types as related to atomic size, ionic charge, and electron configurations, *K. Fajans* (1924) announced several generalizations that aid in predicting what kind of bonding to expect in a given compound. *According to the Fajans Rules, electrovalency is expected if (a) the ions are electronically stable (as explained above), (b) the ionic charges are small, and (c) the cation is large and the anion is small.* The reason for the operation of these principles is that electron loss is best accomplished if only one electron is removed and its position was originally distant from the nucleus (compare Li and Cs, Table 3–5, for example), and electron gain is best made by small atoms in which the attracting nucleus is close. If the compound in question has characteristics opposite the above, electron shared bonds (covalence) is expected. There are many intermediate cases as well in which bonds are said to possess a mixture of electrovalent and covalent character.

Ionic compounds are strongly bonded. They can be thought of as large symmetrical aggregates of ions in which a given ion is attracting and is surrounded by a fixed number of oppositely charged ions. As a consequence the compounds show electrical conduction in the molten condition as well as in aqueous solutions, and the crystals are hard and high melting.

With enough data available one can calculate semiquantitatively whether or not ionic bonds are capable of formation when two free atoms combine. Though this will not be developed further here, one may say first that if the energy of the ionic compound is less than the energy of the starting atoms, bond formation is possible. One then takes into account energy terms related to the heat of reaction and to the production of free atoms from the solid or gaseous elements. Other factors to consider include the cation's ionization potential, the tendency for the electronegative element to gain electrons ("electron affinity"), and the attractive and repulsive forces acting between the resulting ions when the crystal forms (crystal energy). Calculated and measured values for various of these terms show good agreement.

Magnetic Susceptibility

Ionic compounds have been studied in many ways, some of which are given in Chapter 5 (ions in solution) and Chapter 13 (symmetry in crystals). An interesting field of study that will be outlined here for its application later in the discussion of Werner ions is that of *magnetic susceptibility*.

Matter is *ferromagnetic* (limited to materials ordinarily considered magnetic, like Fe, Co, Ni, and their alloys), *paramagnetic*, or *diamagnetic*. The latter effects are much weaker than ferromagnetism. A paramagnetic substance in the solid state or in solution will move in the direction of increasing field strength of an electromagnet, whereas a diamagnetic substance moves out of the magnetic field. Measurements of these effects are made by use of the *Gouy balance* (1889).

It is a fact that substances containing atoms having unpaired electrons are paramagnetic and others are diamagnetic, and, further, that their magnetic moments are directly related to the number of unpaired electrons. The rotational motion of unpaired electrons sets up a weak but measurable moment or field while paired electrons cancel each other's effect. The balance pictured in Fig. 3–9 is capable of distinguishing these effects and their magnitude. From Gouy data the moments can be calculated and are expressed in *Bohr magnetons*, the unit being 9.18×10^{-21} gauss-cm per ion. An ion having x unpaired electrons will have a calculated moment of $[x(x + 2)]^{\frac{1}{2}}$ magnetons. From Fig. 3–5 and magnetic data, one can, for example, deduce the rule of maximum multiplicity. It will be shown in

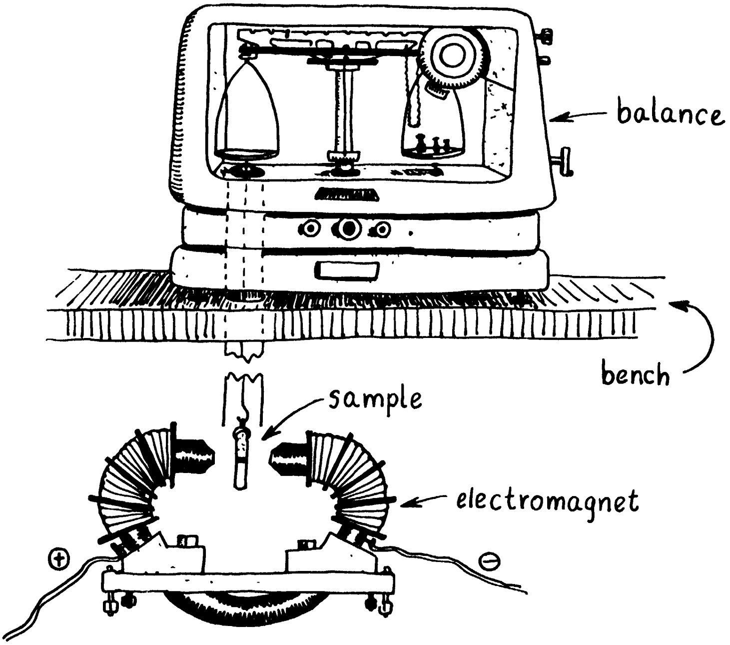


Fig. 3-9. The Gouy balance for determining magnetic susceptibilities. If the sample is paramagnetic it is drawn toward the magnet and more counter weight is added on the balance. If it is diamagnetic, the field repels the sample and less counter weight is needed.

Table 3-9. Magnetic Moments and Electronic Configurations of Representative Ions

Ion	Electronic Distribution						Unpaired Electrons	Calculated Moment, magnetons
	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*		
K^{I}	(:)	(:)	(:)(:)(:)	(:)	(:)(:)(:)		0	0
V^{IV}	(:)	(:)	(:)(:)(:)	(:)	(:)(:)(:)	(·)	1	1.73
V^{III}	(:)	(:)	(:)(:)(:)	(:)	(:)(:)(:)	(·)(·)	2	2.83
V^{II}	(:)	(:)	(:)(:)(:)	(:)	(:)(:)(:)	(·)(·)(·)	3	3.87
Cr^{II}	(:)	(:)	(:)(:)(:)	(:)	(:)(:)(:)	(·)(·)(·)(·)	4	4.90
Fe^{III}	(:)	(:)	(:)(:)(:)	(:)	(:)(:)(:)	(·)(·)(·)(·)(·)	5	5.92
Fe^{II}	(:)	(:)	(:)(:)(:)	(:)	(:)(:)(:)	(:)(·)(·)(·)(·)	4	4.90

the next chapter how magnetic data permit the prediction of complex ion geometry since the deduced electron combinations are known to have certain symmetrical spatial distributions.

COVALENCE

The postulate that atoms may react to form more stable electron distribution through *sharing* rather than actual transfer of electrons was made by *G. N. Lewis* in 1916. He defined a *covalent bond* as a pair of shared electrons counting as part of the outer shells of two atoms. This is a simple idea but a very important one. Instead of ions forming and being held together by electrostatic attraction, covalent compounds are characterized by the formation of *molecules* whose atoms are bonded together by strong, shared electron-pair bonds. Molecules are bonded to other molecules by weaker bonds called *van der Waals forces*, after the man who first discussed them quantitatively. These cohesive forces are a manifestation of attraction of atomic nuclei for electrons of neighboring atoms. Attraction between molecules is directly related to the number of electrons available per molecule but is considerably weaker than other bonding discussed thus far, since there is a substantial compensating force of repulsion on a given atom's electrons by electrons of neighboring atoms. Crystals formed in this way (solid group 0 elements, halogens, most organic compounds, etc.) are called *molecular crystals* to differentiate them from most salts that form *ionic crystals*. As a consequence, typical covalent compounds are insulators and generally give soft crystals having low melting and boiling points.

TABLE 3–10. COMPARISON OF PROPERTIES OF SOME ELECTROVALENTLY AND COVALENTLY BONDED SUBSTANCES

Compound	Elect. Cond. (liquid state)	Bonding	M.p., °C	B.p., °C
NaCl	Strong	Electrovalent	800	1413
MgF_2	Strong	Electrovalent	1400	High
Al_2O_3	Strong	Electrovalent	2000	High
NH_3	0	Covalent	−77.7	−33.4
H_2S	0	Covalent	−82.9	−59.6
AsF_5	0	Covalent	−80	−53

Simple representations showing only the outermost electrons are again convenient in visualizing covalent bond formation. The symbolism usually used is to designate each covalent bond as a line and electrons not used in bonding as X's and dots. Electron shared bonds are known containing 1, 2, 3, 4, and 6 electrons. The 2-, 4-, and 6-electron bonds are the important ones and are respectively called *single*, *double*, and *triple bonds*. The strength of the bond increases and the distance between atoms decreases in the order given.

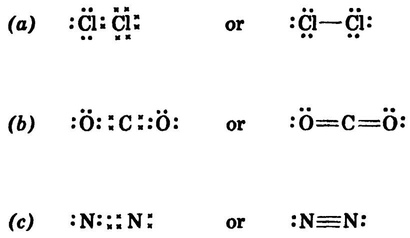


FIG. 3–10. Three types of covalent links: (*a*) single (*b*) double (*c*) triple. Note that each atom attains a noble gas electron arrangement via equal electron donation and sharing, and that some outer orbit electrons are not used in bonding.

With larger atoms, the requirement that a noble gas configuration be formed (*the octet rule*) cannot be maintained since compounds like IF_5, SF_6, IF_7, and OsF_8 are known. Since two 2*s* and three 2*p* orbitals are available in elements Li through F, their maximum covalency is 4; in elements Na through Br, one 3*s*, three 3*p*, and five 3*d* orbitals, a total of 9, are theoretically available, but maximum covalency is 6; in still heavier atoms the maximum observed covalency is 8.

Bond Orbitals and Covalence

One important restriction on the formation of covalent bonds which has not been explained as yet is that only those atoms combine which have at least one orbital containing a single or unpaired electron. The bond then results in a pairing of electron spins. For instance, the electronic structure of nitrogen can be written as $1s^2$, $2s^2 2p 2p 2p$, showing three unpaired 2*p* electrons. Three electrons of opposite spin can enter these orbitals to form three equivalent covalent bonds. In the formation of ammonia, pictured below, these electrons are contributed by three hydrogen atoms.

It was mentioned earlier that while *s* orbitals are spherical or nondirectional, *p* orbitals are figure-8 shaped and at right angles to each other. Since the axes of three-dimensional space are usually designated *x*, *y*, and *z*, *p* orbitals are descriptively labeled in like fashion. For example, the electrons of the N atom are often designated $1s^2$, $2s^2 2p_x 2p_y 2p_z$. In Fig. 3–11 there is pictured an overlapping of *s* and *p* orbitals to effect covalent bonding by pairs of spin compensated electrons.

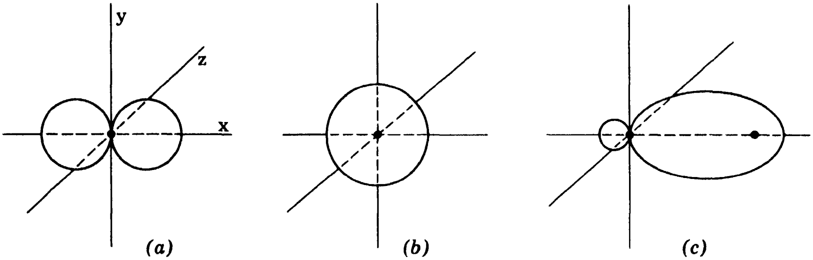


FIG. 3–11. (*a*) One of the three $2p$ orbitals of a nitrogen atom, occupied by a single electron. (*b*) The $1s$ orbital of a hydrogen atom occupied by a single electron. (*c*) One of the three *sp* orbitals of NH_3 formed by overlapping of an *s* and *p* orbital and containing two electrons. The dots are the atomic nucleii.

Carbon is a special case. The structure of the atom is $1s^2 2s^2 2p 2p$, indicating it should be able to form only two covalent bonds, as in carbon monoxide, C=O. A $2s$ electron is capable of *promotion*, however, to the higher energy $2p$ state, giving $1s^2 2s 2p_x 2p_y 2p_z$, the energy for this coming from that released when the extra two bonds form. Investigation of compounds like CH_4, CCl_4, etc., shows that all 4 bonds are equal in length and strength despite an expected difference in one bond, since it presumably involves use of a $2s$ electron while the others are in the $2p$ condition. *Pauling*, *Slater*, *Mulliken*, and others have shown with quantum mechanics that what happens is an amalgamation (*hybridization*) of the 4 orbitals to give 4 equivalent bonds orientated in space to the corners of a regular tetrahedron. This is designated as sp^3 bonding, since one *s* and three *p* electrons are involved, and is always tetrahedral. All the steriochemistry of carbon bears out this as do measurements of carbon bond angles by electron diffraction; 109° 28′ is the tetrahedral angle. Hybridization of other orbitals, particularly in the transition metals, is explained in the next chapter. The sp^3 bonds are unsymmetrically figure-8 shaped, directed toward the corners of a tetrahedron (Fig. 3–11 (*c*)).

Resonance

Another feature of electron-shared bonds is the concept of *resonance*, introduced by Heisenberg in 1926 and widely applied since then by

Pauling and others. For our purposes, it will be sufficient to say that the properties of some substances are best accounted for by the writing of several possible electronic structures whose combination gives a more satisfactory representation than does a single structure. One can think of electron pairs moving very rapidly among the positions pictured in the usual electronic structures. The actual condition is a *single resonance hybrid* or composite, and it is a consequence of wave mechanics that this system has lower energy than otherwise expected and is said to be additionally stabilized to the extent of the *resonance energy* of the system. To aid in understanding resonance there are many analogies that can be made with common experience, though they are all oversimplified. For example, a train (electrons) making continuous round trips among several stations (conventionally pictured electron positions) spends most of its time somewhere among the stations, and if one were asked to draw a picture representing an average condition on this railroad he might draw several diagrams showing the train in each of several locations and then say that the average condition is a combination of all the pictures. If the electrons are considered moving too rapidly to be thought of as individual particles but rather as a zone of charge, then this further analogy is useful: an orange paint (the hybrid) can be made by mixing yellow and red paints (individual electronic states).

As one example of a resonating molecule, ozone, O_3, contains two oxygen–oxygen bonds which by electron diffraction measurements are shown to have equal lengths. If one draws the electronic structure for ozone completing an octet for each oxygen, however, the result is one double and one single bond, which does not explain the experimentally found bond length. By postulating resonance between two such hypothetical structures one says that their composite or hybrid structure is capable of representing the facts.

FIG. 3-12. Two hybrid structures of ozone. Curved arrows represent resonance by electronic shifts in which electron pairs are moved to picture possible states which contribute to the composite. A comma or a double-headed arrow is used between the hybrids to indicate their interconvertability.

Chemists have used these ideas widely, particularly in the formulation of organic reaction mechanisms that are explained on the basis of resonating molecules and ions possessing special energy and structural features.

Partial Ionic Nature of Covalency

Between the extremes of electrovalency like Cs^+F^- and covalency like H:H is considerable room for transition, and most chemical bonds are now known to have mixed characteristics. The resonance theory explains this by showing the possibility of contribution by both covalent and ionic structures to the hybrid structure. Unless the compound is a binary one of a group IA or IB metal and a halogen, oxygen, or sulfur, it is conventional to represent it as a covalent molecule with the understanding that the *covalent bonds have partial ionic character.*

(a) (b)

FIG. 3-13. Two structures which help explain the properties of hydrogen bromide: (*a*) covalent and (*b*) ionic. The H—Br bond is calculated to be about 90% covalent. In water, the bond is broken and HBr becomes a strong electrolyte.

The Electronegativity Table

An aid in estimating the ionic contribution in otherwise covalent bonds has been afforded by Pauling in his development of a *table of electronegativities.* These numbers, derived from measured heats of formation but put on an arbitrary scale from 0.7 to 4.0, give the relative tendencies of atoms to attract electrons in a covalent bond. The following generalizations and uses can be made of the compilation in Fig. 3–14.

(1) The larger the electronegativity value, x, the more powerfully that atom attracts electrons and tends to become a negative ion.

(2) The larger the difference between the electronegativities of atoms A and B, the greater is the ionic character of the bond. Pauling has calculated that if the difference, $x_A - x_B$, is zero units, the ionic character is zero per cent; 0.2 units corresponds to 1%, $0.6 \simeq 7\%$, $1.0 \simeq 18\%$, $1.4 \simeq 32\%$, $1.8 \simeq 47\%$, $1.9 \simeq 50\%$, $2.2 \simeq 61\%$, $2.6 \simeq 74\%$. If the bond is essentially covalent or ionic according to this, it is written accordingly. Thus for sodium chloride, $x_A - x_B = 2.1$, indicating that the compound is predominantly electrovalently bonded.

(3) The larger the electronegativity difference, $x_A - x_B$, the greater generally is the heat of formation of AB and the more stable is the compound.

(4) An electronegativity of less than about 1.8 is a characteristic of metals; amphoteric elements and hydrogen have a value of about 2 and nonmetals have values above 2.

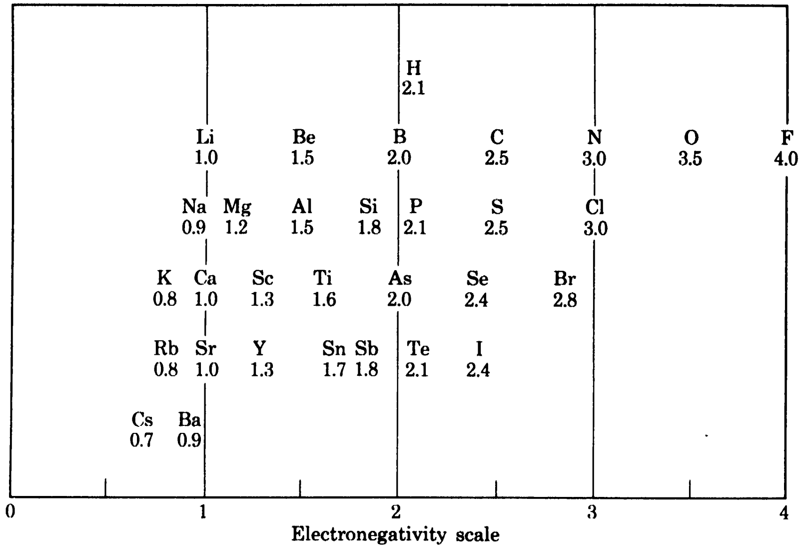


FIG. 3-14. Pauling's electronegativity table. (Adapted by permission from Linus Pauling, *Nature of the Chemical Bond*, Cornell University Press, Ithica, New York, 1944.)

Coordinate Covalence

A coordinate covalent bond is formed when one atom or ion (*donor*), with at least two valence electrons not being shared, donates an electron pair to another atom or ion (*acceptor*) capable of holding them. This capability stems usually from an incomplete octet of valence electrons in the acceptor. Once formed, this bond is equivalent to a covalent bond. Examples and further consequences of coordinate covalence are given in Chapter 4 (coordination compounds) and Chapter 5 (Lewis acid–base theory).

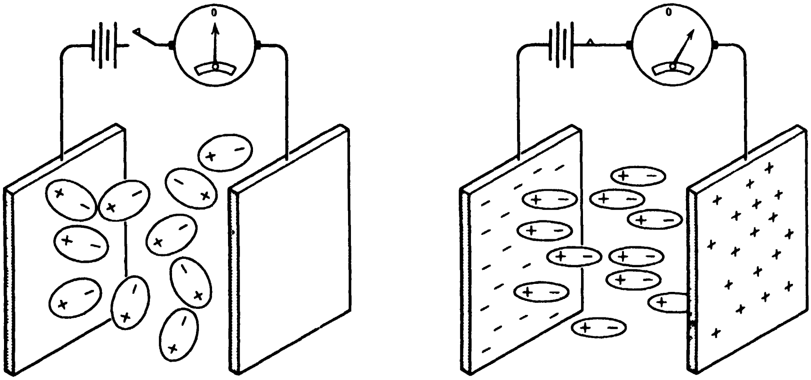
Dipole Moments

Experimental evidence of electronic displacement in bonds and asymmetric electron distribution in molecules is gained by the determination of *dipole moments*, as pointed out in 1912 by *P. Debye*. The magnitude of the dipole moment μ of a bond A—B is dependent upon the electronegativities of A and B and is the product of either of the electronic charges e and the distance l between them, $\mu = el$. Dipole moments are approximately additive (vector quantities acting in the direction of the bond) so that an unsymmetrical molecule will have a permanent dipole (be a *polar molecule*), whereas a symmetrical one will not have a dipole moment and will be a *nonpolar molecule*. Molecules of polar compounds attract each other and hence show mutual solubility, and the pure substances have lower volatility than otherwise expected, since energy is needed to overcome intermolecular attraction. Nonpolar molecules on the other hand are usually more volatile and soluble only in other nonpolar solvents.

Dipole moments are given in electrostatic units or in Debye units, 1 debye = 10^{-18} e.s.u. Values of this magnitude for $e \cdot l$ are realized since the charge of the electron is 4.8025×10^{-10} e.s.u. and the distance l between atoms is about 10^{-8} cm. Methods for obtaining dipole moments are given in physical chemistry texts.

TABLE 3-11. DIPOLE MOMENTS OF REPRESENTATIVE COMPOUNDS

Compound	Moment, debyes	Compound	Moment, debyes
H_2O	1.84	HF	1.91
H_2S	1.10	HCl	1.03
SO_2	1.6	HBr	0.78
CH_3OH	1.68	HI	0.38
NH_3	1.5	CO_2	0.0
HCN	2.9	BCl_3	0.0
H_2O_2	2.1	$SnCl_4$	0.0
C_6H_6	0.0	CCl_4	0.0



(a) (b)

FIG. 3-15. (*a*) Random molecular orientation of polar molecules between uncharged condenser plates. (*b*) Condenser is charged and molecules line up in the field, partially neutralizing the plate charges and increasing the condenser's capacity as measured by the meter. The increase is related directly to the permanent and induced dipoles of the molecules.

Dipole Moments and Molecular Structure

The application of dipole moment data is chiefly that of molecular structure elucidation. From what has been shown previously of *hydrogen bromide* (Fig. 3–13) and *carbon dioxide* (Fig. 3–10), one can surmise that HBr will have a dipole moment, since, due to the different electronegativities of H and Br, the electrons in the bond are displaced toward the halogen. In CO_2, although electronegativity differences exist the molecule is linear, so that the vectors of bond moments cancel and zero dipole moment is the result. *Ammonia* has a high dipole moment, indicating that it does not have a plane triangle shape as does *boron trichloride*, but instead is tripod shaped with the three hydrogens grouped toward one side (Fig. 3–11).

The large dipole moment of *water* shows that that molecule is angle or wedge shaped rather than linear. The use of two *p* orbitals by oxygen should result in a 90° angle between the bonds, but it is actually about 105° due to mutual repulsion of the H's. It can be shown that the ions of a salt are attracted to each other 1/80 as strongly in water as in air, hence in water they may be able to yield to the attraction of the H_2O dipole and go into solution surrounded by solvent molecules. The ions are then said to be *solvated*, and solution proceeds if the forces holding the ions in the crystal (*lattice energy*) are less than the forces of attraction between solvent dipoles and ions (*solvation energy*). The latter is directly related to the solvent's dielectric constant. The somewhat positive hydrogen side of the H_2O molecule is attracted by negative ions and the negative oxygen side, with its unshared electron pairs is attracted by positive ions, thus making water a typical polar solvent and an excellent one for salts.

A further result of the water dipole is its capability of promoting ionization (dissociation) of essentially covalent molecules like HBr and HCl. Bonds in these are partially ionic and break under the solvent's dipole influence. The resulting ions are then covered by a mantle of solvent molecules that hinders recombination and stabilizes the electrolytic solution.

Hydrogen Bonds

The hydrides of the electronegative elements of the first period, NH_3, H_2O, and HF, have unusually high melting and boiling points when compared with hydrides of their own families. For instance, the boiling points of the hydrides of group VIA elements, H_2O, H_2S, H_2Se, and H_2Te, are respectively 100 C, − 59.6 C, − 42 C, and − 1.8 C, and the question is: why should the hydride with the lowest molecular weight require the greatest amount of heat for vaporization? This is answered by considering that an electrostatic attraction exists between the unshared electron pairs on an oxygen atom and the partially ionic hydrogens of an adjacent water molecule. Such bonding creates groups of molecules held together by a force not as strong as formal covalent or ionic bonds but stronger than van der Waals forces. Each water molecule is capable of forming four hydrogen bonds and grouping four other molecules about itself as two electron pairs and two hydrogens are available. Since these bonds are tetrahedrally distributed, one is, incidentally, able to account for the tetrahedral crystal structure of ice. The high dielectric constant for water, hydrogen fluoride, and hydrogen cyanide is also understandable in that hydrogen-bonded aggregates have a greater neutralizing ability on the experimentally applied electrical field than do the individual molecules derived from them.

Density measurements on HF vapor show the gas to be composed of various associated molecules, $(HF)_x$. This and the fact that salts like KHF_2 are well known are evidence of hydrogen bonding in fluorine chemistry. A dotted line is used to designate this type bonding so the trimer $(HF)_3$ would be H—F · · · H—F · · · H—F and the bifluoride ion, (F · · · H—F) .

PROBLEMS

1. Explain briefly by reference to the proper tables and figures:

(*a*) Which element has the configuration $1s^2$, $2s^22p^6$, $3s^23p^4$?

(*b*) Why do the lanthanide series elements all have a valence of + 3?

(*c*) What is the electronic arrangement of Ca and Ca^{+2} in the system used in part (*a*) above?

(*d*) What is peculiar about the electron configuration for yttrium?

(*e*) Why is the electronegativity difference in HCl greater than that in HI?

2. J. P. Slipshod is a man who forms a hasty opinion from little data and has seldom been known to change his mind. Several of his observations follow. How can you answer each?

(*a*) "The idea of electrovalence will not work because when oppositely charged bodies like Na^+ and Cl^- are brought together they discharge and the result is zero charge on both.

(*b*) "The idea that a glowing piece of iron gives a continuous spectrum and a sodium vapor lamp a discontinuous spectrum is wrong. The iron glows red because its radiation is essentially all at the wavelength of red light.

(*c*) "The silicon atom can be represented as $1s^2$, $2s^22p^6$, $3s^23p^2$. The $3s$ electrons are paired and the $3p$ unpaired. With only two unpaired electrons, the valence of Si can only be + 2, and whoever determined the formula of sand and quartz to be SiO_2 had better check his figures.

(*d*) "Substances having the same electronic structure have the same size, since electrons in identical orbitals of different atoms have the same energy and are the same distance from the nucleus. Thus the experimental measurements that give the radii of Cl^-, A, and K^+ (all of which have the electronic structure 2, 8, 8) respectively as 1.81, 1.54, and 1.33 A are obviously wrong. Their values should be identical.

(*e*) "The notion that ions can't have an independent charge greater than +3 is bunk. Otherwise how does one explain Cr being +6 in CrO_4^{-2} and Mn being +7 in MnO_4^-, and how could one balance equations without valences?

(*f*) "The atomic radii of B, C, N, O, and F are respectively given as 0.80, 0.77, 0.74, 0.74, and 0.72. Anybody knows that can't be right since each succeeding element has one more electron and hence must be larger. This also holds for the supposed contraction in size in the rare earth series.

(*g*) "Some people think that elements in a horizontal period show an increase in ionization potential with increasing atomic number because the electrons are added at about the same distance from the nucleus, but the nuclear charge is also increasing and holds ALL electrons more tenaciously. This notion is erroneous. Note for instance that B has a lower value than the preceding element, Be."

3. From the electronegativity table:

(*a*) Predict the stability of BF_3, KBr, CI_4, NI_3, and PI_3.

(*b*) The heats of formation of several hydrogen halides are

$$H_2 + Cl_2 = 2HCl + 44\,\text{kcal};\quad H_2 + Br_2 = 2HBr + 25\,\text{kcal};\quad H_2 + I_2 = 2HI + 3\,\text{kcal}$$

Is this trend consistent with the table? Explain.

4. Write resonance forms for: (*a*) CO_2 showing the possibility of single, double, and triple bonds (*b*) $CO_3^=$ showing why measurement of C—O distances reveals that all are equal.

5. According to the electron notation used in Fig. 3–10, show the bonding in sulfuric acid, $(HO)_2SO_2$, and point out the covalent and coordinate covalent bonds

6. From the table on dipole moments:

(*a*) Argue for or against the proposal that hydrogen peroxide is a linear molecule with the structure H—O—O—H.

(*b*) Are the hydrogen halide values what one might expect by knowing the electronegativities of these atoms? Explain.

(*c*) Can one determine whether the $SnCl_4$ structure is tetrahedral or square planar from the table data alone?

(*d*) The boiling point of $SnCl_4$ is 114 C, and it is appreciably soluble in organic solvents. Is this behavior expected?

(*e*) Two resonance forms for nitrous oxide are $^-{:}N{=}N^+{=}\ddot{O}{:}$ and ${:}N{\equiv}N^+{-}\underset{\cdot\cdot}{\ddot{O}}{:}^-$. Do these help explain why the measured dipole of N_2O is approximately zero?

7. (*a*) Draw a series of simple diagrams showing how H_2O dissolves NaCl. Liquid ammonia is also a solvent that dissolves many salts, giving electrolytic solutions. Explain how this is possible, and again picture the process.

(*b*) Draw a picture of an ice crystal showing the arrangement of water molecules as described in the last section of the chapter. Postulate why it ought to be less dense than liquid water.

8. $CdBr_2$, but not NaBr, is appreciably soluble in organic solvents having low dielectric constants. What can one deduce about these salts? If one had dilute aqueous solutions of both, which would conduct electricity better? Explain.

9. Why doesn't a rare earth series or long period exist in the first two horizontal rows of the periodic table?

10. Give the number of electrons in each shell of Li^+, B^{+3}, Be^{+2}, and C^{+4}. Arrange these ions in order of increasing size and explain. Arrange them in order of decreasing likelihood of independent existence. Explain.

11. Magnetic moments studies show that Cr^{III} and Co^{+2} have 3 unpaired electrons; V^{IV} has one unpaired electron, and Mn^{III} has 4 unpaired electrons. Show the structures of these ions (as illustrated in the examples given on p. 38) to account for the experimental measurements.

12. From Table 3-4 plot three separate graphs of atomic number (abscissa) versus ionic radius; first for group IA ions, second for IIA ions, and third for univalent VIIA ions. Explain the trend in each plot.

13. Using a compass and a scale of 1 A = 1 in., draw circles to represent the group IA and VIIA monovalent ions. Show how LiI and NaCl might look as alternately packed spheres in a face of these salt crystals (the crystals have cubic symmetry). Repeat for KBr and CsF.

14. Explain:

(*a*) How ionization potentials can be used to determine valences of elements.

(*b*) The differences in electron structure between main group and subgroup elements.

(*c*) Whether a neon or an argon lamp (which depends upon ionization of the gas to give light) requires less voltage for starting, and why.

(*d*) On the basis of the size of the central element, why is H_3PO_4 a stronger acid than H_3AsO_4?

(*e*) Why is the dipole moment of O—C—O zero but that of O—S—O is 1.6?

15. (*a*) Plot a graph of electronegativity difference versus % ionic character from data given in the section on the electronegativity table. Extrapolate it to determine the ionic character of the bond in LiF. Predict from this some properties of lithium fluoride.

(*b*) Using this graph, calculate the % ionic character of the compounds listed in problem 3(*a*).

16. Show formation of H_2O by the method of Fig. 3-11. Explain.

17. (*a*) Fajans' rules have been stated in this chapter as conditions that lead to formation of ionic bonds. Restate them as conditions for covalence and briefly explain the reasons for each.

(*b*) In the series LiF, LiCl, LiBr, and LiI, the melting points are, respectively, 870, 614, 547, and 446 C. Is this expected from what was stated in (*a*) concerning the effect of anion size on bond type?

(*c*) In the series NaCl, $MgCl_2$, $AlCl_3$, and $SiCl_4$, the respective melting points are 800, 708, 194 (4.2 atm.), and −70 C. Is this trend expected from what was given in (*a*) concerning the effect of ionic charge?

18. Plot a graph of atomic number (abscissa) versus first ionization potentials of the elements from data in this book. Explain the positions of the group IA and group 0 elements.

19. A device for analyzing O_2 in flue gases does so by continuously measuring the magnetic susceptibility of the sample. This is possible because O_2 has two unpaired electrons. Make a suitable drawing to illustrate the molecule.

20. (*a*) The boiling points of HF, HCl, HBr, and HI are 19.4, −85, −67, and −35.5 C, in that order. Explain the trend.

(*b*) In the series He, Ne, A, Kr, Xe, and Rn, the boiling points show an increase in that order. Explain why one expects this trend rather than that shown in (*a*).

21. Representing last level electrons with dots, show formation of these compounds from their atoms: MgF_2, H_2S, NCl_3, LiBr, SO_3, and SeS. Predict the bonding in each.

22. (*a*) Predict which is more basic: $Pb(OH)_2$ or $Pb(OH)_4$. Explain.

(*b*) Predict the trend in base strength in the series $C(OH)_4$, $Si(OH)_4$, $Ge(OH)_4$ $Sn(OH)_4$, and $Pb(OH)_4$. Give the basis for your predictions.

(*c*) Repeat (*b*) for the series $Ce(OH)_3$, $Eu(OH)_3$, $Ho(OH)_3$, and $Yb(OH)_3$.

23. Some forms of the periodic table list general oxide formulas that are characteristic of vertical groups of elements. Fit these oxides to the proper groups: MO, M_2O, MO_3, M_2O_7, MO_2, and M_2O_3.

24. NO and NO_2 are paramagnetic but N_2O and N_2O_4 are not. What can you deduce concerning their structures?

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4

WERNER IONS AND COMPLEX COMPOUNDS

In 1891 *Alfred Werner*, a German chemist, began studies on *coordination compounds*, the results of which were to open the large field of inorganic structural chemistry, yield important principles for understanding complex substances, and bring Werner a Nobel Prize in 1913.

Early Experiments

Some of Werner's first experiments were with cobalt salts. He found that cobaltous chloride in an aqueous mixture of ammonium chloride and ammonium hydroxide gave a dark solution that yielded three ammoniated derivatives of air-oxidized tripositive cobalt. Chemical analysis showed them to have the molecular formulas of (*a*), (*b*), and (*c*) below:

$$CoCl_2 + NH_4OH + NH_4Cl \xrightarrow{O_2} \underset{(a)}{CoCl_3 \cdot 6NH_3} + \underset{(b)}{CoCl_3 \cdot 5NH_3} + \underset{(c)}{CoCl_3 \cdot 4NH_3}$$

The products were peculiar in these respects:

1. NH_3 could not be readily removed from any of them by reaction with strong base. Werner concluded ammonia was somehow tightly held since strong bases normally liberate weaker ones from their compounds.
2. Upon electrolysis of their solutions, cobalt and ammonia migrated together to the negative pole while chloride went to the positive electrode. This indicated that NH_3 must be attached to Co in some form of positive ion.
3. Compound (*a*) reacted with three equivalents of Ag^+ giving three equivalents of AgCl precipitate and another compound, (*d*), which was

shown to be $Co(NO_3)_3 \cdot 6NH_3$. Both (*a*) and (*d*) had *molal electrical conductances* corresponding to four ions, which was confirmed by freezing point measurements (see Chapter 5). Compound (*a*) should then presumably be written $[Co(NH_3)_6]Cl_3$ to account for the observations. In solution it must exist as $[Co(NH_3)_6]^{+3} + 3Cl^-$. Compound (*d*) should then be $[Co(NH_3)_6](NO_3)_3$.

4. Similarly, (*b*) was found to give three ions and (*c*) only two ions in solution. They were accordingly assigned the formulas $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl$.

Werner called these *coordination compounds*. Thousands of such compounds are now recognized.

The Coordination Theory

From such experimental observations Werner postulated his coordination theory, which is now so well established as a unifying concept for understanding complex compounds that it is referred to as Werner's principle. The main points are:

1. A number of metals, particularly among the transition elements, have two kinds of valence and they hold (coordinate) about themselves groups in two "spheres of attraction." In the first sphere are those groups directly attached to the metal ion. In the second sphere are groups less strongly held. The central metal and its first sphere constitutes one ion in solution; the second sphere contains the remaining ions. Thus in the compound $[Cu(NH_3)_4]SO_4$, the ammonia molecules are in the first sphere, the sulfate in the second, and, in solution, the ions $[Cu(NH_3)_4]^{+2}$ and SO_4^{-2} will be found.
2. Each metal is capable of coordinating characteristic numbers of groups in the first sphere. Common *coordination numbers* are 2, 4, and 6.
3. The central metal is capable of coordinating neutral groups such as NH_3 and H_2O as well as negative groups like Cl^-, CN^-, OH^-, SCN^-, NO_2^-, F^-, etc. The neutral groups do not contribute to the valence of the complex but the negative ions do; for the salt $K[CrCl_4(H_2O)_2]$, $K = +1$, $4Cl^- = -4$, $2H_2O = 0$, so the oxidation state of Cr is (III) to give the molecule neutrality.
4. Formation of complexes depends (as discussed later) upon the size, charge, and electronic distribution of atoms present.

Nomenclature of Werner Complexes

The following rules are a simplified summary of the International Union of Chemistry recommendations set forth in 1940.

1. The cation is named first, then the anion.
2. Coordinated groups which are negatively charged end in "o";

neutral groups have no characteristic ending. H_2O is called aquo and NH_3 is ammine.

3. The order of coordinated groups both in writing and naming is, negative groups, then neutral ones, as $Na[CoCl_4(NH_3)_2]$, sodium tetrachlorodiamminecobaltate(III).

4. Prefixes denoting number are di, tri, tetra, penta, and hexa, respectively, meaning 2, 3, 4, 5, and 6.

5. The central element's oxidation state is designated by a Roman numeral in parenthesis. If the oxidation state is zero, an Arabic (0) is used.

(*a*) For complex *cations*, the number follows the element which is named in its ordinary way: $[Cr(H_2O)_6]Cl_3$ is hexaaquochromium(III) chloride, and $[CoBr_2(NH_3)_4]NO_3$ is dibromotetramminecobalt(III) nitrate.

(*b*) For complex *anions*, the numeral follows the name of the complex which ends in "ate": $H_2[PtCl_6]$, sometimes called chloroplatinic acid, is systematically named (di)hydrogen hexachloroplatinate(IV), and $K_4[Fe(CN)_6]$, known as potassium ferrocyanide, can also be called (tetra)potassium hexacyanoferrate(II). In each of the last two systematic names, either term in parenthesis could be omitted and the names would still be unequivocal. Thus in the last, if 6 CN^- groups are coordinated with Fe^{II}, it is evident 4 K^+'s are needed to complete the molecule.

6. The prefixes bis, tris, and tetrakis are used before names of complex coordinated groups instead of di, tri, and tetra: $[Co(en)_2(NH_3)_2]^{+3}$ is the bis(ethylenediamine)diamminecobalt(III) ion.

7. The symbol μ (mu) is used before the name of each bridging group in polynuclear complexes. The name of $[(NH_3)_5Ni—O—O—Ni(NH_3)_5]SO_4$ is decaamine-μ-peroxydinickel(II) sulfate.

Some groups capable of being coordinated are: amido $—NH_2^-$, bromato $—BrO_3^-$, bromo $—Br^-$, carbonato $=O_2CO^{-2}$, chloro $—Cl^-$, cyano $—CN^-$, fluoro $—F$, hydroxo $—OH^-$, imido $=NH^{-2}$, iodo $—I^-$, nitrato $—ONO_2^-$, nitrito $—ONO^-$, nitro $—NO_2^-$, nitrosylo $—NO$, oxalato $=O_2C_2O_2$, sulfato $=O_2SO_2^{-2}$, thiocyanato $—SCN^-$, and isothiocyanato $—NCS^-$. Many complex organic groups are also known and may act as (chelating) organic reagents for reaction with and possible detection of the central metal. See Chapter 12.

Complexes in the Qualitative Analysis Schemes

The immediate purpose in developing some background in Werner chemistry is to enable one to understand and appreciate the role of complex formation in the laboratory procedures. The types listed below will be encountered.

(1) *Hydrated ions*, or aquo complexes, are the rule in aqueous solution,

and water may be held tightly enough to crystallize with the salt as *water of hydration.* Sometimes the hydrate formula gives the coordination number of the central ion; beryllium compounds, for example, are almost invariably tetrahydrated, suggesting that correct representation would be like $[Be(H_2O)_4]SO_4$.

(2) *Ammonia complexes* are called *ammines.* Ag^{I}, Cu^{II}, Cd^{II}, Ni^{II}, Zn^{II}, Co^{II}, and Co^{III} are ions forming ammines in the analysis described in later chapters. Separations of cations can be effected by means of complex formation. For example, insoluble $Bi(OH)_3$ forms with aqueous NH_3, while copper and cadmium in the same solution give the soluble complexes $[Cu(NH_3)_4]^{+2}$ and $[Cd(NH_3)_4]^{+2}$. The deep blue color of the tetramminecopper(II) ion simultaneously identifies that metal in the sample.

(3) *Sulfido complexes* are numerous in the second cation scheme where Hg^{II}, As^{III}, As^{V}, Sb^{III}, Sb^{V}, Sn^{II}, and Sn^{IV} form soluble sulfides like AsS_3^{-3} and HgS_2^{-2} in alkaline solution, while other group-2 metal ions do not. A separation based on this fact is used.

(4) *Hydroxo complexes* are always possible in basic solution. The amphoteric cations of groups 2 and 3 form hydrated oxides that dissolve in excess strong base due to the formation of hydroxo ions such as $Sb(OH)_6^-$, $Al(OH)_4^-$, and $Zn(OH)_4^{-2}$.

(5) *Cyano complexes* are the basis for a Cu—Cd separation (see group 2) and for the identification by color of both ferrous and ferric iron (see group 3). Typical ions are $Cd(CN)_4^{-2}$ and $Fe(CN)_6^{-4}$.

(6) *Halo complexes* are present in halogen acid solutions of metallic ions, such as $CuCl_4^{-2}$, $SbCl_6^{-3}$, $AlCl_4^-$, etc. Except for fluoro complexes, they usually dissociate upon dilution with water.

(7) Other anions capable of being coordinated and which are used in analysis include *oxalato* as $Fe(C_2O_4)_3^{-3}$, *thiocyanato* as $Fe(SCN)^{+2}$, *tartrato* as $Cu(C_4H_4O_6)_2^{-2}$, and *nitro* as $Co(NO_2)_6^{-3}$.

Ionic Radii and Complex Formation

The metal ions that best coordinate groups around themselves are those with a small radius and large charge. The ratio, *charge/ionic radius* is sometimes called the *charge density*. Stability of complexes is roughly proportional to this value, though other factors are also important. If this ratio is greater than approximately 2 (charge measured in electronic units and radius in Angstrom units. A) the possibility of complex formation is good.

Sidgwick—"The Effective Atomic Number"

It seemed logical that valence characteristics of the central metal ion should be related to its coordination number but in Werner's time little

TABLE 4–1. CHARGE TO RADIUS RATIOS OF SOME METALLIC IONS

Ion	Radius, A	Charge/Radius	Remarks
K^+	1.33	0.71	No complexes
Hg^{II}	1.10	1.8	Few complexes
Cd^{II}	0.97	2.0	Several complexes, ions hydrated
Zn^{II}	0.74	2.7	Generally complexed, ions hydrated
Co^{II}	0.72	2.8	Generally complexed, ions hydrated
Ni^{II}	0.70	2.9	Generally complexed, ions hydrated
Fe^{III}, Cr^{III}	0.64	4.7	Always complexed, ions hydrated
Co^{III}	0.62	4.8	Always complexed, ions hydrated
Pt^{IV}	0.64	6.2	Always complexed, ions hydrated

was known about chemical bonding, and his pure assumption of two bonding "spheres" was the most qualitative aspect of his theory. It is now known that the first sphere is formed largely by *coordinate covalent bonding* as each coordinated group is capable of electron pair donation; the second sphere is held by electrovalence.

The first working approach for correlating electronic configuration and coordination number is credited to *N. V. Sidgwick* (1926). Consider the cobalt atom and its tripositive ion for example. The atom (at. no. 27) has 2 electrons in the *K* level, 8 in the *L*, 15 in the *M*, and 2 in the *N*. The ion has 2 in the *K*, 8 in the *L*, and 14 in the *M*. If the ion were to coordinate 6 $:NH_3$, each ammonia has an unshared electron pair and would furnish a total of 12 electrons to the inner coordination sphere, enough to complete the 18 electron *M* orbit as well as re-establish and fill the *N* orbit with 8 electrons. This gives the closed krypton configuration of 36 electrons, a number referred to by Sidgwick as the ion's *effective atomic number or E.A.N.* Fitting this idea are Zn^{II} and Cu^{I} which coordinate four groups to give the krypton structure, Fe^{II} coordinating six groups to give the same structure, and Pd^{IV} which takes six groups to add 12 electrons and give the xenon arrangement. Some exceptions are Cr^{III}, 6-coordination and E.A.N. = 33, Fe^{III}, 6-coordination and E.A.N. = 35, and Ni^{II}, 6-coordination and E.A.N. = 38. These exceptions were never satisfactorily dealt with by the Sidgwick theory, however, and it wasn't until after the development of quantum mechanics that a better explanation of the linkage in Werner ions was possible.

Pauling—The Quantum Mechanical Interpretation

L. Pauling and others have extended the Sidgwick theory by means of magnetic susceptibility data and a quantum mechanical interpretation

(Chapter 3) to give us our best ideas of bonding in transition metal complexes.

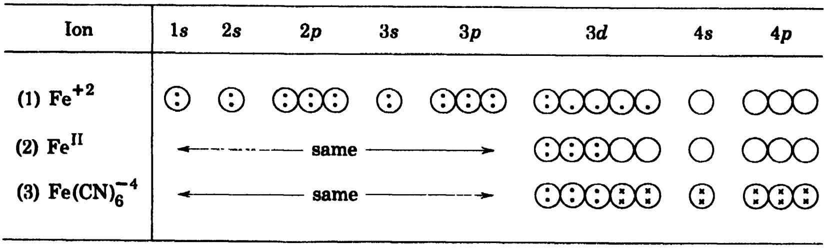

Fig. 4–1. Ferrous ion (1) showing four unpaired electrons, followed by rearrangement (2) and complex formation (3) in which all electrons are paired. Dots represent iron electrons, x's those contributed by six CN$^-$ groups.

For example, FeCl$_2$ has a measured magnetic moment of 5.23 Bohr magnetons, indicating four unpaired electrons. The compound K$_4$[Fe(CN)$_6$], however, has no moment, indicating a pairing of all electrons. *Ferrous ion*, Fig. 4–1 (1), has two paired and four unpaired 3*d* electrons. If it is assumed that the unpaired ones pair up in the first three 3*d* orbitals, Fig. 4–1 (2), then six groups each carrying an available electron pair can coordinate with this metal ion. Quantum mechanics has shown that six equivalent bonds can be formed from the two 3*d*, the single 4*s*, and three 4*p* orbitals, and further that the new bonds are directed spatially to the corners of a regular octahedron. X-ray evidence has proven this geometry in 6-coordinated complexes which are bonded by d^2sp^3* bonds. The final structure of a cyano complex is seen to be the closed krypton configuration which is expected and found to be diamagnetic.

Metals in the first transition series (sometimes called the iron group) have small energy differences among the 3*d*, 4*s*, and 4*p* orbitals (Fig. 3–5), and thus these orbitals can be combined in bonding. Transition metals in the second periodic row (the palladium group) use the 4*d*, 5*s*, and 5*p* orbitals, and the transition elements of the third horizontal row (the platinum group) use combinations of the 5*d*, 6*s*, and 6*p* orbitals, which are also roughly energetically equivalent. The combination d^2sp^3 always means an octahedral configuration.

By the same methods, *zinc ion* (at. no. 30) can be shown to contain no unpaired electrons, its complexes with 4-coordination have the krypton arrangement and the compounds are diamagnetic. Available for holding

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* This means two *d*, one *s* and three *p* orbitals are *hybridized* giving six equivalent electron pair bonds. Table 3–4 gives the electron arrangements of atoms.

the eight electrons donated by the coordinating groups are one 4*s* and three 4*p* orbitals. The geometry of sp^3 hybridization is tetrahedral.

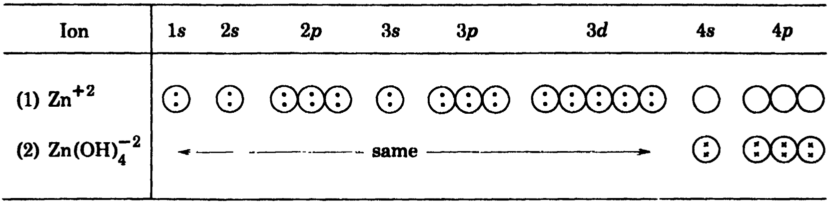


FIG. 4-2. Zinc ion (1), and sp^3 bonding in a tetrahedral 4-coordination hydroxo complex (2).

The situation in cupric compounds is a little different in that *cupric ion* has a magnetic moment associated with one unpaired electron as do its 4-coordination complexes. X-ray examination indicates that cupric complexes are planar meaning that bonding other than sp^3, described above, is in effect. This has been shown to be dsp^2 as follows. Cupric ion has eight paired and one unpaired 3*d* electrons, Fig. 4-3 (1). Instead of utilizing the 4*s* and three 4*p* orbitals, leaving the unpaired electron in the 3*d* state and giving the tetrahedral sp^3 bond type, the odd electron is *promoted* from its original state to a 4*p* orbital as in Fig. 4-3 (2). The eight electrons of the incoming 4X:⁻ groups occupy the vacant 3*d*, 4*s*, and two 4*p* orbitals. Bonds of the type dsp^2 give a square planar structure. The observed magnetic moment for $[Cu(NH_3)_4]SO_4$ is 1.82 and that calculated for the compound on the basis of one unpaired electron is 1.73 Bohr magnetons.

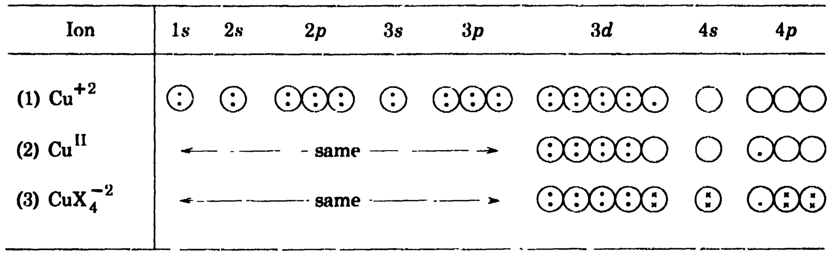


FIG. 4-3. Formation of a square planar cupric complex with dsp^2 bonds.

There are many combinations of orbitals known, resulting in various numbers of bonds and geometrical distributions of groups around a central atom. The bonds which usually form are those having minimum energy (greatest strength), and not infrequently these are hybrid bonds. In addition, the size of coordinating groups and of the central metal is also a factor, maximum coordination number being favored with small groups. Maximum stability of complexes is found within certain ratios of sizes of the atoms present. These points are summarized for several cases in the following table.

TABLE 4–2. COMMON GENERAL TYPES OF WERNER IONS

Ion	Central Metal	Coordination Number	Bond	Geometry	Radius Ratio M/X*
MX_2	Ag^{I}, Hg^{II}, Au^{I}	2	sp	Linear	≥ 0.0
MX_3	Ni^{II}, Cu^{II}	3	sp^2	Triangle planar	≥ 0.15
MX_4	Cu^{II}, $Zn,^{II}$ Ni^{II}, Ag^{II}, Au^{III}, Pd^{II}, Pt^{II}	4	dsp^2	Square planar	≥ 0.41
MX_4	Cu^{I}, Ni^{II}, Al^{III}, Zn^{II}, Cd^{II}, Hg^{II}, Sn^{IV}, As^{V}	4	sp^3	Tetrahedral	≥ 0.22
MX_6	Co^{III}, Co^{II}, Ni^{II}, Fe^{III}, Fe^{II}, Mn^{III}, Sn^{IV}, Al^{III}, Sb^{III}, As^{III}	6	d^2sp^3	Octahedral	≥ 0.41
MX_8	Os^{IV}, W^{IV}, Mo^{IV}, Zr^{IV}	8	d^5sp^3†	Antiprismatical	≥ 0.65

* M stands for the central metal ion and X for the coordinating group. In the column below, the symbol ≥ is read "equal or greater than."

† Of the nine orbitals, only eight are used for bonding.

The most frequently encountered types from Table 4–2 are:

1. *Linear 2-coordination* is illustrated by $[H_3N\!:\rightarrow Ag \leftarrow\!:NH_3]^+$ in group 1 cation analysis and its formation accounts for the solubility of AgCl in NH_4OH. In like manner, when sodium thiosulfate ("hypo") is used in photography to wash unreacted silver halide from film, $[O_3SS\!:\rightarrow Ag \leftarrow\!:SSO_3]^{-3}$ is the soluble complex formed. In cyanide plating baths or the process for dissolving gold and silver in cyanide ore

treatment $[N{\equiv}C{:}\rightarrow Ag \leftarrow{:}C{\equiv}N]^-$ and $[N{\equiv}C{:}\rightarrow Au \leftarrow{:}C{\equiv}N]^-$ are products. In these formulas, arrows represent coordinate covalent bonds.

2. *Planar 4-coordination* is illustrated below in the tetraiodomercury(II) ion. See test 19-9 (*b*) for a preparation of $K_2[HgI_4]$.

3. *Tetrahedral 4-coordination* is pictured below for the hydrated zinc ion. The sp^3 bonds are directional to the corners of a regular tetrahedron.

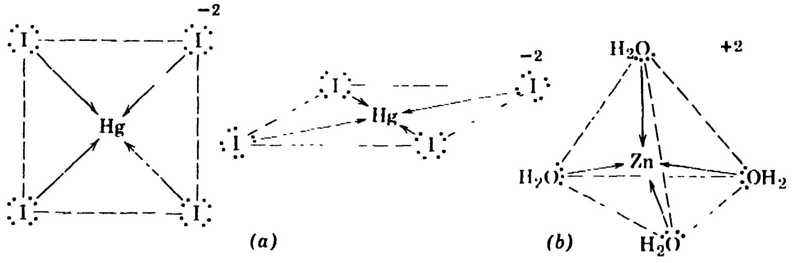


FIG. 4-4. (*a*) Two representations of a planar ion. (*b*) A tetrahedral ion. Dashed lines show the symmetry of the figures; arrows show coordinate covalent bonds.

4. *Octahedral 6-coordination* can be shown in several ways as indicated in the figure.

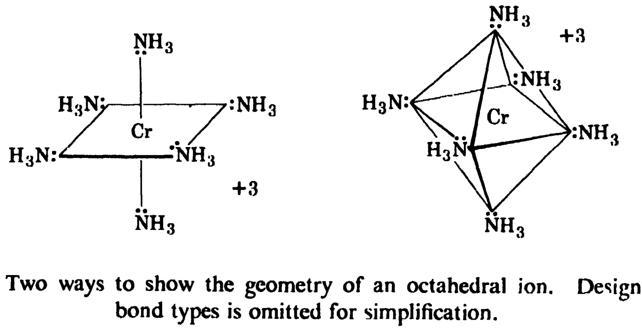


FIG. 4-5. Two ways to show the geometry of an octahedral ion. Designation of bond types is omitted for simplification.

Isomerism in Werner Ions

One of the convincing features of the Werner theory was its ability to predict the possibility of *isomers*, just as the electron orbital idea was later able to predict the geometry of ions from a knowledge of the bonding orbitals that were used and their spatial orientation. *Isomers are substances with the same molecular formula but different arrangements of atoms.* Isomerism was well known in organic chemistry (CH_3—CH_2—OH

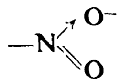
= ethyl alochol, and $CH_3—O—CH_3$ = dimethyl ether, two distinctly different, stable, C_2H_6O compounds), but Werner was the first to apply the same thinking to inorganic chemistry.

1. *Ionization isomerism* refers to isomers that give different ions in solution because of their inclusion in either the tightly held coordination sphere or the readily dissociated second sphere. Two such isomers are $[CoCl_2(NH_3)_4]Br$ and $[CoClBr(NH_3)_4]Cl$. The first will give yellowish AgBr with Ag^+ in solution, whereas the second will give white AgCl.

2. *Manner-of-attachment* (*salt*) *isomerism* is the result of isomeric forms of certain polyatomic ions coordinated with the metal in different ways. Thus nitrite (*a*) and nitro (*b*) are isomeric and will give different series of salts:

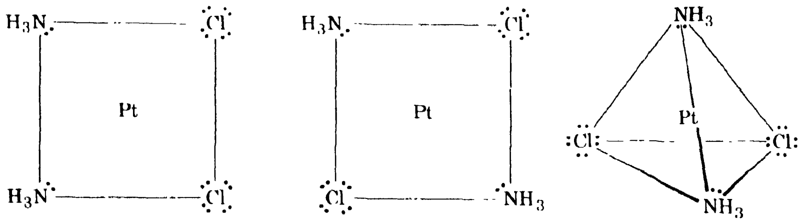
(*a*) $—O—N{=}O^-$

(*b*)



$—N\begin{smallmatrix}\nearrow O^- \\ \searrow O\end{smallmatrix}$

These happen to be interconvertible with the nitro group, the more stable form. "Sodium cobaltinitrite" as prepared in Test 19–7 (*b*) is a nitro compound.



(*a*) *cis* (*b*) *trans* (*c*)

FIG. 4–6. In this example the square planar structure can have two forms and the tetrahedral only one. Since dichlorodiammineplatinum(II) is known in two forms, its geometry is planar. The bonding in Pt^{II} complexes is dsp^2, which is calculated to be planar. Structure (*c*) is therefore incorrect for the ion.

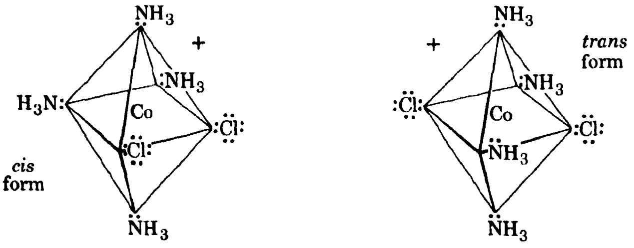


FIG. 4–7. An example of *cis–trans* isomerism. The chlorines are the reference atoms. The solid lines are used to show the symmetry of the ions.

3. *Geometrical isomerism* is also called *cis-trans isomerism.* It can occur with octahedral 6-coordination (complexes like MX_4Y_2) and planar 4-coordination (complexes like MX_2Y_2). The *cis* isomer has two reference groups adjacent to each other, the *trans* form has the groups opposite.

Chelate Compounds

Any complexing group capable of being a donor of two or more electron pairs is called a *chelating agent*, and the substance formed is called a *chelate*. The attachment is again by coordinate covalent bonds and the atoms best known for electron sharing in chelation are oxygen, nitrogen, and sulfur. If a chelating group attaches in two positions in the coordination sphere it is called a *bidentate group* (literally, having two teeth). Tridentate, tetradentate, pentadentate, and hexadentate groups are also known. Ring formation is a characteristic of chelation, and the bond angles of common atoms like C, O, N, and S in chelating groups favor 5- and 6-membered rings. The presence of chelates is detected by (*a*) isolation and analysis of pure compounds (*b*) changes in color (*c*) low conductivity, and (*d*) low solubility in water but high solubility in organic solvents. Chelates are useful in analytical chemistry (see Chapter 12 on organic reagents), in softening water, washing up areas contaminated with radioactive salts, etc. Natural chelates such as chlorophyll and hemoglobin are also known.

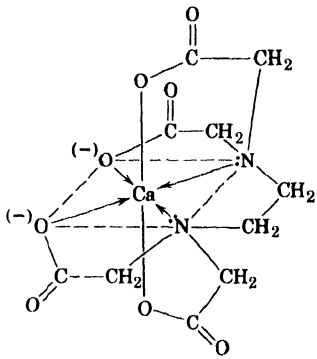
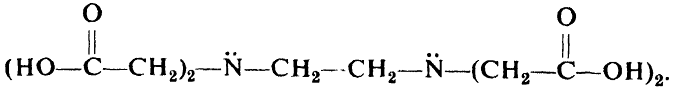


FIG. 4-8. Hexadentate chelation of Versene with Ca^{+2}. The dashed lines are used to aid in showing the octahedral configuration.

A compound of recent practical interest is ethylenediaminetetracetic acid,*



$$(\mathrm{HO}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{CH_2})_2-\ddot{\mathrm{N}}-\mathrm{CH_2}-\mathrm{CH_2}-\ddot{\mathrm{N}}-(\mathrm{CH_2}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{OH})_2.$$

It powerfully complexes divalent metals and is used in titrating Ca^{+2} and Mg^{+2} in water analysis, in dissolving scale from boilers, etc. It can be tetradentate or hexadentate; the latter is illustrated.

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[*] Two trade names are Versene and Sequestrene. Several derivatives of the acid have also received attention.

Stabilization of Oxidation States

Complex formation can stabilize oxidation states of metallic elements that normally cannot exist in aqueous solution. For instance Co^{III} and Co^{IV} are powerful enough oxidants to liberate O_2 from H_2O, but their ammine derivatives are stable in water solution. The chemistry of such unfamiliar oxidation states as Cu^{III}, Ag^{II}, Ag^{III}, Cr^{II}, Mn^{I}, etc., has been conveniently studied in the presence of complexing agents.

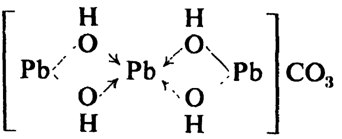
Lattice Compounds

Werner compounds involve definite chemical bonding between the central ion and the groups in the coordination sphere, and the resulting complex ion is largely retained in solution. There is a general class of substances known as *lattice compounds* which from their composition might be taken for coordination compounds but which should be catalogued otherwise. Most inorganic lattice compounds are *double salts*, so called because two salts (plus water frequently) crystallize together in definite molecular ratios to form a stable, symmetrical crystal lattice. Such compounds disappear upon dissolution, however, and all possible ions are free to give their characteristic reactions.

Other Complex Inorganic Compounds

There are many complex inorganic substances, but by comparison to large molecular weight organic compounds they are less numerous. Three examples are given below.

1. *Polynuclear Werner salts* are those containing two or more metallic ions with some coordinated atoms held in common. *Basic salts* generally belong to this class; basic lead carbonate, $PbCO_3 \cdot 2Pb(OH)_2$, for example, is better represented as



2. *Poly acids* are formed by combination of acid anhydride molecules such as V_2O_5, MoO_3, and WO_3 with another acid that furnishes a central ion for the establishment of a complex anion. If only one kind of anhydride molecule is present, the compound is called an *isopoly acid*; if more than one, it is a *heteropoly acid.* These substances are quite complex and capable of wide modification under different experimental conditions. See Chapter 20 and test 22–16 for some specific examples.

3. *Silicates* can be thought of as polymers in which oxygen atoms are coordinated octahedrally around dipositive cations like Mg^{+2} or

tetrahedrally around Si^{IV} or Al^{III}. These are of interest because of the prevalence of silicate minerals.

PROBLEMS

1. (*Library*) There is a generalization which states that in many Werner ions the coordination number is twice the central element's oxidation state. From a reference book, list a number of examples both supporting and contradicting this, and give your conclusions.

2. The ionic radii of several metallic ions are $V^{III} = 0.66$, $Ti^{IV} = 0.68$, $Be^{II} = 0.31$, $Ba^{II} = 1.35$, and $Rb^{I} = 1.69$ A. Calculate the charge densities and predict whether or not each is prone to complex formation and hydration in solution. How many groups will probably coordinate with each?

3. $[Co(NH_3)_6]^{+3}$ is more stable than $[Co(NH_3)_4]^{+2}$ (the latter liberates H_2 from H_2O). Explain the stability difference by both the Sidgwick and Pauling methods. (For the latter, the odd electron of Co^{II} is promoted to the 4*d* state.)

4. Dipositive nickel may under different conditions give either square planar or tetrahedral 4-coordination. As in Fig. 4–1, show the electronic distribution and the orbitals used in bonding from the following hints: (*a*) assume that in the planar configuration, two unpaired 3*d* electrons of Ni^{+2} pair up leaving one open 3*d* orbital, and (*b*) whereas the planar ion is diamagnetic, the tetrahedral ion is paramagnetic to the extent of indicating two unpaired electrons.

5. (*a*) (*Library*) In a dictionary find the definition of the word *chela* and relate to the action of chelating groups.

(*b*) (*Library*) Look up the definition of *sequester* and explain why Sequestrene is a descriptive trade name for ethylenediaminetetraacetic acid.

(*c*) A sodium salt of ethylenediaminetetraacetic acid was suggested once as an internal medicine for dissolving gall stones. Explain. (It required too high a *p*H to be valuable, however.)

6. There is a generalization that says that those metallic ions already having a rare gas configuration tend not to form Werner ions. Cite several specific examples.

7. $[W(CN)_8]^{-4}$ is a stable complex ion; explain this by means of the effective atomic number idea.

8. Four octahedrally coordinated isomers of $CrCl_3 \cdot 6H_2O$ are known. Draw structures from these descriptions: (*a*) gives 4 ions in solution (*b*) gives 3 ions (*c*) gives 2 ions and has a *cis* configuration, and (*d*) gives 2 ions and has a *trans* configuration.

9. Interpret the following: (*a*) $CoCl_3 \cdot 5NH_3 \cdot H_2O$ is not dehydrated at 30 C over a drying agent but from its solution, Ag^+ precipitates three equivalents of AgCl.

(*b*) A certain compound is known to contain platinum, ammonia, and chlorine. When 125.0 mg of it are boiled with a solution of strong alkali, the compound slowly decomposes. The liberated ammonia is absorbed in boric acid and requires 11.25 ml of 0.1097 N HCl to titrate it (see Ammonium, Chapter 19). The residue of platinum in the main reaction flask is washed, filtered off, dried, and found to weigh 60.3 mg. In a separate experiment, a 10^{-3} m solution of the compound has a molal conductance of 265 (see Table 5–3). Show that correct interpretation of this data leads to the conclusion the compound is dichlorotetrammineplatinum(IV) chloride. Write the structural formula.

10. Name the Werner compounds: $Na[Sb(OH)_6]$, $(NH_4)_2[Sn(OH)_6]$, $K_2Na[Fe(CN)_6]$, $[Al(OH)_3(H_2O)_3]$, and $[NiCl_3(NH_3)_3]Br$.

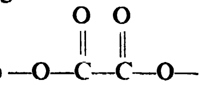
11. (*Library*) Find the structure of (*a*) *hemin* and (*b*) *chlorophyll*. Copy them and explain why they are chelates. (*c*) Find reference to *clathrate compounds*. Define the term and give an example.

12. (*Library*) Find reference to the following types of *water of crystallization*: (*a*) constitutional (*b*) coordinated (*c*) anion (*d*) lattice, and (*e*) zeolitic. Define the terms and give an example of each. The listing here is in the order of decreasing stability. Can you offer any reasons for this order?

13. How could one chemically distinguish among potassium chromium alum, hexamminechromium(III) sulfate, and potassium disulfatodiamminechromate (III)?

14. Predict which member of the following pairs will be more stable and tell why: (*a*) $Na_2[HgCl_4]$ or $Na_2[HgI_4]$ (*b*) $Na_4[NiCl_6]$ or $Na_3[NiCl_6]$.

15. Show electronically that $[Co(NH_3)_6]^{+3}$ is expected to be octahedral because of d^2sp^3 bonding.



16. The oxalato group $—O—\overset{\overset{\displaystyle O}{\|}}{C}—\overset{\overset{\displaystyle O}{\|}}{C}—O—$ is bidentate. Draw the octahedral trioxaltoiron(III) ion. Draw the isomers of dichlorodioxalatoiron(III) ion. Explain why a radiator cleaner sold for rust removal contains oxalate.

17. Converted to standard temperature and pressure, it is found that 56 cc of ferric chloride vapor weighs 811 mg. Calculate the mol. wt and postulate a structure for the compound.

18. (*a*) $[Cd(NH_3)_4]^{+2}$ has no magnetic moment. Give the electronic configuration and draw the ion with its correct geometry. Explain your choices.

(*b*) $[Cr(NH_3)_6]^{+3}$ has a moment associated with three unpaired electrons and the complex is octahedral. Give the electronic structure, and indicate the orbitals used in bonding.

19. A solution contains palladium, ammonia, and chloride. Analysis shows that there is 0.1 g atoms of Pd per 100 ml and that the ratio of Pd to Cl is 1 to 4. Addition of 100 ml of 0.4 F $AgNO_3$ to 10 ml of palladium solution gives a precipitate of 20 mmoles of AgCl. Addition of 10 ml of 0.2 F HNO_3 to another 10 ml portion of sample gives a solution 0.1 F in H^+. What can one deduce concerning the original solution?

20. When 3.27 g of the compound $NaF \cdot CoF_5$ are dissolved in 100 g of H_2O, the solution's freezing point is found to be -0.60 C. In an electrolysis of the solution at room temperature, the cobalt concentration (as measured visually by depth of color) increases around the positive electrode. What can one surmise?

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5

ACID-BASE THEORIES AND THE ELECTRICAL CONDUCTANCE OF ELECTROLYTES

Early Theories of Acids and Bases

The theories developed to explain and correlate the behavior of acids and bases date back to the alchemists. Those early chemists recognized such substances as chemical opposites in that interaction caused a mutual loss of characteristic properties. They also noted that acids tasted sour, changed the colors of plant extracts (the first indicators), etched metals, dissolved some minerals, etc., but, since little was known about chemical composition, it was not until the early part of the nineteenth century that quantitative statements could be made.

Before 1814 it was believed that all acids contained oxygen, but in that year the English electrochemist *H. Davy* provided a method for compound decomposition with new experimental techniques. He showed that *electrolysis* of HCl solution gave only H_2 and Cl_2, and from further experiments on H_2SO_4 and HNO_3 guessed that, since hydrogen was the only element common to all the acids, it might be responsible for their acidic properties.

In 1835 the German chemist *J. Liebig* conducted a number of tests to show acid action on metals and concluded that since H_2 was released, and compounds were formed that contained the metal, acids should be defined as agents containing hydrogen replaceable by metals. In a continuation of electrical experiments in the same year by *M. Faraday*, that famous English chemist found that most acids and bases give electrically conducting solutions that can be decomposed by direct current. He coined the word *electrolyte* for substances yielding conducting solutions.

In the following years electrolytes and electrochemical phenomena were extensively investigated and it soon became apparent that two kinds of electrolytes existed. There were those that showed weak conductivity and those that showed strong conductivity. Furthermore, the *weak electrolytes* were noted to exhibit a gradual increase in conductivity with dilution, whereas the *strong electrolytes* demonstrated excellent conductance at almost any dilution.

Arrhenius

It wasn't until the period 1883–1887, during which *S. Arrhenius* developed his theory of electrolytic dissociation, that a unifying idea was able to explain most of the observations. The Swedish chemist proposed that in water solutions, strong electrolytes (strong acids and bases and most salts) exist largely as charged particles called *ions* rather than as molecules. These free moving ions are capable of carrying current, and move toward the oppositely charged electrodes during electrolysis. His conclusions were based partly upon experiments he had made of the freezing points of solutions of electrolytes in which it was noticed, for example, that an HCl solution gave about twice the expected freezing point lowering and Na_2SO_4 about three times the expected effect. This meant that more particles were in solution than was obvious from the molecular formulas.

Arrhenius therefore defined acids as substances of the type HX *dissociating* in aqueous solution to yield H^+ and X^-, bases like MOH as substances giving M^+ and OH^-, and *neutralization* as the result of these ions combining:

$$HX = H^+ + X^-$$

$$MOH = M^+ + OH^-$$

$$H^+ + OH^- = H_2O$$

He visualized that these ions would be separated by a *polar solvent* like H_2O, since coulombic forces between ions is low and further, that increasing dilution should encourage ionization since the ions would become more independent. This concept satisfied all observations on weak electrolytes admirably and is still held today. He showed by electrical conductivity methods (special experiment 1 and Table 23–1) that the conductivity of an equivalent weight of a weak electrolyte increased gradually with dilution and reached a maximum value in very dilute solution, at which point presumably all molecules of solute had dissociated into ions.

When Arrhenius applied the same experimental methods to strong electrolytes he ran into trouble, however. For instance he found from conductivity and freezing point data that 0.1 *M* HCl is apparently 89% dissociated, 0.01 *M* is 96%, and 0.001 *M* is 98%. He never did explain the basis for the differences in the two types of electrolytes and could not therefore answer the question: why aren't strong electrolytes always 100% dissociated? The dilemma was finally solved 35 years later by Debye and Hückel, but this does not detract from the insight and original thought he gave the problems. Briefly, the Arrhenius contributions are these:

(1) Explained why compounds in solution conduct electricity.

(2) Gave consideration to the role of polar and nonpolar solvents in aiding or hindering dissociation.

(3) Explained the results of electrolysis experiments: ions migrate to electrodes of opposite sign.

(4) Permitted characterization of compounds on the basis of the maximum conductance their ions give at a dilution when further addition of water gives no further dissociation ("*infinite dilution*").

(5) Formulated an explanation of why solutions of strong electrolytes give abnormally large changes in boiling and freezing points and osmotic pressures (since these *colligative properties* depend upon the number of particles in solution).

(6) Showed that compounds that can give several ions in solutions will, in the case of weak electrolytes, dissociate in steps:

$$H_3PO_4 = H^+ + H_2PO_4^- \qquad (5\text{–}1)$$
$$H_2PO_4^- = H^+ + HPO_4^{-2} \text{ etc.}$$

This also accounted for neutralization of one or more H^+ by stepwise titration with base and for the formation of salts such as NaH_2PO_4, etc.

(7) Explained why solutions containing a given ion all have reactions characteristic of that ion. Thus, both NaCl and HCl solutions give a precipitate of AgCl with Ag^+, but $HClO_4$ does not since its dissociation, $HClO_4 = H^+ + ClO_4^-$, gives no Cl^-. CCl_4 also gives no reaction with Ag^+ because it is a nonelectrolyte. Carrying the last illustration a step further, if CCl_4 is a nonelectrolyte, then chloroform $CHCl_3$ is by analogy expected to be a nonelectrolyte and hence not acidic, which is the case.

(8) Formed a foundation for the treatment of weak electrolytes by mass action law (Chapters 6 and 7) by picturing them in solution as a mixture of undissociated molecules and ions, the latter increasing as the solution is diluted. Acetic acid as a typical compound is therefore correctly described by,

$$\underset{\text{Molecules}}{HAc} \leftrightharpoons \underset{\text{Ions}}{H^+ + Ac^-} \qquad (5\text{–}2)$$

Recognition of Interionic Forces

Strong electrolyte interpretation was reconsidered by three investigators in the period 1900–1912. *S. Jahn* surmised that since ions in solution are charged particles, unlike charges will attract each other and perhaps decrease the over-all conductance efficiency.

G. N. Lewis showed that because of interionic attractions and repulsions, corrected concentrations should be used in calculations. He called these *effective concentrations*, or *activities*, and their use is the basis for refined treatment today.

G. B. B. M. Sutherland, in similar work, attempted mathematically to define three forces at work in solutions that complicate affairs by tending to immobilize ions: (*a*) ion-solvent attraction (*b*) ion-ion attraction and (*c*) solution viscosity. His results were only semiquantitative, however.

Although none of these men gave a complete explanation of the characteristics of electrolytic solutions, their contributions greatly aided their successors and some parts of their thinking are still retained.

Debye and Hückel

As will be explained in Chapter 13, the development of X-ray diffraction in the decade 1912–1922, which made structural chemistry an exact science, gave chemists the data needed for continuation of many problems *P. J. W. Debye* and *E. Hückel* (1923) began with the knowledge from X-ray study on salts that both solid and gaseous NaCl is composed exclusively of ions Na^+ and Cl^- and is to be considered 100% ionic at all times. Whereas Arrhenius had thought the situation to be one of equilibrium between undissociated molecules and ions (which is true for weak electrolytes), as $NaCl = Na^+ + Cl^-$, Debye and Hückel proved that in solution the picture is better given by

$$Na^+Cl^- = Na^+ + Cl^- \qquad (5\text{–}3)$$

The left side specie is sometimes called "*bound ions*" to signify decreased mobility by interionic attraction, and the right side, "*free ions*," meaning those far enough apart to behave as individuals.

Brönsted and Lowry

With weak electrolytes explained by Arrhenius, strong ones by Debye and Hückel, and in the meantime considerable information on chemical bonding having become known, attention was turned to refining acid-base generalizations.

J. N. Brönsted and also *T. M. Lowry* (1923) recognized limitations in defining acids and bases simply in terms of H^+ and OH^- because closely related phenomena were not correlated. For example, although H_3PO_4

was called an acid, its ion, $H_2PO_4^-$, which also could give H^+, was not always classed as an acid, nor was it classed as a base when it combined with H^+ to reform H_3PO_4. Accordingly *they defined an acid as any substance which can donate a proton* (H^+), *and a base as any substance that can accept a proton*:

$$\begin{aligned} \text{Acid} &= H^+ + \text{base} \\ HCl &= H^+ + Cl^- \qquad (5\text{–}4) \\ H_2PO_4^- &= H^+ + HPO_4^{-2} \text{ etc.} \end{aligned}$$

In an aqueous solution of an acid the base is H_2O, whose unshared electron pairs make it capable of holding the proton. The typical system is an *equilibrium* in which two bases compete to the extent of their base strengths for protons from the two acids present:*

$$\begin{aligned} HCl + H_2O &= H_3O^+ + Cl^- \qquad (5\text{–}5) \\ \text{Acid 1} + \text{base 2} &= \text{Acid 2} + \text{base 1} \end{aligned}$$

In Brönsted nomenclature, acid 1 and base 1, and acid 2 and base 2 respectively constitute two *conjugate pairs*, the members of each pair differing only by an H^+. Acids may be cations like H_3O^+, anions like HSO_4^-, and molecules like HAc in this system, since any of these can give protons. Substances like HSO_4 may be acidic in a basic environment or basic in an acidic environment and are said to be *amphiprotic* or are called *ampholytes*.

Acid-base strengths† are capable of comparison by the Brönsted theory. In this matter the role of water as a proton donor or acceptor is of prime importance. With a base stronger than water itself, H_2O dissociates and acts as an acid:

$$\underset{B1}{S^{-2}} + \underset{A2}{H_2O} = \underset{A1}{HS^-} + \underset{B2}{OH^-} \qquad (5\text{–}6)$$

With an acid stronger than itself, water is capable of proton acceptance:

$$\underset{A1}{HSO_4^-} + \underset{B2}{H_2O} = \underset{A2}{H_3O^+} + \underset{B1}{SO_4^{-2}} \qquad (5\text{–}7)$$

By measuring pH (Chapter 6) of a series of reactions like the two above, one can establish a list of approximate acid and base strengths.

Strong acids and bases cannot be evaluated in this manner, however,

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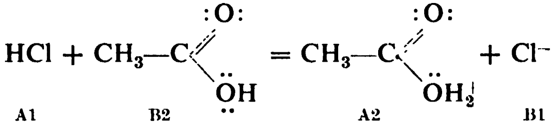
* This means that Brönsted calls the acid in aqueous solution H_3O^+ the *hydronium ion*. Though this will be inferred in following discussions, H^+ will be used instead of H_3O^+ in most cases. The simplification is made because the extent of proton hydration varies and because certain conventional expressions like pH (instead of pH_3O) have been retained. Where H_3O^+ is vital to the text, it is shown.

† Quantitative aspects are considered in Chapter 7.

since they all appear equally strong. It is then necessary to resort to measurements in solvents with lower acid strength for the examination of strong bases and with lower base strength for the investigation of strong acids to obtain a spread in proton transfer ability. Acetic acid is a solvent of the latter type. It has acidic properties of its own of course but is forced into the role of a base when confronted with stronger proton donors:



$$\underset{A1}{HCl} + \underset{B2}{CH_3{-}C(=\ddot{O}{:})\ddot{\underset{\cdot\cdot}{O}}H} = \underset{A2}{CH_3{-}C(=\ddot{O}{:})\ddot{O}H_2^+} + \underset{B1}{Cl^-} \qquad (5\text{–}8)$$

Acid strength of A1 (dry HCl gas) in this solution is measured by electrical conductivity, since strong acids will shift the system to the right with the production of ions. Experiments show the strength order of several common acids is $HClO_4 > HI > HBr > HCl > HNO_3$, though in H_2O they appear equally strong.

Franklin

E. C. Franklin's research in the United States during the first quarter of this century began by considering that in water a *solvent-solvent reaction* is possible:

$$\underset{A1}{H_2O} + \underset{B2}{H_2O} = \underset{A2}{H_3O^+} + \underset{B1}{OH^-} \qquad (5\text{–}9)$$

This idea should carry over into other *solvent systems* as liquid ammonia and anhydrous acetic acid. For example:

$$\underset{A1}{NH_3} + \underset{B2}{NH_3} = \underset{A2}{NH_4^+} + \underset{B1}{NH_2^-} \qquad (5\text{–}10)$$

$$\underset{A1}{HAc} + \underset{B2}{HAc} = \underset{A2}{H_2Ac^+} + \underset{B1}{Ac^-} \text{ etc.}$$

He successfully developed a system of ammonia chemistry which clearly showed the value of general acid-base theory for understanding a great variety of reactions. For instance in liquid ammonia, the reaction between sodium amide and ammonium chloride (the reverse of eq. 5–10) is thought of as a neutralization, analogous to NaOH and HCl reacting in water, since a solvent and a salt is the result:

$$NaNH_2 + NH_4Cl = NaCl + 2NH_3 \qquad (5\text{–}11)$$

Lewis

Between the years 1915 and 1938, the American chemist *G. N. Lewis* carried on acid-base studies and from these discovered many examples in support of four *criteria of acids and bases* on which his work dwelled:

(1) Neutralization reactions are rapid.

(2) Stronger acids and bases will replace weaker acids and bases from their compounds.

(3) Titrations using indicators to find equivalence points are feasible.

(4) Both acids and bases frequently function as catalysts.

The Lewis concepts are more general than those of Brönsted because H^+ is not invariably necessary. Instead, Lewis considered the mode of bond formation as the characteristic feature of acid-base interaction, and the presence or absence of unshared electron pairs as the distinguishing feature of bases and acids themselves. *He defined an acid as any substance that can accept an electron pair (frequently it has only six of its normal octet of valence electrons), and a base as any substance capable of donating the electron pair (it has an octet of electrons but not all are used in bonding).* Reaction between the two results in the formation of a coordinate covalently bonded product (Chapter 3). This view incorporates previous examples as well as others, including reactions in the gas and solid phases, and of many organic compounds. A few examples follow.

$$\underset{\substack{\text{Acid}\\(\text{needs } e \text{ pair})}}{\mathrm{H^+}} + \underset{\substack{\text{base}\\(\text{has unshared } e)}}{:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}\mathrm{H}^-} = \underset{\substack{\text{Neutralization product}\\(\text{has coordinate covalent bond})}}{\mathrm{H} \leftarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}\mathrm{H}} \qquad (5\text{–}12)$$

$$\mathrm{BF_3} + :\mathrm{NH_3} = \mathrm{F_3B} \leftarrow :\mathrm{NH_3} \qquad (5\text{–}13)$$

$$\mathrm{SiO_2} + \mathrm{MgO} = \mathrm{MgSiO_3} \qquad (5\text{–}14)$$

Usanovich

The latest (1938) and most inclusive acid-base ideas are due to the Russian chemist, *M. I. Usanovich. He has defined an acid as any substance capable of (a) yielding a cation (b) combining with electrons or an anion, or (c) giving a salt when it neutralizes a base. A base is any substance which can (a) give electrons or anions (b) combine with a cation, or (c) neutralize an acid to yield a salt.* This incorporates all older theories and extends them again, but because it is so general, the Brönsted and Lewis views still are used for most acid-base interpretations.

Electrical Conductance of Electrolytes

As has been inferred, electrical conductance studies did much to not only advance acid-base ideas but our general understanding of all electrolytic solutions. Since ions transfer current through a solution, their number will be directly proportional to the conductance (and vice versa) under specified conditions. (See special experiment 1 for typical procedure and experimental data.)

The *specific resistance*, ρ (rho), of a solution is the ohm resistance measured between parallel faces of a cube of solution 1 cm on an edge. The reciprocal of the specific resistance or resistivity is the *specific conductance*, kappa, or $\kappa = 1/\rho$. Conductance is expressed in reciprocal ohms (ohms^{-1}) which are also called mhos. If the temperature is constant, the conductance of a solution will vary with concentration and the speed with which the ions carry the current, since different ions have different *mobilities*. As one might suspect, H^+ and OH^- have greater speed or mobility in water solution than do other ions. To study mobility, a standard quantity of solute must be defined for reference and the gram equivalent weight is used. The conductance of this quantity is called the *equivalent conductance* at the particular dilution, and abbreviated with a capital lambda, Λ. To get Λ, one measures the conductance of 1 cc of solution then multiplies it by V, the cc volume needed to contain the gram equivalent weight, or $\Lambda = V\kappa$.

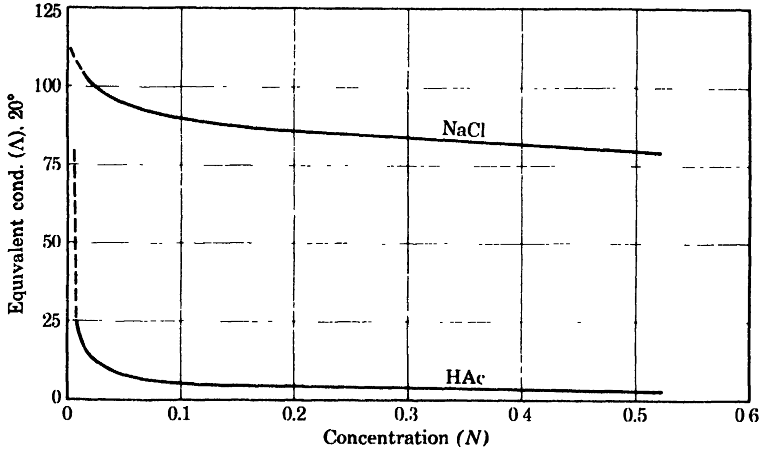


FIG. 5-1. Equivalent conductance vs. concentration for a typical weak and strong electrolyte.

Table 5-1 shows that the equivalent conductance of both strong electrolytes (NaCl, K_2SO_4, KOH, HCl) and weak electrolytes (NH_4OH, HAc) increases with dilution, but only values for the former are high at all concentrations. Both types of electrolytes (in more dilute solution) attain a maximum value, after which, further dilution has no effect on Λ. The equivalent conductance at this "*infinite dilution*" or "zero concentration" is abbreviated Λ_0. At that concentration all solute ions function unencumbered by interionic repulsions or attractions.

In practice one measures conductance of a strong electrolyte at a number of reasonable dilutions, then plots Λ versus the normal concentration N, and *extrapolates* to zero concentration. This is not feasible for weak electrolytes since the graphical extrapolation is too uncertain and the method described below is used.

TABLE 5-1. TYPICAL EQUIVALENT CONDUCTANCE DATA, 18 C

Normality	V, cc	NaCl	$\frac{1}{2}K_2SO_4$	KOH	NH_4OH	HCl	HAc
1.0	10^3	74.2	71.5	184	0.89	300.5	1.32
0.1	10^4	91.8	94.8	213	3.3	350.1	4.60
0.01	10^5	101.7	115.6	228	9.6	369.3	14.3
0.001	10^6	106.3	126.7	234	28	377	41

The Law of Independent Ion Migration

From conductance studies carried out in the years 1870–1890, the German chemist *F. Kohlrausch* assumed that the equivalent conductance of any electrolyte at "zero concentration" is the sum of the zero concentration (or limiting) equivalent conductance of its cation λ_0^+ and anion λ_0^-. These *ionic mobilities* are independent of each other and can be added directly to obtain Λ_0 for the compound. Ionic mobilities are related to the speed with which ions move under an applied voltage and are calculated (in physical chemistry courses) from Λ_0 and *transport numbers*, which are the fractions of current carried by each ion.

TABLE 5-2. LIMITING EQUIVALENT CONDUCTANCES OF SOME IONS AT 18 AND 25 C

Cation	λ_0^+, 18 C	λ_0^+, 25 C	Anion	λ_0^-, 18 C	λ_0^-, 25 C
H^+	315	348	OH^-	174	192
K^+	64.6	73.4	$\frac{1}{2}SO_4^{-2}$	68.5	79
NH_4^+	64.5	74.5	Br^-	67.3	77
$\frac{1}{2}Ba^{+2}$	55	65	Cl^-	65.5	75.5
$\frac{1}{2}Ca^{+2}$	51	60	$\frac{1}{2}C_2O_4^{-2}$	63	73
Ag^+	54.3	61.9	NO_3^-	62	70.6
Na^+	43.5	49.8	Ac^-	35	40.8

Calculation of Dissociation by the Conductivity Method

The equivalent conductance of a weak electrolyte at some normality, Λ_N, is a measure of the number of ions present in solution, and since Λ_0 is the maximum value, meaning 100% dissociation, the ratio Λ_N/Λ_0 is the fraction ionized at concentration N. This is also called α, the *degree of ionization*, and the *percent of ionization* is then 100α, or

$$\%\ \text{ionization} = 100(\Lambda_N/\Lambda_0) \qquad (5\text{–}15)$$

Example 5–1. At 18 C a 0.001 N soln. of HAc has a sp. resistance of 25,000 ohm cm. Calculate the sp. cond. and cc vol. needed to contain a g equiv. wt of solute at the given normality; also, the equiv. cond., the equiv. cond. at inf, diln., the degree of ioniz., and the percent of ioniz.

The sp. cond. is the reciprocal of the sp. resistance:

$$\kappa = 1/\rho = 1/25{,}000 = 4.00 \times 10^{-5}\ \text{ohm}^{-1}\ \text{cm}^{-1} \qquad (\textit{Ans.})$$

The vol., V, needed to contain a g equiv. wt is 1,000,000 cc (*Ans.*) because the 10^{-3} N solution only contains 10^{-3} g equiv./liter. Since κ is the cond. of 1 cc, the cond. Λ_N of the g equiv. wt is,

$$\kappa V = \Lambda_N = (4.00 \times 10^{-5})(10^6) = 40.0 \qquad (\textit{Ans.})$$

The value for the equiv. cond. representing 100% dissoc., Λ_0, is obtained by Kohlrausch's law and the 18 C values of limiting ionic mobilities from Table 5–2:

$$\Lambda_0 = \lambda_0^+ + \lambda_0^- = 315 + 35 = 350 \qquad (\textit{Ans.})$$

The ioniz. degree, α, is

$$\alpha = \Lambda_N/\Lambda_0 = 40.0/350 = 0.114 \qquad (\textit{Ans.})$$

and the percent dissoc. is

$$100\alpha = (100)(0.114) = 11.4\% \qquad (\textit{Ans.})$$

Molal Conductance and The Identity of Salts

The molal conductance of a solution is the conductivity of a mole of solute at the given molal dilution. If the conductivity of 1 cc of solution is measured, one multiplies by the number of cubic centimeters needed at that dilution to contain 1 g formula weight of solute. The following approximate room temperature data have been found from measurements on several 10^{-3} m salt solutions.

These molal conductance generalizations were of great assistance to Werner in the determination of coordination compound formulas. For instance, at the above dilution a solution of $PtCl_2 \cdot 4NH_3$ showed a molal conductance of 240 and gave 2 equivalents of AgCl when treated with excess Ag^+. From this he could deduce that the compound contained

TABLE 5-3. MOLAL CONDUCTANCES OF SALT TYPES (10^{-3} *m* SOLUTIONS)

Salt Type	Number of Ions	Approximate Molal Conductance
AB	2	95–110
A_2B	3	215–265
A_3B	4	390–450
A_4B	5	515–560
A_5B	6	590–630
AQ	0 (nonelectrolyte)	0

three ions, two of which were Cl^-, so the complex ion must have been $[Pt(NH_3)_4^{+2}]$.

Calculation of Dissociation by the Freezing Point Method

It was known to Arrhenius from the previous work of *C. Blagden* and contemporary accurate measurements of *F. M. Raoult* and *E. Beckmann* that a gram mole of any nonvolatile, nonionized solute dissolved in 1000 g of solvent (1 molal solution) raises the solvent's boiling point and lowers its freezing point characteristic amounts, and that the changes are due to the *number* of particles in solution and not their kind. These values for 1 *m* solutions are called *cryoscopic constants*. ΔT_b is the molal boiling point constant and ΔT_f the molal freezing point constant, and they vary with solvent used. Most of Arrhenius' work was done using ΔT_f, by which he showed, for example, that HCl gave about twice the expected lowering a nonionic material should give, Na_2SO_4 three times as much, etc. Such experimental results were excellent support for his ionization theory.

TABLE 5-4. SOME SOLVENTS FOR CRYOSCOPIC STUDIES

Solvent	Normal B.P., °C	ΔT_b, °C	Normal F.P., °C	ΔT_f, °C
Acetic acid	118.5	3.07	16.7	3.9
Benzene	80.15	2.53	5.5	5.12
Camphor	208.25	5.95	178.4	40
Carbon disulfide	46.13	2.34	−111.5	
Phenol	181.2	3.56	42	7.27
Water	100.00	0.52	0.00	1.86

From this type of data one can calculate whether or not a substance is a strong or weak electrolyte, and, if the former, then how many ions it dissociates into. One can also find the degree of apparent ionization of strong electrolytes and apparent molecular weights of any solutes. Weak electrolyte ionization cannot be studied easily because it furnishes too few ions to effect much freezing point change.

Example 5–2. A 0.112 molal soln. of $BaCl_2$ begins depositing ice at −0.381 C. Find the apparent % dissoc.

We may let x be the molality of Ba^{+2} in soln. Then $2x$ will be the molality of Cl^-, and $0.112 - x$ will be the molality of the 'undissoc.' $BaCl_2$:

$$\underset{0.112-x}{BaCl_2} \;=\; \underset{x}{Ba^{+2}} \;+\; \underset{2x}{2Cl^-}$$

The total molality of solute particles is $(0.112 - x) + x + 2x = (0.112 + 2x)$. When this is multiplied by the f.p. constant, ΔT_f, of the solvent, it should give the f.p. drop of the soln., or $(0.112 + 2x)1.86\text{ C} = 0.381\text{ C}$. Solving for x gives 0.0465 molal Ba^{+2}. The fraction "dissoc." is 0.465/0.112 and the % is 100 times that, or 41.5% apparent dissoc. (*Ans.*)

How could one check this answer? Verify it by your method.

PROBLEMS

1. X-ray diffraction measurements demonstrate that perchloric acid monohydrate (m.p. 50 C) is a crystalline substance isomorphous (see problem 5, Chapter 13) with ammonium perchlorate. This has been offered as evidence of the existence of the hydronium ion. Explain.

2. In the chapter, a number of acid-base theories were described and named after their discoverers. Five of the more important ones are also known as (*a*) the proton theory (*b*) the positive-negative theory (*c*) the electron theory (*d*) the solvent system theory, and (*e*) the water theory. Match them with the men's names and briefly explain why the descriptions are appropriate.

3. Explain the following reaction in terms of the Lewis theory. Why doesn't the Brönsted theory cover it?

$$(CH_3)_3N + BCl_3 = (CH_3)_3NBCl_3$$

(The final product is called trimethylamine boron trichloride.)

4. Select several pairs of values from the first two columns of Table 23–1 and confirm the data given in the next five columns by calculation.

5. From Table 5–1, plot for NaCl and $\frac{1}{2}K_2SO_4$, $N^{\frac{1}{2}}$ versus Λ_V as best you can, and extrapolate each line to zero concentration. Check the results from Table 5–2 using Kohlrausch's law. Explain the purpose of the graphical method.

6. (*a*) From Table 5–1, calculate the apparent ionization of NaCl, KOH, and HCl at each concentration and present this data in table form.

(*b*) Why is the word "apparent" used in this connection?

7. (*a*) According to Table 5–1, at what temperature should 0.1 and 1.0 *N* NaCl solutions begin to freeze?

(*b*) Will the entire solution freeze at the temperatures calculated? If not, why not?

(*c*) Why do you suppose Arrhenius studied freezing point changes in preference to boiling point changes?

8. What is peculiar about camphor as a solvent for measuring freezing point depressions of its solutions? What is the advantage of using it?

9. Interpret each of the following by the (*a*) Lewis theory, (*b*) Brönsted theory, and (*c*) Usanovich theory:

$$
\begin{aligned}
&(1)\ Cu^{+2} + 4NH_3 = Cu(NH_3)_4^{+2}\\
&(2)\ HS^- + H^+ = H_2S\\
&(3)\ Ag^+ + Cl^- = AgCl\\
&(4)\ HCl + AlCl_3 = H^+ + AlCl_4^-
\end{aligned}
$$

10. The freezing point of a 1.0 *N* KCl solution is −3.35 C. Calculate the apparent molecular weight of the salt from this and explain why it differs from the actual molecular weight.

11. Designate the conjugate pairs in the following:

$$
\begin{aligned}
&(a)\ HNO_2 + H_2O = H_3O^+ + NO_2^-\\
&(b)\ HF + NH_2OH = NH_3OH^+ + F^-
\end{aligned}
$$

12. (*a*) What is the difference between molal and equivalent conductances?

(*b*) A solution of $PtCl_4 \cdot 2NaCl$ at a dilution of 1 mole/1000 liters has a molal conductance of 229. Electrolysis of a more concentrated solution gives no Pt or Cl at the negative pole. What can one deduce about the compound's formula?

13. What would be the approximate freezing point of 0.10 *M* potassium hexacyanoferrate(II)? Explain how this freezing point determination would aid in deducing the salt's formula.

14. (*Library*) Beckmann invented his thermometer to measure cryoscopic changes with an accuracy of ± 0.002 C. Find reference to this instrument, sketch it, and explain how it functions.

15. One has solutions of the following salts in 0.001 *m* concentrations. Plot a rough graph of molal conductance vs. the charge on the complex ion (scale from +3 to −3), and explain how the graph would aid one in establishing the formulas of other Werner compounds: $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_4Cl_2]Cl$, $[Co(NH_3)_3Cl_3]$, $Na[Co(NH_3)_2Cl_4]$, $Na_2[Co(NH_3)Cl_5]$, and $Na_3[CoCl_6]$.

16. (*a*) A solution made by dissolving 1.28 g of sulfur in 50.0 g of CS_2 begins boiling at 46.36 C. Explain.

(*b*) The same quantities of solute and solvent are mixed again, but this time the solute is phosphorous and the boiling point of the mixture is 46.61 C. Explain.

17. A class determines the f.p. of 1.00 *m* $LiNO_3$ to be −3.40 C. J. P. Slipshod knows each $LiNO_3$ can give two ions, so he figures that a f.p. drop of (1.86 C)(2) = 3.72 C means 100% ionization. He calculates the apparent ionization in the solution by setting up the proportion 100%/3.72 C = x%/3.40 C, from which $x = 91.4\%$. Everybody else in class gets 82.8%, so J. P. figures he is the only one who saw through the math. Who is right?

18. Hydrazine hydrate, $H_2N—NH_2 \cdot H_2O$, in aqueous solution turns red litmus to blue. Explain.

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6

REACTION RATES AND CHEMICAL EQUILIBRIUM

Early chemists recognized that not all reactions take place at the same speed or proceed to completely consume the reacting materials. It was found that some reactions begin rapidly, slow, and finally stop, and it was believed that motion of all particles had halted because evidence of further action was not visible. It is now known that molecular motion never ceases and that the apparent cessation of many chemical processes is due to the advent of a reverse combination by reaction products to reproduce original reactants. The speed of this reverse reaction is slow at first, since not many product molecules are available for reaction, but, as the forward reaction increases their number, the probability of their reaction increases. When the rates* of the opposing reactions are equal, the system comes to its apparent rest. In other words, a state of *dynamic* (instead of static) *equilibrium* is established between reactants and products so no net material transport takes place. The determination of the concentration ratio (products/reactants) can be made by quantitative analysis of the equilibrium mixture, and under specified conditions is a constant for a particular system. As will be seen, this *equilibrium constant* is the starting point for many useful calculations which form the theoretical foundations of analytical chemistry.

Factors Affecting Reaction Rates

Rates are influenced by a host of factors, only some of which are well

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* *Specific rates* are expressed in moles per liter reacting per second.

understood and can be dealt with quantitatively. The following all exert effects: the nature of reacting substances, their physical state, pressure, the presence or absence of catalysts and their nature, the outside energy available such as heat and light, and the concentrations.

1. Catalytic effects. A *catalyst* is a substance that affects rates and is not changed in the reaction. A catalyst is classed as positive if it accelerates, and negative if it slows attainment of equilibrium. Catalysts may function in *heterogeneous* (two or more phases) systems as in the reaction $2H^+ + 2e^- = H_2$, which is hastened on a surface of finely divided Pt, or in a homogeneous (single phase) system as $2N_3^- + I_3^- = 3I^- + 3N_2$, which is accelerated by such catalysts as SCN^-, S^{-2}, or $S_2O_3^{-2}$ in solution. Catalysts do not alter the final equilibrium state or shift the degree of conversion, however. This means that the yield of reaction products is the same with or without the catalyst.

2. Concentration effects. It was discovered in 1864 by the Swedish chemists *M. Guldberg* and *P. Waage* that the speeds of many reactions are directly proportional to the "active masses" (molar concentrations will be used here) of reactants raised to powers which are their coefficients in the balanced reaction equation. This statement has become known as the *law of mass action.* For example, to test a solution for acetate, one adds a trace of sulfuric acid (catalyst) and some ethyl alcohol. Ethyl acetate (identified by odor) and water form, and as their concentrations increase the reverse reaction becomes important:

$$HAc + C_2H_5OH \overset{H^+}{=} C_2H_5Ac + H_2O$$

The specific rate of reaction to the right s_r is given by

$$s_r = [HAc][C_2H_5OH]k_r \qquad (6\text{–}1)$$

and to the left is

$$s_l = [C_2H_5Ac][H_2O]k_l \qquad (6\text{–}2)$$

The terms k_r and k_l are specific reaction rate constants and are different for different reactions. They can be determined from equilibrium concentration measurements. The values are constant at constant temperature and generally increase as temperature increases. The rate constants represent the fraction of molecules that are colliding and reacting per second. Therefore, k times a molar concentration gives the number of molecules reacting in unit time (1 sec) per unit volume (1 liter).

The square brackets indicate *molar concentrations* (see the section on **concentration conventions,** p. 10). If HAc and/or C_2H_5OH are in abundance, formation of the ester and water will be relatively rapid; if instead the latter are in large excess, then acid and alcohol will be relatively quickly formed. When $s_r = s_l$ at some temperature, reactants and products are formed in equal amounts each second, so concentrations do not change and the system is at equilibrium.

3. Temperature effects. Reacting molecules must have energy for bonding and must approach each other within bonding distance for reaction to occur. It is evident that raising the temperature of a system will increase both the average molecular energy and the molecular collision rate, so in almost every case known, reaction speed increases with increasing temperature. For the average reaction at room conditions, it has been found that the specific rate increases about 10–30% for every 1 C rise in temperature.

Equilibrium and The Mass Action Law

Derivation of this law is developed in physical chemistry courses using methods from thermodynamics discovered by *A. Horstmann* (1873), *J. W. Gibbs* (1876), and *J. H. van't Hoff* (1886). A much simplified presentation will give all that is needed here, however.

For the general reaction,

$$\mathrm{A} + \mathrm{B} = \mathrm{D} + \mathrm{E}$$

as in the preceding section, the rates right and left are equal to the products of molar concentrations times the rate constants:

$$s_r = k_r[\mathrm{A}][\mathrm{B}]$$
$$s_l = k_l[\mathrm{D}][\mathrm{E}]$$

At equilibrium, the forward and reverse speeds are equal,

$$s_r = s_l = k_r[\mathrm{A}][\mathrm{B}] = k_l[\mathrm{D}][\mathrm{E}]$$

Collecting like terms, and letting the ratio of constants be K, the equilibrium constant, we get

$$k_r/k_l = [\mathrm{D}][\mathrm{E}]/[\mathrm{A}][\mathrm{B}] = K \qquad (6\text{–}3)$$

By accepted convention, division is always made by putting the resultants over the reactants (right side terms over left as the equation is written). If the equation contained the coefficients, w, x, y, z, as

$$w\mathrm{A} + x\mathrm{B} = y\mathrm{D} + z\mathrm{E}$$

the equilibrium constant's value is

$$K = [\mathrm{D}]^y \cdot [\mathrm{E}]^z/[\mathrm{A}]^w \cdot [\mathrm{B}]^x \qquad (6\text{–}4)$$

The student may now be surprised to learn that most reactions are more complex than the idealized four particle A + B = D + E, because a number of intermediate reactions often take place before the final products appear. These steps may or may not be known and are not deducible without experimental work to find what species may be present besides A, B, D, and E, and upon what species the rates depend. Such study is the province of *chemical kinetics*, the science of reaction rates and mechanisms, and is too advanced for consideration here. Nevertheless, despite the fact that important omissions were made in the derivation of K, the final expression is correct. This is so because the equilibrium state is independent of the path by which it was attained, as one can deduce from the law of energy conservation. Thus at equilibrium s_r and s_l are equal and equation 6–4 is applicable to all specific equilibrium situations to be encountered even though intermediate chemical processes might be involved about which we know nothing.

The important idea is summarized as follows: *for a reversible reaction at equilibrium at a given temperature, the product of concentrations of resultants raised to powers which are respectively their coefficients in the balanced reaction equation, divided by the product of concentrations of reactants raised to powers which are their respective equation coefficients, is a constant.*

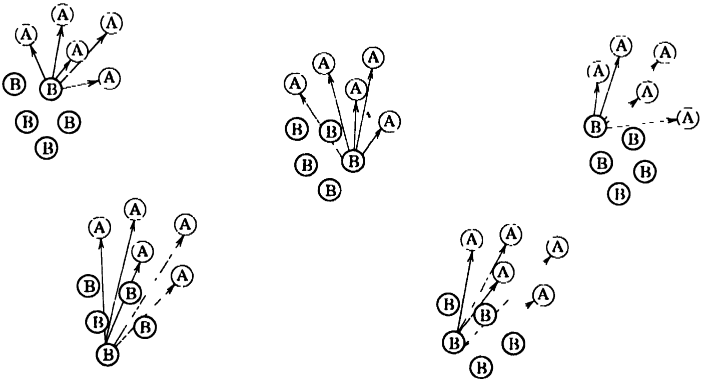

FIG. 6-1. Random distribution of reacting particles showing that if there are x of one type and y of the other, the number of possible reaction collisions is xy.

A simple physical picture is this: suppose ten atoms are in a container, five of type A and five of B. Assuming equal probability of any A and any B colliding and possessing favorable orientation and energy for reaction to form AB, the number of possibilities is (5)(5), or, the rate is proportional to the product of concentrations, [A][B]. By inserting a rate constant k, the actual rate becomes equal to k[A][B].

If the reaction were $A + 2B = AB_2$, then, as above, the rate of AB_2

formation is $k_r[A][B][B-1]$. The last term means that after the first particle of B has reacted, there is one fewer B in the mixture, so the possibility of further reaction is one less, and the rate will be a little slower. If, however, any reasonable quantities of reactants are present, say even a millionth of a mole of B, 6.02×10^{17} particles, the effect of 1 less B is insignificant and one writes for the rate, $k_r[A][B]^2$. Specific examples will later be considered in this way.

Factors Affecting Equilibrium

Changes in temperature T, pressure P, and molar concentration M, can cause a shift in the equilibrium points of a system. The *principle of equilibrium* as described by *H. L. Le Chatelier* (1885) and *F. Braun* (1886) is a qualitative statement of what to expect when such changes are made; namely *if a change is made in P, T, or M of an equilibrium system, the system changes in a direction that tends to compensate for the effect of the change.* The amount of change cannot be predicted from this statement alone, however.

1. Catalytic effects. Catalysts hasten or retard attainment of the state of equilibrium but it is an experimental fact that they do not affect the equilibrium point; that is, the ratio of concentrations at equilibrium will be the same regardless of how long the reaction takes to get there. The positive catalyst thus speeds both forward and reverse rates equally.

2. Pressure effects. These are mainly important in reactions that include gases. For example a solution of carbonic acid decomposes to give water and carbon dioxide gas:

$$H_2CO_3 = H_2O + CO_2$$

If this system is at equilibrium in a closed container and one increases the pressure with a movable piston, the system responds according to Le Chatelier's principle in such a way as to absorb the pressure—which means that the solubility of the gas is increased and reaction goes from right to left. Decreasing the pressure (as for example in opening a bottle of carbonated water) has the opposite effect.

3. Temperature effects. If one knows whether heat (expressed in kcal/mole) is absorbed or given off in a reaction he can predict by the Le Chatelier principle the effect a temperature change will have on an equilibrium system. It is known for example that when one dissolves silver nitrate in water, the solution absorbs heat and gets cold, or negative heat is a product:

$$AgNO_3 + H_2O \rightarrow \text{Solution} - \text{kcal}$$

Rewriting gives

$$\text{kcal} + AgNO_3 + H_2O \rightarrow \text{Solution}$$

This shows that if one heats the mixture, the reaction now proceeds from left to right; i.e., at the higher temperature the salt has greater solubility. That is the direction in which heat is absorbed as the system tries to re-establish its previous equilibrium point. At a new temperature the process is still a reversible one but the rates of the forward and reverse reactions may change different amounts so different equilibrium constants are expected at different temperatures.

*4. **Concentration effects.*** Consider the reversible reaction that takes place when ammonia is dissolved in water:

$$NH_3 + H_2O = NH_4^+ + OH^-$$

If either the ammonia or water concentrations are increased, the reaction velocity toward the right is increased and more ions will appear in solution. Adding either ammonium or hydroxide ions shifts the reaction toward the left. Thus, addition of a strong base (furnishing many OH^- in solution) to an ammonium salt solution will aid one in identifying the latter, since NH_3 (which is detected by odor) is liberated.

Concentration Conventions

For the purposes of equilibrium discussion, the concentrations of solids are considered to be unchanging. They are given the value of unity and cancel from, or simply are not written in, expressions involving the equilibrium constant K. For the reaction of a slightly soluble compound dissolving in water, as,

$$Ag_2C_2O_4 = 2Ag^+ + C_2O_4^{-2} \qquad (6\text{–}5)$$

one may write $K = [Ag^+]^2[C_2O_4^{-2}]/[Ag_2C_2O_4]$ or $K[Ag_2C_2O_4] = [Ag^+]^2[C_2O_4^{-2}]$, and dropping the solid term, $K = [Ag^+]^2[C_2O_4^{-2}]$. The square brackets indicate molar concentrations of the ions. Though this reaction takes place in water solution, H_2O is not a reactant and is not shown.

For *gases*, molar concentrations or partial pressures may be used. The term K_c denotes the equilibrium constant in the former case and K_p is used in the latter. For example, heating solid $CaCO_3$ in a previously closed and evacuated container gives decomposition, the extent of which at equilibrium is expressed by the pressure of CO_2:

$$CaCO_3 = CaO + CO_2 \qquad (6\text{–}6)$$

Since the calcium compounds are solids, the equilibrium statement is simply

$$K_p = p_{CO_2}; \qquad \text{or } K_c = [CO_2]$$

Most systems discussed in the following chapters and illustrated in laboratory work concern *ions* and *molecules dissolved in water.* Usually the solutions are dilute and the use of molar concentrations in equilibrium calculations will give results that are close to those obtained from laboratory experimentation. Calculations applying only the simple approach thus far described on more concentrated solutions may give quite erroneous answers, however, because these solutions do not behave ideally and K changes with concentration. An *ideal solution* in this respect is one in which the ions are far enough apart so their random movement is not affected by interionic attractions or repulsions.

For practical purposes this means that only dilute solutions are ideal and it was from these that the mass action law was derived. A physical picture for one non-ideal system is this: if solid $Ag_2C_2O_4$ is at equilibrium with its ions as in equation 6–5, the system behaves ideally because it is very dilute. If some $NaNO_3$ is added, ions from the latter will hinder, by mechanical interference and ionic attraction, the equilibrium traffic between Ag^+ and $C_2O_4^{-2}$ on the solid's surface and Ag^+ and $C_2O_4^{-2}$ dissolved in solution, so that more $Ag_2C_2O_4$ must dissolve to re-establish the original reaction velocity.

K actually varies with the valence, size, and population of ions in the solution, and in refined calculations* cognizance is taken of these factors, though we will ignore them. The equilibrium constants used in problems here are all of "classical," rather than thermodynamic, derivation.

Partition—an Example of Heterogeneous Equilibrium

Heterogeneous equilibria systems are those containing two or more phases, several examples of which have been mentioned. One more is given here in greater detail because of its importance as a method for quantitatively studying the equilibrium phenomenon.

If two immiscible liquids are in contact, and if a common solute is added and the mixture shaken, the solute distributes itself between the two solvents in the ratio of its solubility in each. It is capable of doing this because its molecules are moving in all directions and pass through the liquid-liquid interface.

Suppose Br_2 is shaken with a mixture of two immiscible solvents, H_2O and CCl_4, until no further concentration changes are found. The organic layer is noted to be a darker brown than the aqueous layer, showing that Br_2 is more soluble in CCl_4. If s_1 is the rate at which Br_2 leaves the water layer, s_1 is proportional to $[Br_2(H_2O)]$, the concentration of Br_2 in water, and equal to this times a rate constant, k_1:

$$s_1 = k_1[Br_2(H_2O)] \tag{6–7}$$

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* See any physical chemistry text on "activities," "activity coefficients," and "ionic strengths."

In the same way, if s_2 is the rate at which Br_2 leaves CCl_4, s_2 is equal to the concentration of Br_2 in CCl_4 multiplied by another rate constant:

$$s_2 = k_2[Br_2(CCl_4)] \tag{6-8}$$

At equilibrium the two rates are equal and collection of terms gives an equilibrium constant which is called the *distribution* (*D*) *constant* or *partition coefficient*:*

$$k_1/k_2 = K_D = [Br_2(CCl_4)]/[Br_2(H_2O)] \tag{6-9}$$

Experimental determination of the layer concentrations will give the value of K_D, which may then be used to predict partition when different weights and volumes of the three substances are mixed. The value of this K_D at 20° has been found to be 23.

See Example 9-3 for an illustration of how K_D can be used in solving equilibrium problems.

The Dissociation of Water—an Example of Homogeneous Equilibrium

Water (*W*) ionizes slightly and this reversible process is one of the most important ones in chemistry:

$$2H_2O = H_3O^+ + OH^- \qquad \text{or } H_2O = H^+ + OH^-$$

The "concentration" of water is considered constant in dilute solutions and is incorporated in the equilibrium constant:

$$K = [H^+][OH^-]/[H_2O] \qquad \text{or } K[H_2O] = [H^+][OH^-]$$

and the *water constant* has the definition,

$$K_W = [H^+][OH^-] = 1 \times 10^{-14} \tag{6-10}$$

This constant can be determined from measurements on salt hydrolysis (Chapter 10), electrochemical cells (Chapter 11), and electrical conductance. The last method involves the preparation of water of the highest purity by means of ion exchange resins and low pressure distillations to remove all impurities including dissolved gases. This is followed by finding the conductance, as explained in Chapter 5 and in special experiment 1. The solution is dilute enough to consider it at infinite dilution. At 25 C the conductance of a centimeter cube of H_2O is 5.53×10^{-8} $ohms^{-1}\ cm^{-1}$. The equivalent conductances at infinite dilution are $H^+ = 348$ and $OH^- = 192$. The *cc* of H_2O thus contains $5.53 \times 10^{-8}/348 + 192 = 1.00 \times 10^{-10}$ g equivalents of H^+ and of OH^-. A *liter*

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* The convention here is to put the concentration in the extracting phase in the numerator and the concentration in the extracted solution in the denominator.

of water at 25 C consequently contains H^+ and OH^- at 1.00×10^{-7} molar concentrations, or from equation 6–10,

$$[H^+][OH^-] = K_W = (1.00 \times 10^{-7})^2 = 1.00 \times 10^{-14} \qquad (6\text{–}11)$$

K_W increases with an increase in temperature; it is 0.61×10^{-14} at 18 C and 50×10^{-14} at 100 C. *The value* 1.00×10^{-14} *will be used in our calculations.*

pH, pOH, pK_W

Because small molar concentrations of H^+ and OH^- are common, *S. P. L. Sorenson* in 1909 proposed that a convenient way to express them would be as their negative logarithms. This is denoted by the small letter *p*. The relationships (in fairly dilute solutions) from equation 6–10 are,

$$pH = -\log [H^+] = \log (1/[H^+])^* \qquad (6\text{–}12)$$

$$[H^+] = 10^{-pH} \qquad (6\text{–}13)$$

$$pOH = -\log [OH^-] = \log (1/[OH^-]) \qquad (6\text{–}14)$$

$$[OH^-] = 10^{-pOH} \qquad (6\text{–}15)$$

$$pH + pOH = pK_W = 14.00 \qquad (6\text{–}16)$$

$$pK_W = -\log K_W \qquad (6\text{–}17)$$

Due to the equilibrium expressed in equation 6–10, it is seen that when a solution contains equal numbers of H^+ and OH^-, the *p*H at room conditions will be 7.00 and such solutions are called neutral. If $[H^+] > 10^{-7}\,M$, $pH < 7$, and the solution is acidic. If $[H^+] < 10^{-7}\,M$, then there is more OH^- than H^+ since the equilibrium must be maintained, so $pH > 7$ and the solution is basic (alkaline). The usual limits of the *p*H scale are from 1 *M* H^+ ($10^{-14}\,M$ OH^-) to 1 *M* OH^- ($10^{-14}\,M$ H^+), or from *p*H 0 (*p*OH 14) to *p*H 14 (*p*OH 0).

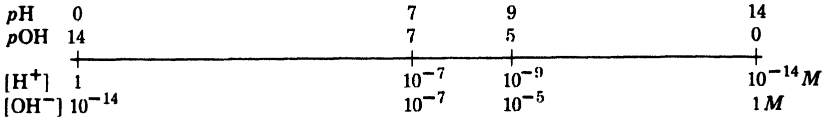

FIG. 6–2. The *p*H scale showing a few representative values.

Example 6–1. One dissolves 0.0092 g of $Ca(OH)_2$ (mol. wt 74) to make a liter of soln. Calculate $[OH^-]$, $[H^+]$, *p*H, and *p*OH.

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* See Appendix A3 on handling logarithms.

The molarity of the soln. is $9.2 \times 10^{-3}/7.4 \times 10 = 1.24 \times 10^{-4}$. One may assume this dilute, strong base is completely dissoc. so

$$[\mathrm{OH^-}] = (2)(1.24 \times 10^{-4}) = 2.48 \times 10^{-4}\,M \qquad (\textit{Ans.})$$

From 6–10,

$$[\mathrm{H^+}][\mathrm{OH^-}] = 1.00 \times 10^{-14}, \qquad [\mathrm{H^+}] = 4.03 \times 10^{-11}\,M \qquad (\textit{Ans.})$$

Then from equation 6–12

$$p\mathrm{H} = -\log(4.03 \times 10^{-11}) = -0.60 + 11.00 = 10.40\,p\mathrm{H} \qquad (\textit{Ans.})$$

pOH is found from either equations 6–14 or 6–16 to be 3.60 pOH (*Ans.*)

Example 6-2. Methyl orange added to an HCl soln. gives a yellow-orange color. Approx. the formality of the HCl.

From the appendix table of indicators, A17, $p\mathrm{H} \simeq 4.4$, so $4.4 = -\log[\mathrm{H^+}]$, or $[\mathrm{H^+}] = 10^{-4.4}$. Since log tables do not provide for negative mantissas, the number is written as $[\mathrm{H^+}] = 10^{-5} \times 10^{0.6} = 10^{-5} \times \text{antilog}\,0.6 = 4 \times 10^{-5}$ for both the hydrogen ion molarity and hydrochloric acid formality. (*Ans.*)

*p*H Measurement

pH is determined most often by indicators or a pH meter, as illustrated in special experiment 2.

The water equilibrium and the effect of pH on several systems will be developed in the next chapters.

PROBLEMS

1. Write expressions for the equilibrium constant K for each of the following, utilizing only those substances whose concentrations may change:

(*a*) $N_2 + 3H_2 = 2NH_3 + 34\ \mathrm{kcal}$

(*b*) $4HCl + O_2 = 2H_2O + 2Cl_2$

(*c*) $\mathrm{C} + O_2 = CO_2 + 94.4\ \mathrm{kcal}$

(*d*) $H_2 + I_2 = 2HI + 12\ \mathrm{kcal}$

(*e*) $\mathrm{BaSO_4 = Ba^{+2} + SO_4{}^{2}}$

(*f*) $\mathrm{HSO_4^- = H^+ + SO_4{}^{2}}$

(*g*) $\mathrm{H_2O + C_2O_4^{-2} = HC_2O_4^- + OH^-}$

(*h*) $\mathrm{HNO_2 = H^+ + NO_2^-}$

(*i*) $\mathrm{CuBr_4^{-2} = Cu^{+2} + 4Br^-}$

(*j*) $\mathrm{NH_4^+ + H_2O = NH_3 + H_3O^+}$

2. Kp for $CaCl_2 \cdot 2H_2O = CaCl_2 + 2H_2O$ is 10^{-8} atm at 0 C. Explain.

3. For reactions (*a*), (*c*) and (*d*), in problem 1, explain the effect of making these independent changes: (*a*) add heat (*b*) lower the total pressure (*c*) remove the products as formed (*d*) add one of the reactants, and (*e*) pump an inert gas like helium into the otherwise closed reaction chamber.

4. The all-gas system in (*d*) of problem 1 was one which was carefully studied when equilibrium concepts were originally being formulated (*Bodenstein*, 1894). A sealed reaction flask mixture of 0.9151 g of I_2 and 0.0197 g of H_2 was allowed to come to equilibrium in a bath of boiling sulfur (444.6 C), then quenched in ice to retain the equilibrium concentrations. The vessel was broken open, the HI and I_2 absorbed in aqueous solutions, and the H_2 collected in a gas buret. Corrected to standard conditions, the H_2 had a volume of 143 cc. Calculate the moles of each constituent at equilibrium and K_c.

Why doesn't flask volume matter in this calculation?

$$H_2 = 0.00638, \quad HI = 0.00694, \quad I_2 = 0.00014, \quad K_c = 53.5 \qquad (\textit{Ans.})$$

5. Using K_c from problem 4, calculate the equilibrium concentrations in a 2-liter-flask at 444.6 C into which originally was placed 10 g of I_2 and 0.059 g of H_2.

6. J. P. Slipshod calculates the *p*H of 10^{-8} *F* HCl as follows:

$$10^{-8}\,F\,\mathrm{HCl} = 10^{-8}\,M\,\mathrm{H}^+ \qquad p\mathrm{H} = -\log 10^{-8} = \log 10^{8} = 8\,p\mathrm{H}$$

He then remembers that a *p*H greater than seven means a basic solution and he cannot figure out why HCl should be basic. What happened?

7. A mixture of 10.0 g of HAc and 8.00 g of C_2H_5OH is held at 45 C until equilibrium is established. Analysis shows 2.00 g of H_2O and 9.68 g of $CH_3CO_2C_2H_5$ are present (see reaction above equation 6–1). (*a*) Find *K*. (*b*) If a mole of each reactant had been present initially, what weights of products would have been produced?

8. Organic chemists are interested in the partition application of chemical equilibrium since if they wish to extract a compound from one solvent with another immiscible solvent, they are able to calculate the efficiency of the process. If M_0 = original weight of a solute in water, M_n = final weight of solute in water after *n* extractions, K_D = the distribution constant, V_O = the volume of organic solvent used in each extraction, and V_W = the volume of water solution it can be shown that

$$M_n = M_0[(V_W/K_D)/(V_O + V_W/K_D)]^n$$

It is known that Br_2 is 80 times more soluble in CS_2 than in H_2O and that these solvents are practically immiscible. Calculate: (*a*) K_D. (*b*) The mg of Br_2 left in the water layer if 200 cc of H_2O containing 40 mg of Br_2 are shaken with 30 cc of CS_2. (*c*) The mg of Br_2 left in the water layer under the same conditions, except this time three extractions with CS_2 are made, using 10 cc each time. (*d*) What generalization can you form by comparing the results from (*b*) and (*c*)?

9. Complete the table for solutions A, B, C, and D.

	A	B	C	D
pH	7.45			
*p*OH		2.17		
$[H^+]$			0.25	
$[OH^-]$				3.2×10^{-5}

10. (*a*) A solution has a *p*H of − 1.0. Explain. (*b*) Could any solution have a *p*H > 14? Explain. (*c*) What does 10^{-pH} equal?

11. J. P. Slipshod reads that $K_{W'}$ is 50×10^{-14} at 100 C and calculates the *p*H of boiling water to be 6.15. This gets both him and his Uncle Frisbee excited enough to form a corporation for the purpose of cleaning scale from boilers without the use of expensive chemicals or manual labor. J.P.S. and U.F. reason that if hot water is run through the tubes it should dissolve carbonates because its *p*H indicates it is acidic. On their first job they circulate hot tap water for six days without visible results and are shown the door. J.P. then alibis that salts in the tap water threw off his computations and distilled water will be used on their next caper. What about this?

12. Consider the reaction in equation 6–6 to be at equilibrium. What is the effect of adding more CaO? Explain.

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7

EQUILIBRIUM AND WEAK ACIDS AND BASES

In the last chapter it was stated that chemical equilibrium principles can be broadly applied to soluble weak electrolytes in solution but not to strong ones. The former ionize gradually in a predictably progressive fashion with dilution, but the latter, already largely in the form of freely moving and individually functioning ions at moderate concentrations, do not exhibit the same regularity. This is easily demonstrated.

A Weak and a Strong Base Compared

By the method described in Chapter 5 and illustrated in special experiment 1, one may obtain conductivity data on various dilutions of potassium and ammonium hydroxides, for example. From this one can calculate the equivalent conductance, Λ, for each compound at each dilution, and get the figures shown in the accompanying table. By knowing that at

TABLE 7–1. CONDUCTANCE DATA FOR KOH AND NH_4OH SOLUTIONS

Molarity	KOH Λ, 18 C	NH_4OH Λ, 18 C
1.0	184	0.89
0.10	213	3.3
0.01	228	9.6

infinite dilution the limiting ionic conductance of $NH_4^+ = 64$, $K^+ = 64$, and $OH^- = 174$ and applying Kohlrausch's law as in Chapter 5, one finds that both compounds have the same equivalent conductance at infinite dilution, $\Lambda_0 = 238$. The ratio Λ/Λ_0 is the apparent degree of dissociation or fraction of substance in the free ionic form. This is shown in Table 7-2. Both KOH and NH_4OH apparently increase in their amounts of ionization but the two are not similar phenomena, as will be shown.

TABLE 7-2. APPARENT FRACTION OF FREE MOVING IONS IN KOH AND NH_4OH SOLUTIONS

Molarity	KOH Λ/Λ_0	NH_4OH Λ/Λ_0
1.0	0.774	0.00374
0.10	0.895	0.0139
0.01	0.958	0.0403

The Ionization of NH_3 in H_2O

Ammonia, NH_3, dissolved in water forms hydrates, but there is no way at present to differentiate between $NH_3 \cdot H_2O$ and NH_4OH. While the latter has not been proven to exist, it is convenient to use it in equation writing and the student should understand that these two expressions are equivalent:

$$NH_3 + H_2O = NH_4^+ + OH^-$$

$$NH_4OH = NH_4^+ + OH^-$$

The latter will be used most often here.

Considering the 1.0 *M* NH_4OH solution first, from Table 7-2 one sees that the degree of dissociation is 0.00374. This is the fraction of a mole which is ionized, so the concentration of NH_4^+ is (0.00374)(1 mole) = 0.00374 *M*. Since OH^- is formed in equal amount, its concentration is also (0.00374)(1 mole) = 0.00374 *M*. The NH_4OH left undissociated is the difference between unity and that dissociated, 1.00 − 0.00374 or 0.996, and its concentration is (0.996)(1 mole) = 0.996 *M*. In the general case when α, the degree of dissociation, is known one finds the concentrations of the various species in solution by multiplying α and $1 - \alpha$ by the appropriate molarity. It is handy to put these values beneath the respective terms of the reaction equation for reference in problem solving. Thus for some weak electrolyte HQ, which gives ions H^+ and Q^- in solution and whose degree of ionization is α at an HQ concentration of M, one writes:

$$\underset{(1-\alpha)M}{HQ} \leftrightarrows \underset{M\alpha}{H^+} + \underset{M\alpha}{Q^-} \qquad (7\text{–}1)$$

For the particular case under study,

$$\underset{(0.996)(1)}{NH_4OH} \leftrightarrows \underset{(0.00374)(1)}{NH_4^+} + \underset{(0.00374)(1)}{OH^-} \qquad (7\text{–}2)$$

The ionization constant, K_B, for the base may be found from these figures, and as was pointed out is a special case of the general equilibrium constant. The concentration of water is essentially constant since a large excess exists in dilute aqueous solutions, and it will be considered incorporated in the equilibrium constants but not appear as such:

$$K_B = [NH_4^+][OH^-]/[NH_4OH] = (0.00374)^2/0.996 = 1.40 \times 10^{-5} \quad (Ans.)$$

At 0.10 M, the degree of dissociation (fraction ionized or dissociated) is 0.0139 and the undissociated fraction is 1 minus this value or 0.986. As above, one obtains the equilibrium concentrations of all species, then solves for K_B:

$$\underset{(0.986)(0.1)}{NH_4OH} \leftrightarrows \underset{(0.0139)(0.1)}{NH_4^+} + \underset{(0.0139)(0.1)}{OH^-}$$

$$K_B = [(0.0139)(0.1)]^2/(0.986)(0.1) = 1.96 \times 10^{-5} \qquad (Ans.)$$

At 0.01 M the same reasoning leads to

$$K_B = [(0.0403)(0.01)]^2/(0.959)(0.01) = 1.70 \times 10^{-5} \qquad (Ans.)$$

The three results for K_B are in fair agreement with one another and in other dilute solutions at the same temperature, the result of more measurements gives K_B values clustering about 1.8×10^{-5}. One concludes that the chemical equilibrium law is suited to describe the behavior of this typical weak electrolyte. (These calculations are all approximate: three significant figures and many times only two are justified.)

The picture one should have of this type weak electrolyte in solution is, molecules $\rightleftharpoons$ ions, the equilibrium shifting toward the right with dilution. One deduces this from Le Chatelier's principle: dilution decreases the ionic concentration so the molecules dissociate further to make up the deficiency and restore equilibrium. It is only at high dilution that this approaches 100% or that $\alpha \simeq 1$.

The Ionization of KOH

If one assumes that KOH behaves as does NH_4OH and that considerable undissociated KOH is present in solution along with its ions, $KOH \rightleftharpoons K^+ + OH^-$, calculations can be made in the same way. At

1.00 M, $K_B = 2.65$, at 0.10 M, $K_B = 0.764$, and at 0.01 M, $K_B = 0.218$. These results show a decrease of K_B with dilution and one concludes that chemical equilibrium principles do *not* apply in this case. The failure is due to the fact that KOH as a typical strong electrolyte, is ionic all the time but in fairly concentrated solutions the ions are too close together to completely escape each other's attraction and so the conductivity is lower than expected. We thus apply equilibrium calculations only to *weak* acids and bases in this chapter.

Weak Monoprotic Acids

The mathematical treatment of weak acids of the type HQ is similar to that shown for NH_4OH and the general results and conclusions are the same. Again increased ionization compensates for increased dilution over a wide concentration range and K_A, the ionization constant for a weak acid, is a constant.

K_A for acetic acid, $(CH_3CO_2)H$ (abbreviated hereafter HAc) is 1.8×10^{-5} at 25 C, showing it to be comparable in strength (or weakness) as an acid, to NH_4OH as a base, and solutions of the same concentration of these substances contain equal numbers of ions. Suppose one wishes to know the per cent of ionization of 0.2 M HAc solution. The problem can be solved in several ways.

Example 7-1. (*Method* 1). If α is the degree of dissoc. of HAc into ions, then $(1 - \alpha)$ will be the degree of nondissoc. The amount of H^+ and Ac^- at equil. will each be 0.2α and the concn. of HAc will be $(0.2)(1 - \alpha)$ as in equation 7-1:

$$\underset{(0.2)(1-\alpha)}{\mathrm{HAc}} \leftrightharpoons \underset{0.2\alpha}{\mathrm{H}^+} + \underset{0.2\alpha}{\mathrm{Ac}^-} \qquad (7\text{-}3)$$

$$K_A = [H^+][Ac^-]/[HAc] = 1.8 \times 10^{-5} = (0.2\alpha)^2/(0.2)(1 - \alpha) \qquad (7\text{-}4)$$

Collecting terms and dividing through by 0.4, one obtains $\alpha^2 + 9.0 \times 10^{-5}\alpha - 9.0 \times 10^{-5} = 0$. This is a quadratic equation of the form,

$$\alpha^2 + b\alpha - b = 0 \qquad (7\text{-}5)$$

which is common in these problems but for which there is generally no simpler solution than the *quadratic formula*

$$\alpha = - b \pm (b - 4ac)^{\frac{1}{2}}/2a \qquad (7\text{-}6)$$

where a, b, and c are coeff. of the general quadratic $a\alpha^2 + b\alpha + c = 0$. Usually in our calcns. $a = 1$ and $b = - c$, as above.

Substituting:

$$\alpha = - 9.0 \times 10^{-5} \pm [(9.0 \times 10^{-5})^2 - (4)(1)(- 9.0 \times 10^{-5})]^{\frac{1}{2}}/(2)(1)$$

$$\alpha = - 9.0 \times 10^{-5} - 1.9 \times 10^{-2}/2 \cong - 0.95 \times 10^{-2}$$

and $$\alpha = - 9.0 \times 10^{-5} + 1.9 \times 10^{-2}/2 \cong + 0.95 \times 10^{-2}$$

The latter root is the only one with significance since a neg. degree of ioniz. is impossible. *The lowest value α can have is* 0, *the highest*, 1.00 (why?). This degree of ioniz. is convertible to % ioniz. since α is the decimal equiv. of the per cent, or $100\alpha = \%$. The ioniz. in this soln. is 0.95%. (*Ans.*)

Example 7–2. (*Method* 2). Let $x =$ the molar concns. of both H^+ and Ac^- since these are formed in equal quantity. Then $(0.2 - x) =$ the molar concn. of HAc left undissoc.

$$\underset{(0.2-x)}{HAc} \leftrightharpoons \underset{x}{H^+} + \underset{x}{Ac^-} \qquad (7\text{–}7)$$

$$K_A = 1.8 \times 10^{-5} = x^2/(0.2 - x) \qquad (7\text{–}8)$$

This leads to another quadratic from which one obtains

$$x = 1.9 \times 10^{-3}\, M\ H^+ \text{ and } Ac^-$$

The fract. ionized is $1.9 \times 10^{-3}/0.2 = 9.5 \times 10^{-3}$ (this is α from the first method), and one again finds the dissoc. to be 0.95%. (*Ans.*)

Example 7–3. (*Method* 3.) Either of the above methods may be simplified by the assumption that weak electrolytes are not going to ionize greatly at concns. usually employed. So one may say in *Method* 1 that if α is small, $(1 - \alpha) \cong 1$; and in *Method* 2 if x is small, $(0.2 - x) \cong 0.2$. This assumption is often made when the % ioniz. is going to be $<$ 10% or the concn. is $>$ 10^{-3} *M*. Going back to *Method* 1, the new values are,

$$\underset{(0.2)(1)}{HAc} \leftrightharpoons \underset{0.2\alpha}{H^+} + \underset{0.2\alpha}{Ac^-} \qquad (7\text{–}9)$$

$$K_A = 1.8 \times 10^{-5} \cong (0.2\alpha)^2/0.2 \cong 0.2\alpha^2$$

$$\alpha \cong (1.8 \times 10^{-5}/0.2)^{\frac{1}{2}} \cong 9.5 \times 10^{-3} \text{ as before.} \quad (\textit{Ans.})$$

Since the same approx. is made each time one works this type problem, the last step can be generalized,

$$\alpha = (K_A/C)^{\frac{1}{2}} \qquad (7\text{–}10)$$

where C is the original molar concn. of weak acid or base.

Applying the approx. to *Method* 2, gives

$$\underset{0.2}{HAc} \leftrightharpoons \underset{x}{H^+} + \underset{x}{Ac^-}$$

$$K_A \cong 1.8 \times 10^{-5} \cong x^2/0.2$$

$$x \cong [(0.2)(1.8 \times 10^{-5})]^{\frac{1}{2}} = 1.9 \times 10^{-3} \text{ as before.} \quad (\textit{Ans.})$$

A generalization* can be discovered in the last step again by recognizing that

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* *Formulas of general interest for solving type problems will be developed to call attention to reasoning processes and to show relationships that might be overlooked if only isolated, specific examples are given. The student is not encouraged, however, to lean heavily on memorized equations or set patterns for other than simple problems. It is always better to spend time learning the reasoning and principles involved, since these are the best tools for attacking the "different" problem, where no obvious solution is at once evident. It is the problem where no formula is given that separates thinkers from memorizers.*

0.2 is the weak acid's original molar concn. and 1.8×10^{-5} is the ion constant. Using the abbreviations as above,

$$[H^+] = (C \cdot K_A)^{\frac{1}{2}} \qquad (7\text{–}12)$$

The approximate solutions are as good in these examples as the more exact ones since both x and α are small. At higher dilutions more difference will be noted, but for most purposes this shorter method is preferred.

*p*H of Weak Acid and Base Solutions

In the last two sections, enough data was presented in the examples to have calculated the *p*H of the NH_4OH and HAc solutions, since the ionization constants and the concentrations were known. This is worthy of illustration.

Example 7–4. Calculate the $[OH^-]$, $[H^+]$, *p*H and *p*OH of 0.30 *M* NH_4OH. If we let $x = [NH_4^+] = [OH^-]$, and if we assume the concn. of those ions is insignificant compared to 0.30 *M*, then the concn. of NH_4OH is not altered by the dissoc.

$K_B = 1.8 \times 10^{-5} = x \cdot x/0.30$, and $x = 2.32 \times 10^{-3}\ M = [OH^-]$ (*Ans.*)

From the water constant (Chapter 6) $K_W = [H^+][OH^-] = 10 \times 10^{-15}$, $[H^+]$ then is found to be $4.32 \times 10^{-12}\ M$. *p*OH and *p*H are respectively $-\log [OH^-] = 2.63$ and $-\log [H^+] = 11.37$ (*Ans.*)

The latter may also be found from the identity, *p*H + *p*OH = 14.00.

If one is working with an unknown weak acid or base whose concentration and *p*H are known, K_A or K_B can be found. This is of interest to research workers who have need of characterizing new substances. (See special experiment 2.)

Example 7–5. A new, weak monoprotic acid HQ, has been discovered. When 2.304 g are dissolved to make 50.00 ml of solution, the *p*H of the mix. as measured with a *p*H meter is 2.45 and 35.40 ml of 0.2640 *N* NaOH are equiv. to this amount of acid in a titration. Show that the easily obtained data leads to calcn. of the mol. wt of HQ, K_A, and α.

From $V_A N_A = V_B N_B$ (Chapter 2) one finds the normality of the HQ soln. $N_A = (35.40)(0.2640)/50.00 = 0.1869\ N$. Since the acid is monoprotic, $N = M$. The acid soln. contained 2.304 g/50 ml, which is equiv. to 46.08 g/liter. This means that 46.08 g is 0.1869 part of a g mole or the mol. wt of HQ is 247. (*Ans.*)

From the *p*H of 2.45, one calcs. the $[H^+]$ to be $3.55 \times 10^{-3}\ M$, and since one Q^- is formed with each H^+, $[Q^-] = 3.55 \times 10^{-3}\ M$ also.

The equil. concn. of HQ is the original concn. minus the quantity dissoc. or $0.1869 - 0.00355 = 0.1834\ M$. The fraction dissoc., α, will be $0.00355/0.1869 = 1.90 \times 10^{-2}$ (*Ans.*) and the ioniz. constant will be,

$$K_A = [H^+][Q^-]/[HQ] = (3.55 \times 10^{-3})^2/1.83 \times 10^{-1} = 6.89 \times 10^{-5} \quad (\textit{Ans.})$$

Some Electrolytes Compared

The magnitude of K values for weak electrolytes and the pH of their solutions depends upon the extent of dissociation as just illustrated. The dividing line between strong and weak electrolytes is somewhat arbitrary, but those which obey the mass action law when dilution is the only variable are classed as weak, and most of the common ones are listed in Tables A20 and A21 with their K_{ion} values.* In general they have ion constants smaller than 10^{-2} and their 0.1 M solutions are less than about 30% ionized. From those tables and the methods given in this chapter, one can calculate such things as the % ionization and pH of weak electrolyte solutions and find the changes with changes in concentration and K_{ion}. For example, K_A for HSO_4^- is 1.26×10^{-2}, pH of a 0.1 M solution is found to be 1.53, and the acid is 29.6% ionized, whereas K_A for HCN is 4.0×10^{-10}, pH of a 0.1 M solution is 5.2, and it is 0.0063% ionized, etc. The student should verify these calculations, given concentration and K_A.

Some generalizations concerning the *strength of oxygen acids* can be made from the K_{ion} table and are useful to know as a means of getting first approximations. Acids of the type H_aXO_a (such as H_3BO_3) in which a is an integer and X generally a nonmetal, usually have first ion constants less than 10^{-7}. Acids of the type H_aXO_{a+1}, as HNO_2, are moderately weak and have first ion constants of about 10^{-3}. Strong oxygen acids having first ion constants approximately equal to 10^3 have formulas H_aXO_{a+2}, as HNO_3, and there are a few very strong acids, $K_{\text{ion}} \sim 10^8$, such as $HClO_4$, whose general formula is H_aXO_{a+3}.

Effect of Foreign Ions on Weak Acid and Weak Base Equilibria

So long as the weak electrolyte is alone with its ions in aqueous solution, the type calculations illustrated thus far handle the possible problems. If other substances are present, however, they may affect the dissociation. Three cases are encountered.

*1. **Indifferent, Nonreacting Ions.*** If KCl is added to an HAc solution, the ions K^+ and Cl^- are "indifferent" or "uncommon" to the original system. Offhand it would seem that they should have no effect on $HAc = H^+ + Ac^-$, but, as pointed out in the preceding chapter, any added ions interfere with the weak electrolyte's equilibrium and decrease the *effective* H^+ and Ac^- concentrations by interionic attractions that hinder the latter's recombination. Therefore HAc must dissociate to a greater than normal degree to refurnish the solution with equilibrium ion concentrations. K_{ion} will thus be larger than normal. This is known as the

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* K_{ion} is the general term for the *ionization constant.* K_A will be used to denote the ionization constant of a weak acid and K_B used for weak bases.

indifferent or uncommon ion effect. Enough is known of this effect so that in advanced work correction can be made for it, but we will not pursue it further.

2. ***Indifferent, Reacting Ions.*** If to a weak base is added an acid, or to a solution of weak acid is added a base, the added substance contains ions indifferent or uncommon to the original solute but capable of reacting with it. If the added substance gives a precipitate or forms a complex with the original, a reaction again occurs that will alter concentrations. Some examples of this are,

$$HCN + OH^- = H_2O + CN^-$$

$$HCN + Cu^+ = CuCN + H^+$$

$$4HCN + Ni^{+2} = Ni(CN)_4^{-2} + 4H^+$$

In all of these, the original HCN concentration is decreased and its ionization promoted because a demand is created by the added reagent for H^+ or CN^-. Some reactions of this type will be included in further discussion.

3. ***Common Ion Effect.*** One can predict from Le Chatelier's principle, that if ions common to those found in a solution of weak acid or base are added to it, ionization of the weak electrolyte is inhibited. Thus adding either HCl or NaCN to a solution of HCN increases respectively the concentration of H^+ and CN^-, shifting the reaction $HCN \rightleftharpoons H^+ + CN^-$ to the left. The reason for this is that the system was originally in equilibrium with a much smaller quantity of its ions ($K_A = 4 \times 10^{-10}$) and now must readjust to the new conditions. If H^+ is added, CN^- will react with it. This increases the HCN concentration proportionately, and when equilibrium is again attained, the $[CN^-]$ will be very small. If CN^- is added, H^+ will react with it to increase the HCN concentration again, and incidental to this will be a rise in the pH caused by a disappearance of H^+. These changes are due to the *common ion effect* which is the most important effect of the three mentioned. Application is made in buffer solutions.

Simple Buffer Solutions and the Common Ion Effect

A solution of weak acid(s) or weak base(s) plus salt(s) of weak acids or bases is called a buffer solution. Frequently the salt is a derivative of the same acid or base in the solution. By furnishing a comparatively large quantity of common ion to the solution it depresses the $[H^+]$ from the weak acid or the $[OH^-]$ from the weak base by the common ion effect. These solutions come to equilibrium at some definite pH and despite small additions of strong acid or base are able to maintain that pH through equilibrium shifts. Such solutions are said to be *buffered* against *p*H change, though large additions of strong acid or base will use up the *buffer capacity*. Buffer systems are important in biochemical processes (blood contains the system H_2CO_3—HCO_3^-) as well as in certain laboratory procedures where *p*H regulation is needed during chemical reactions.

Buffers may be classed as *acidic buffers*, weak acid plus a salt, and as *basic buffers*, weak base plus a salt. A typical basic buffer is the system

$$\left.\begin{aligned} NH_4OH &= NH_4^+ + OH^- \\ NH_4Cl &= NH_4^+ + Cl^- \end{aligned}\right\}$$

and a typical acidic buffer is

$$\left.\begin{aligned} HAc &= H^+ + Ac^- \\ NaAc &= Na^+ + Ac^- \end{aligned}\right\} \qquad \begin{aligned} &(7\text{–}13) \\ &(7\text{–}14) \end{aligned}$$

Consider adding a little HCl to a solution containing the last pair. The increase in H^+ disturbs the system (7–13) since $[H^+]$ is momentarily abnormally high. Equilibrium is soon reestablished however as Ac^- combines with H^+ to produce more HAc. There is plenty of Ac^- available in solution for this purpose from the reaction shown in equation 7–14. In this way, H^+ is used up and the buffer's *p*H is not much affected. Consider adding base to the same system. The OH^- is neutralized by H^+ (see equation 7–13), causing the reaction to shift right and give more H^+ since the original equilibrium H^+ concentration was greater. Such shift is possible because acetic acid is present primarily as undissociated molecules and much H^+ is stored in that form, ready for release if the solution *p*H is raised. Again, the added substance is nullified as a *p*H disturbance. The student should consider similar reactions with the basic buffer.

For our purposes, approximate solving of buffer problems will be satisfactory, and the following approximations are useful in simplifying the calculations. One assumes that

(1) Since the solutions are dilute, molarities can be used validly and K_A remains constant. The uncommon ion effect will not be considered.

(2) The salt in the buffer is 100% dissociated into free ions. Since the weak acid or base is negligibly dissociated, the common ion concentration will therefore be calculated from the salt concentration.

(3) If a small amount of strong acid or base is added to the buffer mixture, the strong acid or base is completely used up, leaving a buffer solution similar to the original but of different concentration. Since the solutions are dilute, volumes are additive.

Example 7–6. A soln. is 0.10 *M* in HAc and NaAc. To 90 ml of this is added 10 ml of 0.01 *M* HCl. Calculate (*a*) *p*H of original buffer and (*b*) *p*H of final mixt.

Assuming that the weak acid is so little ioniz. that the concn. of HAc molecules in 0.1 *M* HAc is about the same as in the buffer soln., namely [HAc] $\cong$ 0.1, and that the common ion, acetate, is furnished almost entirely from the salt which exists as free ions, then $[Ac^-] \cong 0.1$. Knowing K_A for HAc, only $[H^+]$ is unknown so

$$1.8 \times 10^{-5} = [H^+][Ac^-]/[HAc] = [H^+](0.1)/(0.1)$$

and

$$[H^+] = 1.8 \times 10^{-5}\ M, \text{ from which } pH = 4.75 \quad (\textit{Ans.})$$

Mixing this buffer with HCl has two effects; first, the solns. mutually dil. each other and second, the addn. of H^+ momentarily unbalances the equil. so that H^+ and Ac^- react to form HAc and reestablish equil. concns.

At equil., the mixt. vol. is 100 ml and the concn. of HAc will reflect both the fact that 90 ml of 0.10 *M* HAc is dil. to 100 ml and that 10 ml of 0.01 *M* HCl dil. to 100 ml produces some HAc, by $H^+ + Ac^- = HAc$. Its equil. concn. is $[HAc] = (90/100)(0.1) + (10/100)(0.01) = 0.091\ M$. The equil. acetate concn. will be approx. the original minus the amount used by H^+, or reasoning as above $[Ac^-] = (90/100)(0.1) - (10/100)(0.01) = 0.089\ M$. Note the fundamental assumption is that $H^+ + Ac^- = HAc$ is a 100% conversion. Again the hydrogen ion concn. is the unknown in the equil. constant expression for the weak acid:

$$1.8 \times 10^{-5} = [H^+](0.089)/(0.091)$$

from which *p*H is found to be = 4.73 (*Ans.*).

Thus despite addition of strong acid the buffer *p*H is essentially unchanged. The same type calculation shows buffer mixtures equally well able to compensate for additions of strong base. Had the added strong acid or base been 0.1 *M* instead of 0.01 *M* in this problem, one can show that $[H^+]$ will still only change about 20%. Three related points worthy of consideration are given in the next sections.

*p*H Changes in Unbuffered Solutions

In solutions that contain no substances that can react to use up H^+ or OH^-, *p*H changes are great upon strong acid or base addition.

Example 7–7. To 90 ml of H_2O are added 10 ml of 0.01 *M* HCl. Calculate the initial and final *p*H.

The *p*H of water is 7.00. (*Ans.*) After mixing, the $[H^+]$ in 100 ml is $(10)(0.01)/100 = 10^{-3}\ M$, and the *p*H by inspection is 3.00. (*Ans.*)

Compare this change of 4 *p*H units with the change of 0.02 units from Example 7–6. (Why is there such a difference?)

Buffer Range

The effectiveness with which a buffer system resists *p*H change is directly proportional to its concentration. In general laboratory practice, these solutions are employed in the range 0.02–2.0 *M* with a ratio of weak electrolyte to salt in the range 1/10–10/1. While moderate dilution will not alter the solution *p*H, the ratio of weak electrolyte to salt will.

Example 7–8. Calculate the useful *p*H range covered by the buffer system salicylic acid, $H(C_7H_5O_3)$, a weak monoprotic acid, ($K_A = 1.1 \times 10^{-3}$) and its sodium salt, $Na(C_7H_5O_3)$.

Let us abbreviate the radical Sa^-, then

$$K_A = [H^+][Sa^-]/[HSa] \qquad \text{or} \qquad [H^+] = K_A\,[HSa]/[Sa^-]$$

Since almost all Sa^- comes from the salt, if we let

[A] = acid concn. and [S] = salt concn. then in a general case,

$$[H^+] = ([A]/[S])K_A \tag{7–15}$$

and

$$pH \cong -\log\,[([A]/[S])K_A] \tag{7–16}$$

If the ratio [A]/[S] is 1/10,

$$pH = -\log\,(1/10)(1.1 \times 10^{-3}) = 3.96 \qquad (\textit{Ans.})$$

and if that ratio is 10/1, then

$$pH = -\log\,(10/1)(1.1 \times 10^{-3}) = 1.96 \qquad (\textit{Ans.})$$

One could therefore expect to use this buffer to hold *p*H's between 2 and 4. Some uses of buffers in analysis are illustrated in the next chapter, where it will be demonstrated that certain precipitations are *p*H regulated and *p*H is in turn dictated by a buffer mixture. The precipitation reaction may be such that it would normally change the *p*H and come to equilibrium with a low product yield, as $Zn^{+2} + H_2S = ZnS + 2H^+$. A basic buffer, by reacting with H^+, promotes the forward reaction, since by Le Chatelier's principle, if the $[H^+]$ is kept low the equilibrium point is displaced to the right.

Adjustment to Given *p*H

By way of a corollary to the last paragraph, if a solution *p*H is selected, one may predict which buffer solutions give about that *p*H and what specific mixture should be prepared. In practice one uses the approximate methods already outlined for the calculation, mixes the solution, measures the *p*H with a *p*H meter, and adjusts the *p*H as needed with small additions of acid and base.

Example 7–9. How many g of NH_4Cl (mol. wt 53.5) are needed in a liter of 0.20 *M* NH_4OH to give a soln. of *p*H 9.0?

The concn. of common ion NH_4^+ will be about the same as the salt concn.

and is the unknown in this problem. If the $pH = 9.0$, $[H^+] = 10^{-9}\,M$, and $[OH^-] = 10^{-5}\,M$. At equil., $[NH_4OH] \cong 0.20\,M$, and $K_B = 1.8 \times 10^{-5} = [NH_4^+](10^{-5})/0.2$, from which $[NH_4^+] = 0.36\,M$. The g of salt needed per liter are $(0.36)(53.5) = 19.3$. (*Ans.*)

A quick method of selection of the logical weak acid or weak base to use in a buffer for a certain pH *is this:*

$$K_A \cong \textbf{the desired } [H^+]\textbf{, and } K_B \cong \textbf{the desired } [OH^-] \qquad \textbf{(7–17)}$$

The ratio weak electrolyte to salt is then $\cong 1$ and effective buffering action is assured.

Some Buffer Mixtures

Many buffer combinations are known and used. They may be made from salts and weak acids and bases as already illustrated, or simply by reaction between acids and bases in which at least one weak electrolyte is derived. Thus, upon mixing such reactants as $NaOH + H_3PO_4$, $KOH + H_3BO_3$, $Na_2B_4O_7 + HCl$, $NaOH + NaH_2PO_4$, $KH_2PO_4 + Na_2HPO_4$, $Na_2CO_3 + NaHCO_3$, $H_2C_2O_4 + KOH$, etc., buffer solutions are established. Calculations involving polyfunctional ions like $H_2PO_4^-$, HPO_4^{-2}, PO_4^{-3}, etc., are considered in quantitative analysis courses and will not be treated in much detail here. Approximations in these systems are usually justified and simplify otherwise lengthy calculations involving several simultaneous equations.

Polyprotic Weak Acids

Polyionic acids and bases introduce a complicating feature into problems. Such substances ionize in steps and an ionization constant can be found for each step. The first ionization always proceeds to a greater degree than the second and the second greater than the third, so the ion constants for the consecutive steps are in the order $K_1 > K_2 > K_3$. Not infrequently the latter dissociations are so weak that only the first is important to the problem. The reason for the decrease in acid strength is that with one less H^+, the negative ion's attraction for the remaining hydrogen is greater since it is concentrated on fewer of them. A secondary cause is the common ion effect, the H^+ now in solution acts to repress further dissociation. For a number of diprotic (also called dibasic) acids, the ratio of K_1/K_2 is approximately $1/10^{-5}$ or $1/10^{-6}$, and for several triprotic acids, the ratio of $K_1/K_2/K_3$ is about $1/10^{-5}/10^{-10}$. Appropriate examples are *sulfurous acid*,

$$H_2SO_3 = H^+ + HSO_3^- \qquad K_1 = 1.25 \times 10^{-2}$$
$$HSO_3^- = H^+ + SO_3^{-2} \qquad K_2 = 5.6 \times 10^{-8}$$

and *arsenic acid,*

$$H_3AsO_4 = H^+ + H_2AsO_4^- \qquad K_1 = 2.5 \times 10^{-4}$$
$$H_2AsO_4^- = H^+ + HAsO_4^{-2} \qquad K_2 = 5.6 \times 10^{-8}$$
$$HAsO_4^{-2} = H^+ + AsO_4^{-3} \qquad K_3 = 3.0 \times 10^{-13}$$

H_2S

In qualitative analysis the most important weak polybasic acids are hydrosulfuric, H_2S, and carbonic, H_2CO_3, the former being of particular interest because it is the precipitating agent for cation groups 2 and 3. Its dissociations and constants (see reference 11, p. 126) are

$$H_2S = H^+ + HS^- \tag{7-18}$$
$$K_1 = [H^+][HS^-]/[H_2S] = 1.0 \times 10^{-7} \tag{7-19}$$
$$HS^- = H^+ + S^{-2} \tag{7-20}$$
$$K_2 = [H^+][S^{-2}]/[HS^-] = 1.3 \times 10^{-13} \tag{7-21}$$

Since K_1 is roughly 10^6 times larger than K_2, almost all the $[H^+]$ comes from equation 7–18 and further, since so little HS^- reacts in equation 7–20 $[H^+] \simeq [HS^-]$. It follows that if the latter concentrations are calculated as shown in equation 7–19 and substituted in equation 7–21, they will cancel, or $[S^{-2}] \simeq K_2$. *When $K_1 \gg K_2$ for any weak diprotic acid, the molar concentration of the divalent ion has about the same magnitude as K_2.*

For calculations involving the overall ionization,

$$H_2S = 2H^+ + S^{-2}$$

an equilibrium statement is obtained by multiplying equation 7–19 by 7–21.

$$K_1K_2 = K = [H^+]^2[S^{-2}]/[H_2S] = 1.3 \times 10^{-20} \tag{7-22}$$

This is further simplified by learning that at room conditions of temperature and pressure, the solubility of H_2S gas in H_2O is such that the solution is about 0.1 *M* in H_2S. *For problems in which saturated* H_2S *solutions under laboratory conditions are described or inferred, one may use*

$$\mathbf{[H^+]^2[S^{-2}] = 1.3 \times 10^{-21}} \tag{7-23}$$

or

$$[H^+] = (1.3 \times 10^{-21}/[S^{-2}])^{\frac{1}{2}} \tag{7-24}$$

It is evident that the solution *p*H will have a profound effect upon the $[S^{-2}]$ and precipitations using sulfide ion will need *p*H regulation. If too little S^{-2} is present (*p*H too low), metallic sulfides may not form or will be incompletely precipitated. If pH is too high $[S^{-2}]$ will be comparatively large and some metals which one wants to retain in solution may precipitate.

Example 7–10. Calculate the $[H^+]$ in satd. H_2S soln.

Since $[S^{-2}] \cong K_2 = 1.3 \times 10^{-13}$, substitution in equation 7–24 of $[S^{-2}]$ should give us $[H^+]$; $[H^+] = (1.3 \times 10^{-21}/1.3 \times 10^{-13})^{\frac{1}{2}} = 1.0 \times 10^{-4}\,M$ H^+ (*Ans.*)

One could have obtained the same result via equation 7–19, since if $[H^+] \cong [HS^-]$, then $[H^+] \cong (K_1 \cdot [H_2S])^{\frac{1}{2}}$. The student should verify this.

Example 7–11. Calculate the $[S^{-2}]$ in satd. H_2S and compare it to the $[S^{-2}]$ in satd. H_2S contg. enough HCl to make the $[H^+]$ 2 *M*.

Since $K_2 \cong [S^{-2}] = 1.3 \times 10^{-13}\,M$, the first part is solved by inspection. (*Ans.*)

Substitution of 2 *M* for $[H^+]$ in equation 7–23 gives $[S^{-2}]$ in the more acidic soln. $\cong 3.3 \times 10^{-22}\,M$. (*Ans.*) The latter figure is about 10^{-9} times smaller and illustrates the ease with which the concn. of the divalent ion of the weak acid can be changed with changes in pH.

H_2CO_3

The carbonate ion is the precipitating agent for cation group 4 but the acid H_2CO_3 is not as important to us as H_2S. As one could predict from the foregoing, two dissociations are possible:

$$H_2CO_3 = H^+ + HCO_3^-$$

$$K_1 = [H^+][HCO_3^-]/[H_2CO_3] = 4.16 \times 10^{-7}$$

$$HCO_3^- = H^+ + CO_3^{-2}$$

$$K_2 = [H^+][CO_3^{-2}]/[HCO_3^-] = 4.84 \times 10^{-11}$$

$$K_1K_2 = K = [H^+]^2[CO_3^{-2}]/[H_2CO_3] = 2.01 \times 10^{-17}$$

A water solution saturated with CO_2 at room conditions is about 0.034 *M* in H_2CO_3. *For such solutions one may incorporate the saturation concentration in the last equation and get*

$$[H^+]^2[CO_3^{-2}] = \mathbf{6.85 \times 10^{-19}} \qquad (7\text{–}25)$$

and,

$$[H^+] = (6.85 \times 10^{-19}/[CO_3^{-2}])^{\frac{1}{2}}$$

As approximated in the H_2S case, we may say $[H^+] \cong [HCO_3^-]$ and $[CO_3^{-2}] \cong K_2$. These are the identities most often used in carbonate problems.

Carbonates are in general much more soluble than the corresponding sulfides and hence a greater $[CO_3^{-2}]$ than $[S^{-2}]$ is needed for their precipitation. From equation 7–25 one should observe that carbonates are formed at high pH and dissolved at low pH. This will be considered further in the next chapter.

Strong Polyprotic Acids

If one is dealing with stronger acids than H_2S and H_2CO_3, wherein the several ionization steps make significant contribution to the final total ionic population, then all the ionization constants become important to the problem. The most common example of this is sulfuric acid. It is assumed that in dilute solution, dissociation of one H^+ is complete:

$$H_2SO_4 \rightarrow H^+ + HSO_4^-$$

The second dissociation, however, is weak enough so that equilibrium principles may be applied to it, yet not so weak that it can be ignored as a source of H^+:

$$HSO_4^- = H^+ + SO_4^{-2}$$

$$K_2 = [H^+][SO_4^{-2}]/[HSO_4^-] = 1.26 \times 10^{-2} \qquad (7\text{-}26)$$

Example 7-12. Calculate the approx. concn. of each ion in 0.10 M H_2SO_4 and the approx. pH.

Since the first dissoc. step is assumed to be complete, momentarily $[H^+] = [HSO_4^-] = 0.10\,M$. Bisulfate ion then undergoes ioniz. giving more H^+ and sulfate ion. If we let x be the molar amt. dissoc. at equil.

$$\underset{(0.10-x)}{HSO_4} \leftrightarrows \underset{(0.10+x)}{H^+} + \underset{x}{SO_4^{-2}} \qquad (7\text{-}27)$$

Substituting in equation 7-26 gives

$$1.26 \times 10^{-2} = (0.10 + x)(x)/(0.10 - x)$$

From the quadratic, $x \simeq 0.01\ M$.

From equation 7-27 one gets the following for the ionic concns.:

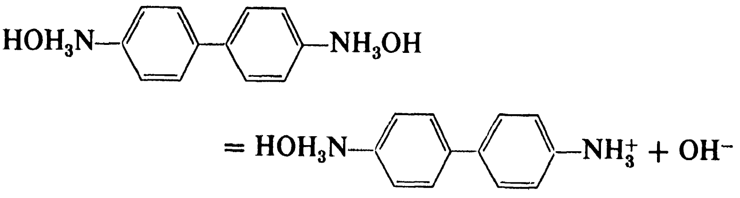
$[SO_4^{-2}] \cong 0.01\ M$, $[HSO_4] \cong 0.099\ M$, and $[H^+] \cong 0.11\ M$

corresponding to a pH of 0.96. (*Ans.*)

Polyhydroxy Bases

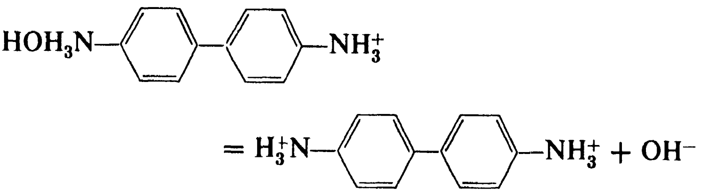
For most purposes in qualitative analysis, calculations concerning equilibrium constants of strong polyhydroxy bases such as $Ca(OH)_2$ and $Ba(OH)_2$ are of little interest and are handled as we handled the sulfuric acid case. Most other polyhydroxy bases are only sparingly soluble in water, such as $Fe(OH)_3$, $Al(OH)_3$, etc., and will be considered in the next chapter, as their uniqueness lies in their insolubility rather than their base strength. Weak soluble polybases are almost all organic nitrogen compounds and the calculations in which they appear are similar to those with H_2S and H_2CO_3.

Benzidine, abbreviated $B(NH_3OH)_2$, is representative of this class and its ionization resembles that of ammonium hydroxide:



$$K_1 = [BNH_3OHNH_3^+][OH^-]/[B(NH_3OH)_2] = 9.3 \times 10^{-10}$$

(7–28)



$$K_2 = [B(NH_3)_2^{+2}][OH^-]/[BNH_3NH_3OH^+] = 5.6 \times 10^{-11}$$

(7–29)

Indicators

Indicators for *p*H determination are organic weak acids and bases that change color by an alteration of structure upon accepting or donating H^+. By knowing their ionization constants one can calculate such things as their *p*H *range*. Consider some indicator HIn, a weak acid:

$$HIn = H^+ + In^-$$

$$K_A = [H^+][In^-]/[HIn] \qquad \text{or} \qquad [H^+] = K_A([HIn]/[In^-])$$

The colored forms are HIn (color at lower *p*H) and In^- (color at higher *p*H). The intensity of color observed is proportional to the concentration of these substances and, when they are in equal concentration, they cancel from the equation above, and $[H^+] = K_A$. The corresponding *p*H is the midpoint of the indicator's *p*H range. The observed color is a mixture of the colors of the two forms. The eye cannot distinguish well between the two colors unless one colored form has a concentration about ten times the other form, hence the range for indicators of this type is given by, $[H^+] = K_A \cdot (10/1)$ and $[H^+] = K_A \cdot (1/10)$, or $pH = pK_A \pm 1$.

PROBLEMS

1. Explain in a paragraph, using complete sentences, equations, diagrams, etc. as needed, how the system, $NH_4OH + NH_4NO_3$ resists a *p*H change when small amounts of strong acid or base are added.

2. For ratios 1/10 and 10/1 of weak electrolyte to salt, calculate the *p*H range for the buffer in problem 1. What assumptions are made in your method?

3. At 18 C and a potential of 110 volts, 0.041 amperes flow through a resistance cell (with a cell constant of 1.00) dipping into a 0.002 *M* solution of weak acid HA. At infinite dilution, the equivalent conductance of A^- is 35.0. Calculate (*a*) specific resistance and conductance of the solution (*b*) ml volume necessary to contain 1 g equiv. wt of HA at 2×10^{-3} *M* (*c*) equivalent conductance of solution (*d*) equivalent conductance of HA at infinite dilution and (*e*) % ionization of HA at 2×10^{-3} *M*. [Ans. (*a*) 2.69×10^3, 3.73×10^{-4} (*b*) 5×10^5 (*c*) 186 (*d*) 350, and (*e*) 53.4.] See methods, p. 90–91 Chapter 5.

4. Use (*a*) a more exact and (*b*) an approximate method for calculating the % ionization in 0.005 *M* HAc. Compare the results by giving a % deviation in (*b*) from the other answer. Explain why the answers are different.

5. HX is a weak acid, $K_A = 6.4 \times 10^{-5}$. At what concentration is HX 2.5% dissociated? (Ans. 0.10 *M*).

6. A solution is prepared by mixing 100 ml of 0.2 *M* HNO_2 with 100 ml of 0.1 *M* NaOH. Calculate the approximate *p*H of the mixture and list each assumption you made in working the problem.

7. To 100 ml of a solution 0.2 *M* in HAc and 0.1 *M* in KAc is added 20 ml of 0.02 *M* NaOH. Calculate the initial *p*H, the final *p*H and the % change in *p*H.

8. Calculate the original and final *p*H:
(*a*) 100 ml of 0.04 *M* HAc diluted to 4 liters
(*b*) 100 ml of 0.04 *M* HBr diluted to 4 liters
Explain why these solutions change *p*H by different amounts, and why the original *p*H's are not identical, whereas the original concentrations of acids are.

9. Calculate the approximate concentration of each ion, including OH^- in:
(*a*) 0.01 *M* H_2SO_4
(*b*) 100 ml of 0.01 *M* H_3AsO_4

10. At 18 C, Λ_0 for HCl = 380, for NaAc = 78, and for NaCl = 109. From these alone calc. Λ_0 for HAc. (Ans. 349).

11. One hundred ml of 0.10 *M* HAc are mixed with 100 ml of 0.04 *M* NaOH and 100 ml of H_2O. Calculate the final $[H^+]$, $[OH^-]$, *p*H, and *p*OH.

12. At 18 C, Λ_0 for NaCl = 109. For other dilutions of NaCl, $\Lambda_{.01\,N} = 102.8$ and $\Lambda_{.1\,N} = 92.5$. Calculate the apparent % ionization and *K* at each dilution. Explain why *K* changes with concentration.

13. Calculate the degree of ionization in 10^{-3} *M* HCN. At what concentration is the ionization 10%?

14. Equation 7–16 was developed for an acid-type buffer. Develop a general formula for finding *p*H of a base-type buffer.

15. What concentration of HAc has a pH of 5.25? What concentration of HCl has a pH of 5.25?

16. For a weak acid HQ, if [B] = [HQ] show that approximately, $[H^+]^2/[B] = K_A$.

17. From the result in 16, show that $[H^+] = ([B]K_A)^{\frac{1}{2}}$, and derive a general formula for pH from that. For what cases could it be used?

18. Four mmoles of $H(CO_2H)$, formic acid, and 5.5 mmoles of $Na(CO_2H)$ are dissolved in H_2O to make 50 ml of solution. Calculate the pH.

19. How much solid NaAc must be added to 3 ml of 0.28 M HCl so that when the solution is saturated with H_2S, $[S^{-2}] = 10^{-14}$ M?

20. To what volume must 10 ml of 0.3 M HAc be diluted to give a solution of pH 4.32? (Ans. 23.4 liters.)

21. An unknown weak, monoprotic acid has a pH of 4.76 in 0.01 M solution. Calculate K_A and from the table of ionization constants, determine which acid it might be. (Ans. HClO, experimental $K_A = 3.03 \times 10^{-8}$).

22. One has 100 ml of 0.02 M NH_4OH. Which of the following would be most effective in lowering the pH: (*a*) 100 ml of 0.002 M HCl (*b*) 0.2 moles of NH_4Cl (*c*) 900 ml of H_2O? Explain with calculations.

23. A solution of HAc is 0.074 M and has an equivalent conductance at 25 C of 6.09. With the aid of Table 5–2 calculate the pH of the solution.

24. Will 50 ml of 0.2 M HAc require more, less, or the same amount of NaOH to react with it stoichiometrically than 100 ml of 0.1 M HNO_3? Explain.

25. One has a 0.1 M solution of the theoretical weak acid H_2Q, $K_1 = 10^{-3}$ and $K_2 = 10^{-9}$. Calculate the approximate $[Q^{-2}]$. Explain any shortcuts. (Ans. 10^{-9} M)

26. From the data in 25, (*a*) explain why the answer was independent of the solution concentration and (*b*) calculate the value of $[H^+]^2[Q^{-2}]/[H_2Q]$. (Ans. (*b*) 10^{-12})

27. The actual pH of 0.10 M H_2SO_4 is 1.1. Why is the pH calculated in example 7–12 not the same?

28. (*a*) One has two HCl solutions, one of pH 3, the other of pH 2. If 10 ml of each are mixed, what is the resulting pH?

(*b*) A hundred ml of 0.1 M HCl is mixed with 100 ml of 0.1 M HAc. Calculate the pH of the mixture. Explain any assumptions.

29. (*a*) Describe an experiment by which one could determine the ionization constant of a monoprotic weak acid.

(*b*) Describe another experiment whereby one could determine which of two weak acids is the weaker, given 0.1 M water solutions of each.

30. Arrange these in order of increasing acidity: H_2O, 0.2 M HAc, 10^{-5} M HCl, 2 M NH_4^+ in 10^{-3} M NH_4OH, 0.1 M H_3PO_4.

31. Jackson Slipshod knows that 0.1 M HAc is 1.34% dissociated. To 1 liter of such solution he adds 0.1 mole of solid NaAc. He wants to calculate a value for K_A from the known concentrations and reasons that $[H^+] = (0.1)(0.0134)$, $[Ac^-] = (0.1)(0.0134) + 0.1$, and $[HAc] = (0.1)(0.9866)$. Putting these figures into $K_A = [H^+][Ac^-]/[HAc]$ he obtains an answer larger than the accepted K_A. What is wrong with the Slipshod method?

32. A certain indicator of the type HIn has a blue color at *p*H 4.5 and yellow color at *p*H 6.5. Find the ionization constant of the indicator.

33. Under what conditions may one write equation 7–1 as

$$\underset{M}{HQ} \leftrightharpoons \underset{\alpha M}{H^+} + \underset{\alpha M}{Q^-}$$

34. Equations 7–10 and 7–12 were developed for a weak acid. Develop analogous equations for a weak base and explain under what circumstances the equations can validly be utilized.

35. An indicator is a weak base, InOH, $K_B = 1.5 \times 10^{-6}$. (*a*) Give formulas for the colored forms. (*b*) Calculate its *p*H range. (*c*) Name an acid and a base that could be properly titrated using the indicator.

36. With reference to the section on strengths of oxygen acids, "guessimate" K_A for the following and check your answers with the appropriate table: HBrO, $H_2C_2O_4$, HClO, H_2SO_3.

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8

EQUILIBRIUM AND SLIGHTLY SOLUBLE ELECTROLYTES

Water is an excellent solvent, as described in Chapter 3. When it dissolves substances, energy is released as ions become hydrated and this energy is used to overcome interionic forces in salt crystals. If the *hydration energy* is greater than the *lattice energy*, the solid dissolves; if not, low solubility is the result. A given amount of water at a fixed temperature will dissolve a definite amount of solid when excess solute is shaken with it. The reason variable solubility is not noted under these conditions is that the solubility process is reversible and is ultimately balanced by a counter reaction in which ions are reprecipitated on the surface of the excess solute. If the ionic concentrations in solution are changed say by dilution, the compound will dissolve more and the system will re-establish the equilibrium concentrations again. It is found that many of the ideas of general homogeneous system chemical equilibrium can be related to heterogeneous systems when the solvent is water and the solute is a sparingly soluble electrolyte. It is the purpose of the following paragraphs to apply this quantitatively to some problems stemming from the laboratory part of the course.

The Solubility Product Constant

When one causes a precipitate like AgBr to form in the laboratory, he may believe that if stoichiometric quantities were used all Ag^+ and Br^- have been removed from solution. This is not the case for any precipitation. The solution remains saturated, though sparsely populated, with ions, and equilibrium is set up between them and ions on the precipitate's surface. Simultaneous dissolution and reprecipitation are pictured as going on at the surface and the ideas of Chapter 6 are logically extended to include this reversible process:

$$\mathbf{AgBr} = \mathrm{Ag}^+ + \mathrm{Br}^-$$

The equilibrium statement will be

$$K = [\mathrm{Ag}^+][\mathrm{Br}^-]/[\mathbf{AgBr}], \qquad \text{or } K[\mathbf{AgBr}] = [\mathrm{Ag}^+][\mathrm{Br}^-]$$

We will consider all solids to have a constant concentration of unity so such terms as $K[\mathbf{AgBr}]$ are constants, and will henceforth be designated K_{SP}, or *the solubility product constant*:

$$K_{SP} = [\mathrm{Ag}^+][\mathrm{Br}^-] \tag{8–1}$$

As with equilibrium applications in the two previous chapters, if several similar ions are involved as

$$\mathbf{Bi_2S_3} = 2\mathrm{Bi}^{+3} + 3\mathrm{S}^{-2}$$

then the coefficients are used as powers in the K_{SP} expression:

$$K_{SP} = [\mathrm{Bi}^{+3}]^2[\mathrm{S}^{-2}]^3 \tag{8–2}$$

If the several ions produced on dissociation are all different, then coefficients do not appear, as

$$\mathbf{Mg(NH_4)PO_4} = \mathrm{Mg}^{+2} + \mathrm{NH}_4^+ + \mathrm{PO}_4^{-3}$$

$$K_{SP} = [\mathrm{Mg}^{+2}][\mathrm{NH}_4^+][\mathrm{PO}_4^{-3}] \tag{8–3}$$

At a given temperature and in the absence of substantial concentrations of other ions, K_{SP} is constant for a given sparingly soluble salt and is equal to the product of the molar concentrations of the ions each raised to a power which is its coefficient in the equation, showing the compound's dissociation into ions.

Factors Affecting Solubility

A number of commonly encountered influences affect solubility and are of concern to the analyst because of the many times he must dissolve precipitates or must precipitate a substance quantitatively in a state of high purity and suitable for centrifuging or filtering.

*1. **Temperature.*** In most cases, the solubility of salts (and hence K_{SP}) increases with increasing temperature, though some salts like NaCl show little solubility change and a few, such as $\mathrm{Ce(SO_4)_2}$, show decreasing solubility. If the heat of solution is negative (the solution becomes cooler as salt is dissolved), the compound's solubility increases as the temperature is raised, and, if the heat of solution is positive, then raising the temperature decreases the compound's solubility. This is another illustration of Le Chatelier's principle. If some solid salt having a positive heat of solution is in equilibrium with its saturated solution, and the system's temperature is lowered, more solid goes into solution evolving heat to restore the original temperature. By similar reasoning one can deduce the opposite is true for compounds having negative heats of solution. Tables in this book will give K_{SP} values at room temperature.

2. ***Indifferent ions.*** The K_{SP}'s in the table were determined for saturated solutions of single compounds in pure water. If soluble salts, furnishing indifferent or uncommon ions, are present they change the ionic character of the solution and increase the solubility of slightly soluble salts by the salt effect (see Chapter 7). A simple explanation for this is that the concentrations of ions of the low-solubility salt in solution are effectively diminished due to interionic attractions that slow their movement. If such is the case then the rate of reprecipitation falls below the rate of solution. Solubility product constants will thus change slightly, but this refinement is omitted in beginning work and we shall use the K_{SP} values as given, and molar concentrations, in calculations concerning them.

3. ***Different solvents.*** Discussion, application, and data will be limited to water as a solvent but different solvents obviously change the solubility of a given substance. Organic solvents like alcohol are frequently added to water solutions of salts to precipitate the salts, and the reverse is also done—salts like NaCl being added to aqueous solutions of organic compounds (as soap) to precipitate them—a process known as *salting out.*

An application of the use of a nonaqueous solvent can be made in the separation of $SrCrO_4$ and $CaCrO_4$ in the cation group 4 procedure. Both chromates are fairly soluble in water and both are insoluble in alcohol. By making the proper mixture of these solvents, however, one is able to precipitate only the less soluble strontium chromate and leave the calcium compound in solution.

4. ***Complex formation.*** It is clear that if ions are present which will form complexes with ions from the low-solubility salt, the solubility of the latter may become great. Thus the solubility of AgBr in H_2O is low, $K_{SP} = 3.3 \times 10^{-13}$, but, if NH_4OH is present, the solubility increases markedly due to formation of $Ag(NH_3)_2^+$, which is moderately stable.

5. ***Particle size.*** Small particles of a given precipitate are more soluble than large particles, in some cases as much as a thousand times more

soluble.* The reason for this behavior is that the small particles have a higher surface tension than the larger crystals and the tendency is toward reduction of this energy by reorganization to produce larger crystals of smaller surface area. Crystalline substances such as $BaSO_4$ and CaC_2O_4 when precipitated rapidly contain many small crystals which are difficult to separate from the solution but which will increase in size if allowed to *age* or *digest*, that is, come to equilibrium with solution and the rest of the precipitate in such a way as to reach a fairly coarse average particle size.

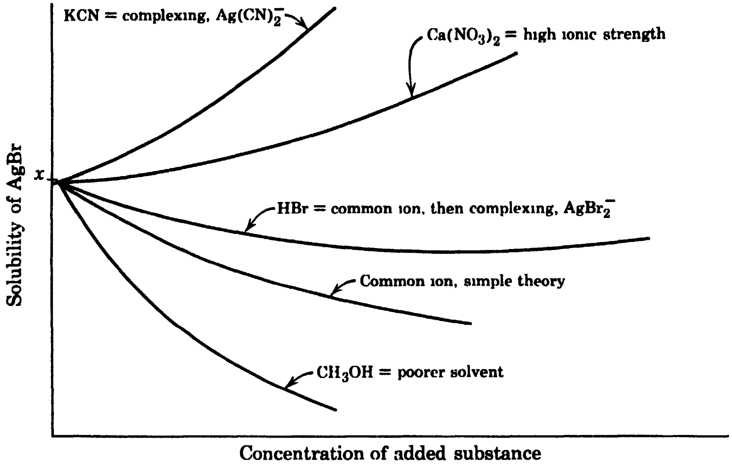

FIG. 8-1. Schematic review of important factors affecting the solubility of a salt. Point *x* represents the saturated aqueous AgBr solution.

Solubility product constants are given only for this stable condition. Amorphous precipitates like hydrated oxides have no definite orientation as precipitated, and on standing may change solubility considerably, commonly getting less soluble with time.

6. *Common ions.* The effect in the solution of ions that are common to ones in the slightly soluble salt will at first decrease the solubility of the latter as explained in the last two chapters. Thus, in precipitating a substance from solution, a little excess precipitating agent is used for its *common ion effect*. This shifts the equilibrium by the mass action principle to produce a maximum yield of desired precipitate. A large excess is

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* The relationship is given by $(RT/\text{mol. wt}) \ln S_r/S = 2\sigma/dr$, in which R is the gas constant, T absolute temperature, S_r the solubility of fine particles of radius r, S the solubility for coarse equilibrium particles, σ the surface tension, and d the density of the particles. The formula is derived by thermodynamics.

avoided, however, because of the salt effect or possibility of complex formation, as

$$HgI_2 + 2I^- = HgI_4^{-2}$$

*7. **Hydrolysis.*** If the cation of the sparingly soluble salt is derived from a weak base and/or the anion is derived from a weak acid, either or both ions may react with water (in a manner detailed in Chapter 10) to give hydrolysis products and a resulting increase in solubility. For example CaC_2O_4 is expected to hydrolyze some due to the weakness of oxalic acid:

$$CaC_2O_4 + H_2O = Ca^{+2} + C_2O_4^{-2} + H_2O = Ca^{+2} + HC_2O_4^- + OH^-$$

The result is that CaC_2O_4 is more soluble than if hydrolysis did not occur. The effect can be quite appreciable in these very dilute solutions, particularly with sulfides since the K_A for H_2S is so small.

Determination of Solubility Product Constants

K_{SP}'s are calculated from solubility data gathered by several methods, some of which are explained below.

*1. **Electrical conductivity.*** As with weak acids and bases, one can use electrical conductivity of the solution to determine the ionic concentrations in it. In Chapter 5 the formula $\Lambda = \kappa V$ was developed in which Λ is the equivalent conductance, κ the specific conductance, and V the cc volume needed to contain 1 g equivalent weight of solute. If we let S be the solubility of the slightly soluble salt expressed in gram equivalent weights per cubic centimeter, then V, which was the cc per g equivalent weight, is its reciprocal, or $\Lambda = \kappa/S$. Since the solution is so dilute, Λ approaches its maximum value Λ_0, which is the equivalent conductance at infinite dilution. One can obtain its value from addition of ionic conductances given in Table 5–2. The formula then becomes $S = \kappa/\Lambda_0$. Since a more useful solubility than gram equivalent/cubic centimeter would be gram equivalent/liter, let S' be the solubility in these concentration terms. Then $S/1000 = S'$, and the formula now derived for greatest usefulness becomes

$$S' = 1000\kappa/\Lambda_0 \qquad (8\text{–}4)$$

Example 8–1. The sp. cond. of AgBr at 18 C is 1.23×10^{-6} ohm^{-1}cm^{-1}, and the sp. cond. of H_2O at that temp. is 1.16×10^{-6} ohm^{-1}cm^{-1} (a correction that is significant at these dilns.). For AgBr alone, $\kappa = 0.07 \times 10^{-6}$. Calculate the K_{SP} of AgBr from that.

From Table 5–2, $\Lambda_{Ag^+} + \Lambda_{Br^-} = 121.6 = \Lambda_0$ for AgBr, and $S' = (1000)(7 \times 10^{-8})/121.6 = 5.76 \times 10^{-7}$ g equiv./liter. This figure will be the same as the molar solub., since the equiv. and mol. wts of AgBr are equal. Dissociation being approx. 100% at such low concn., $[Ag^+] = 5.76 \times 10^{-7}\ M = [Br^-]$ and,

$$K_{SP} = [Ag^+][Br^-] = (5.76 \times 10^{-7})^2 = 3.32 \times 10^{-13} \qquad (\textit{Ans.})$$

2. ***Electrochemical cells.*** By measuring the voltage of properly designed cells, one is able to relate it to the concentration of ions in a saturated solution of a slightly soluble salt and thus to calculate K_{SP}. (The calculation is similar to that of Example 11–5.)

3. ***Radioactive tracers.*** The number of curies* of radioactivity, determined by a counter, emitted by a gram of radioactive material is defined as the *specific activity* of the material. Because the number of nuclear disintegrations that radio elements undergo per second is very large, only traces of the elements or their ions need be present to give a detectable count. Various elements have been easily determined in microgram† per liter amounts. Since the count is related directly to the amount present, if one knows the specific activity of the element and the activity in a saturated solution of a slightly soluble salt containing it, he is able to determine the solubility and K_{SP}. Solutions may also be evaporated and the activity of the residue checked.

4. ***Simple evaporations.*** Where salts are soluble enough to yield a weighable residue upon evaporation of a reasonable volume of their saturated solutions, this is the most direct method of determining solubility product constants. See problem 2 and Example 8–2.

Example 8–2. It is found that a liter of satd. $BaSO_4$ (mol. wt 233) at 18 C leaves a residue of 2.3 mg of salt upon evap. Find the K_{SP}.

The molar solub. is $2.3 \times 10^{-3}\ g/233 \simeq 9.9 \times 10^{-6}$ moles/liter. The dissoc. is complete so this is also the molarity of Ba^{+2} and of SO_4^{-2} in equil. at 18 C with solid $BaSO_4$ and

$$[Ba^{+2}][SO_4^{-2}] = (9.9 \times 10^{-6})^2 = K_{SP} = 9.8 \times 10^{-11} \qquad (\textit{Ans.})$$

5. ***Turbidimetry and nephelometry.*** The first of these methods concerns the detection of solubility limits. One causes one dilute solution to react with another until turbidity due to the appearance of a precipitate is just noticed. This is the saturated solution, and K_{SP} is calculated from knowing the concentrations. Turbidity is determined by shining a beam of light through the solution; only when the first very fine solid particles are present will the beam be scattered by particles and appear to extend through the suspension as a shaft of light.

The second method involves shaking a known quantity of solid solute with an increasing volume of water and measuring the light scattering due to undissolved suspended solid. This is done, as above, by means of

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* 1 curie = 3.7×10^{10} disintegrations/sec.

† 1 microgram, $\mu g \doteq 10^{-6}$ g.

an optical instrument known as a nephelometer. The dilution beyond which solvent addition results in no further reduction in light scattering is the saturated solution and K_{SP} follows by calculation.

6. Ultramicroscopy. In this method, one studies successive dilutions of solid in water using the ultramicroscope to determine which dilution just fails to show any solid phase. This is the saturated solution, and again K_{SP} is calculated from the known concentrations.

7. Colorimetry. Sometimes the substance being studied lends itself to a colorimetric measurement that enables one to determine equilibrium concentrations of ions in the saturated solution. This is illustrated in special experiment 3 wherein the K_{SP} of CaF_2 is found with the aid of a sensitive organic reagent for fluoride. Many experiments can be designed using that general principle—see problems 3 and 4, for example.

K_{SP} and Solubility

K_{SP} values can be misleading in the sense that they do not express solubility directly, although they are related to it. The following example illustrates both this and the method for determining solubilities from the K_{SP} table.

Example 8–3. CuI and Ag_2CrO_4 both have about the same K_{SP} value, 1.1×10^{-12}. Calculate the molar and g/liter solub. for both.

Taking CuI first, if we let x be the molar concn. of Cu^+ in the satd. soln., then x is also the concn. of I^-, since the two ions are dissoc. in equal numbers.

$$[Cu^+][I^-] = K_{SP} = (x)(x) = 1.1 \times 10^{-12} = x^2$$

and $x = 1.05 \times 10^{-6}\ M$. This is also the number of moles of CuI which will dissolve to make a liter of satd. soln., so the molar solub. $= 1.05 \times 10^{-6}$ moles/liter (*Ans.*), and the g/liter solub. is obtained by multiplying by the mol. wt, 190.5, giving 2.0×10^{-4} g/liter. (*Ans.*)

If y is the molar concn. of CrO_4^{-2} in a satd. soln. of Ag_2CrO_4, then $[Ag^+]$ will be $2y$ since $2Ag^+$ are present with each CrO_4^{-2}:

$$Ag_2CrO_4 = \underset{2y}{2Ag^+} + \underset{y}{CrO_4^{-2}}$$

Substituting in the K_{SP} statement and solving for y,

$$[Ag^+]^2[CrO_4^{-2}] = K_{SP} = (2y)^2(y) = 1.1 \times 10^{-12} = 4y^3$$

$$y = (1.1 \times 10^{-12}/4)^{1/3} = (275 \times 10^{-15})^{1/3} = 6.5 \times 10^{-5}\ M$$

Since y moles of CrO_4^{-2} come from y moles of Ag_2CrO_4, the molar solub. of this salt is 6.5×10^{-5} moles/liter (*Ans.*), and the g/liter solub. is $(6.5 \times 10^{-5})(331.8) \cong 2.2 \times 10^{-2}$ (*Ans.*).

Thus though the K_{SP}'s were about the same, the squared term in the Ag_2CrO_4 case and the difference in molecular weights of the two salts led to the fact that the solubilities are not identical.

The opposite case is true also; if one has two salts such as AB and C_3D which have the same solubility in grams per liter, one can see that different molecular weights will lead to different molar solubilities and the cubed term will give a considerably different K_{SP}.

Conditions for Precipitation

A common problem in analytical chemistry is that of discovering conditions of concentration under which precipitation will or will not occur. If such knowledge is available, schemes of gravimetric separations follow. Since the K_{SP}'s are calculated from data on saturated solutions it should be clear that any greater concentration of ions involved than those which give the K_{SP} value by proper manipulation, are in excess of equilibrium concentrations and precipitation will take place (assuming supersaturation does not occur). This type of problem reduces itself to a comparison between the magnitude of the K_{SP} and the product of the ionic concentrations (properly handled algebraically to match the K_{SP} definition for the compound being studied, cubing, squaring, etc., as needed). The product of ionic concentrations so manipulated is called the *ion product, I.P.* Three cases arise:

I.P. $> K_{SP}$; *precipitation takes place until I.P.* $= K_{SP}$.
I.P. $= K_{SP}$; *no apparent reaction; solution is saturated.*
I.P. $< K_{SP}$; *no precipitation; precipitate already present dissolves until I.P.* $= K_{SP}$.

It should now be added that the precipitate must not only be theoretically capable of appearance, but sufficient quantity must be present for the observer to see. If one is using a milliliter of test solution, he is capable of detecting no less than between 0.1 and 0.01 mg of average precipitate suspended in it. If precipitates have an average molecular weight of about 150, this means that the concentration of precipitate to be detected must at least be in the approximate range $7 \times 10^{-4} - 7 \times 10^{-5}$ *M*.

Example 8–4. A certain tap water is known to contain 300 parts per million (ppm = mg/liter for dil. aq. soln.) sodium chloride. If to 50 ml of this are added 50 ml of 0.02 *M* $AgNO_3$, will AgCl pptn. take place?

All one needs do is to compare the *I.P.*, $[Ag^+][Cl^-]$ in the mixt. to the K_{SP}, whose value from the table is 2.8×10^{-10}. If *I.P.* $> K_{SP}$, a ppt. results. The NaCl concn. in the tap water is 3.00×10^{-1} g/liter divided by the mol. wt, 58.5, or 5.13×10^{-3} *M*. Since each soln. dilutes the other in mixing, then, momentarily, prior to reaction the NaCl concn. is 2.56×10^{-3} *M* and the $AgNO_3$ is 10^{-2} *M*. Therefore $[Ag^+] = 10^{-2}$ *M* and $[Cl^-] = 2.56 \times 10^{-3}$ *M*, and the *I.P.* $[Ag^+][Cl^-] = 2.56 \times 10^{-5}$, which is larger than the K_{SP} so AgCl does ppt. AgCl continues to form until *I.P.* $= K_{SP}$. (*Ans.*) One can further calc. that the amount of ppt. formed is sufficient to be visually detected. (How is this done?)

Fractional Precipitation

If a solution contains two or more ions that can form slightly soluble compounds upon addition of some oppositely charged ion, the precipitates will form in the order which their K_{SP}'s are exceeded. If one is to effect good separations in this way, the quantity of the first precipitating compound still remaining unprecipitated must be very small when the *I.P.* of the next precipitating compound just exceeds its K_{SP}. Naturally the greater the difference in solubilities of the two or more compounds to be precipitated the more readily and clean cut may the separation be made. For practical purposes, the equilibrium ratio between two ions to be separated in this way should be at least 10^5 or 10^6 to 1, a ratio one can determine with the aid of K_{SP} data. The precipitation of a selected species from solution in this manner is called *fractional precipitation* or *fractional crystallization*, and is a principle used frequently in analytical chemistry. Two applications from this course follow.

1. ***Group 2 and Group 3 Sulfide Separations.*** If one calculates the solubilities of the group 2 sulfides from K_{SP} data and compares them with the solubilities of the group 3 sulfides, he finds the latter are considerably more soluble. Thus for a given $[S^{-2}]$, more group 3 metal ions are needed in solution for equilibrium than group 2 ions, hence through proper regulation of $[S^{-2}]$ it is possible to precipitate only group 2 sulfides and leave group 3 metals still in solution. When the former have been removed by centrifugation, the latter are precipitated using the same precipitant, H_2S, but regulating conditions to produce more $[S^{-2}]$. This is most easily done with *p*H control since $[H^+]$ is related to $[S^{-2}]$ by the H_2S equilibrium. A solved problem should clarify these generalizations.

Example 8–5. Calculate the approx. mg of Cu^{+2} (typical group 2 ion) and mg of Fe^{+2} (typical group 3 ion) that could remain unpptd. in 1.0 ml of soln. that is 0.3 *M* in H^+ and is kept satd. with H_2S (i.e., is under group 2 pptn. conditions).

From $[H^+]^2[S^{-2}] = 1.3 \times 10^{-21}$ for satd. H_2S, one can determine the sulfide in equil. with 0.3 *M* H^+ to be 1.4×10^{-20} *M*. (See Chapter 7 on H_2S.) This being the $[S^{-2}]$ available for pptn. it remains only to find from their respective solub. product constants the quantity of metallic ions that can be tolerated simultaneously in soln.

For CuS, $K_{SP} = 4 \times 10^{-36} = [Cu^{+2}][S^{-2}]$ and substituting 1.4×10^{-20} *M* for $[S^{-2}]$ gives a value of 2.8×10^{-16} *M* which corresponds to 1.8×10^{-14} mg of Cu^{+2} left unpptd. in 1 ml of soln. (*Ans.*) By the same method, using 4×10^{-17} for the K_{SP} of FeS one calcs. that the equil. $[Fe^{+2}]$ is 2.8×10^3 *M*, corresponding to 1.6×10^5 mg of Fe^{+2}/ml left unpptd. (*Ans.*)

It is evident that essentially all Cu^{+2} precipitates and no Fe^{+2} can precipitate (regardless of how much was originally in solution), as the theoretical equilibrium $[Fe^{+2}]$ greatly exceeds the solubility of any ferrous salt. These being typical ions of the two analytical groups, one sees how effective and important fractional precipitation methods can be.

The problem just solved was done in a very approximate way and a refinement should be noted now. Since the Cu^{+2} precipitation is found to be all but complete

$$Cu^{+2} + H_2S = CuS + 2H^+$$

shows that as reaction proceeds, the *p*H of the solution continues to drop. This increase in $[H^+]$ is considerable if a large amount of CuS precipitates, and since $[H^+]$ is a major factor in sulfide precipitations it is advisable to work such problems allowing for $[H^+]$ change, as below.

Example 8–6. One has a 0.3 M H^+ soln. contg. 10 mg Cu^{+2}/ml. If one keeps 1 ml of this saturated with H_2S, calculate the $[Cu^{+2}]$ in soln. at equil., taking into account the fact that the $[H^+]$ will increase.

From Example 8–5 one may expect that almost all the copper will be pptd. as the sulfide. The original $[Cu^{+2}]$ is $10/63.5 = 0.158\ M$, and since two H^+ are formed for each Cu^{+2} pptd., the H^+ increases from 0.3 M to $0.3 + (2)(0.158) \cong 0.62\ M$. From K_A for satd. H_2S, one calculates that 0.62 M H^+ depresses the ioniz. to the point where $[S^{-2}]$ is only $\cong 3.4 \times 10^{-21}\ M$. From the K_{SP} of CuS one then finds that the $[Cu^{+2}]$ in equil. with this amount of sulfide is $\cong 1.2 \times 10^{-15}\ M$. (*Ans.*) Due to the very small value of the K_{SP}, the $[Cu^{+2}]$ is still minute, so in this case the additional $[H^+]$ did not hinder the pptn. noticeably.

In another situation where different concentrations and a more soluble sulfide were considered, the more exact calculation might demonstrate that precipitation would never take place quantitatively.

The next example shows another method for handling this type of problem.

Example 8–7. Calculate the ratio $[Fe^{+2}]/[Cu^{+2}]$ that could exist in soln. when, as in Example 8–6, the $[H^+]$ is 0.62 M and $[S^{-2}]$ is 3.4×10^{-21} Show that the ratio is greater than 10^6 to 1, hence separation by fractional pptn. is feasible.

If one simply multiplies each term of the desired ratio by $[S^{-2}]$, the expression becomes a ratio of K_{SP}'s of the two sulfides. These being given, the problem is solved in one step:

$$\begin{aligned}[Fe^{+2}]/[Cu^{+2}]\cdot[S^{-2}]/[S^{-2}] &= [Fe^{+2}][S^{-2}]/[Cu^{+2}][S^{-2}]\\ &= K_{SP}\text{FeS}/K_{SP}\text{CuS}\\ &= 4\times 10^{-17}/4\times 10^{-36}\\ &= 1\times 10^{19}/1 \quad (\textit{Ans.})\end{aligned}$$

The ratio of metal ions left in soln. being much greater than 10^6 to 1, separation by fract. pptn. is feasible. (*Ans.*)

Multiplication by factors like $[S^{-2}]/[S^{-2}]$ to simplify the computation by producing expressions whose values are known challenge the alertness of the student and allow for some quick and original solutions to problems.

2. Mg^{+2} and Group 4 Separation. A further illustration in *p*H control, which regulates in turn the concentration of ions causing precipitation, is afforded in the case of Mg^{+2}, whose hydroxide precipitation is prevented in group 4, though the solution is basic with an NH_4Cl—NH_4OH buffer.

Example 8–8. One has 2.0 ml of soln. contg. 10 mg of Mg (~ 0.21 *M* Mg^{+2}), 2.0 *M* NH_4^+, and 0.30 *M* NH_4OH. Show that $Mg(OH)_2$ cannot ppt.

From the last two concns. and K_B for NH_4OH, one obtains $K_B = 1.8 \times 10^{-5} = (2.0)[OH^-]/(0.30)$, from which $[OH^-] = 2.7 \times 10^{-6}$ *M*. The *I.P.* is then determined as $[Mg^{+2}][OH^-]^2 = (0.21)(2.7 \times 10^{-6})^2 \cong 1.5 \times 10^{-12}$. The K_{SP} is 8.9×10^{-12}, so since $I.P. < K_{SP}$, no pptn. occurs. (*Ans.*)

Further Regulations of Solubility; Fractional Solubility

We have seen above that certain ions may be precipitated under given circumstances and others held in solution, even though under different concentration conditions they too could be precipitated with the added reagent. Similar calculations can be used to determine whether or not a precipitate once formed will redissolve if factors of concentration and/or chemical environment are favorable.* Calculations can show which precipitates, if any, in a mixture will dissolve under the given conditions. Separations effected in this manner are by a process which can be called *fractional solution* or *fractional solubility*. As before, the ratio of the solubility of two precipitates involved must be about 10^6 to 1 to get a separation clean enough for qualitative analysis.

Example 8–9. One has a few mg of a mixt. of ZnS and HgS. It is stirred with several ml of 2.0 *M* HCl. Is a separation possible by fract. solub.?

Though the H_2S will be unknown at equil., one might assume as a first approx. that one sulfide will dissolve and furnish enough hydrogen sulfide to sat. the soln. Then from $[H^+]^2[S^{-2}] = 1.3 \times 10^{-21}$, the $[S^{-2}]$ in the 2 *M* H^+ soln. is found to be $\cong 3.3 \times 10^{-22}$ *M*, and from the K_{SP} of ZnS which is 1×10^{-20} the equil. $[Zn^{+2}]$ is $\cong 30$ *M*. This value is so large that the few mg of ZnS in the sample will dissolve in the HCl.

The K_{SP} of HgS is 1.1×10^{-50} and the $[Hg^{+2}]$ in equil. with the available S^{-2} is only $= 3.3 \times 10^{-29}$ *M*. For practical purposes HgS is not going to

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* This assumes the precipitate itself does not change character as some sulfides and hydrous oxides do on standing. The K_{SP} values are generally listed only for freshly prepared, though well digested, precipitates.

dissolve at all in 2 *M* HCl (or in any other acid soln. for that matter in which H_2S is a by-product) since the K_{sp} of HgS is so small.

The Solubility of HgS in Aqua Regia

After the foregoing calculation one may recall that HgS is separated in cation group 2A by fractional solubility, since it is insoluble in HNO_3, while the other members of the subgroup are soluble. The student may wonder why in the next step HgS dissolves in aqua regia when before it was insoluble in either HCl or HNO_3 individually. There are two factors favoring displacement of equilibrium to give that result: (*a*) HNO_3 oxidizes sulfide to elemental sulfur, a reaction which keeps $[S^{-2}]$ very low and (*b*) a reasonably stable tetrachloromercury(II) complex forms that keeps $[Hg^{+2}]$ very low. The over-all reaction is

$$3HgS + 8H^+ + 2NO_3^- + 12Cl^- = 3HgCl_4^{-2} + 2NO + 4H_2O + 3S$$

It is not correct to say that aqua regia produces oxidants more powerful than the original substances. Though NOCl and Cl_2 may be present in aqua regia, they are not the whole explanation for the above reaction.

Colloids

The student will become aware soon after starting the laboratory work that not all precipitates form quickly and settle completely, even after heating, prolonged stirring, centrifugation and perhaps some profanity. Sulfur and certain metallic sulfides are prone to form many very small particles rather than a lesser number of large particles. If the particle diameters are in the range 10^{-5} and 10^{-7} cm*, the particles are *colloidal*. They will not settle by gravity since they are small enough to be kept in motion (*Brownian movement*) by collisions with solvent molecules and by mutual repulsion due to their possessing similar surface charge. They are also too small to be filterable by ordinary means. A homogeneous appearing suspension like this is called a *sol*. Particles in this range may coagulate and form long strings (*micelles*) of atoms that trap liberal amounts of solvent to give a second type of colloidal suspension called a *gel*. There are a number of familiar gels in analytical chemistry, most of them being hydrous oxides, as those of Fe^{+3}, Al^{+3}, Si^{IV}, and Cr^{+3}.

Precipitation of Colloids

From the analyst's viewpoint the most significant feature of colloidal particles is their great surface area per unit weight and the ability of that

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* 1 micron, $\mu = 10^{-4}$ cm, 1 millimicron, $m\mu = 10^{-7}$ cm, and 1 Angstrom unit, $A = 10^{-8}$ cm. These units are used in discussing small dimensions.

surface to collect (*adsorb*) ions from solution. Sols adsorb primarily ions of one charge or the other, so a given sol will be composed of particles whose surface charge is similar. Clustered about this *primary layer* of adsorbed ions is a less tightly held *secondary layer* of *counter ions*.

Sols may be shown in two simple experimental ways to be charged, both depending for evidence on the idea that if the surface charge is neutralized, *coagulation* or *flocculation* of the colloid will take place. The first method involves adding a salt to the colloidal suspension to force adsorption of a secondary layer, which neutralizes the primary layer. The valences of the salt ions of proper charge are in direct proportion to their coagulative effectiveness (and one experimental technique for determining the valence of complex ions actually uses such an application). If this precipitate is then washed with pure water instead of with a dilute salt solution, the ionic layer that caused flocculation can be removed and the solid may return to its former dispersion by a *deflocculation* process called *peptization*. The second method of colloid precipitation involves electrolysis of the sol; if it is positively charged, it moves toward the negative electrode and coagulation is noted there as the sol's charge is neutralized. This is the principle used in precipitating smoke particles in chimneys to prevent air pollution.

Coprecipitation

Coprecipitation is the term given the process in which a substance that is precipitating carries with it other substances from the solution that normally would not come down. These coprecipitants and extent of contamination by them depend upon the substances involved, their valences, the surface area available for adsorption, speed of reaction, temperature, time allowed for digestion, etc. There are several mechanisms by which coprecipitation can take place, the most important being that of adsorption (described above). Adsorption causes trouble for the analyst in that the adsorbed ions may be the ones sought in a later test or they may be such as to make confirmatory tests on the main precipitate difficult. Coprecipitation can be minimized by adding the precipitant slowly and with good stirring to a fairly dilute, hot solution. This is followed by a hot digestion period and washing of the precipitate with a dilute solution of a volatile electrolyte. These precautionary measures favor large, pure crystals with minimum surface, and slow tendency toward adsorption and peptization. (See problem 25, this chapter.)

Uses of the Adsorption Phenomenon

Once the mechanisms of adsorption are understood, conditions can be regulated to increase or decrease the phenomenon and it can be put to work in the chemist's behalf. One use is illustrated by the *adsorption complexes* (*lakes*) formed between certain inorganic precipitates and organic color reagents (type D, Chapter 12). Another use is in *chromatographic separation methods.* In this technique, a solution moves over an insoluble medium, on the surface of which solution components concentrate in the order of their ability to be adsorbed. The solution may percolate through a column of adsorbant (*column chromatography*) or move by capillary action over a strip of paper (*paper chromatography*). Adsorbance of colored substances is followed simply by the color banding; colorless materials require color reagents or ultra violet light to locate their positions. The zones holding adsorbed material are cut out and the desired components washed out (*eluted*) by proper solvents (special experiment 9). The chromatographic method has recently been applied to gases that are identified by thermal conductivity after desorption.

The analyst may also utilize adsorption to collect or concentrate small quantities of precipitates for further testing. For instance, by precipitating $BaSO_4$ on filter paper, one decreases the paper's average pore size to a degree that colloidal precipitates (such as Prussian blue from a test for Fe^{+3}) can be removed from suspension by filtration. Detection by spot paper techniques is generally of a higher order than detection in solution, due partly to the paper's adsorptive effect.

PROBLEMS

1. The K_{SP} of $SrCrO_4$ is 3.6×10^{-5}. Arbitrarily select six values of $[Sr^{+2}]$ between 10^{-1} and 10^{-4} *M* and calculate the equilibrium $[CrO_4^{-2}]$. Prepare a graph of $[Sr^{+2}]$ vs. $[CrO_4^{-2}]$. Explain the hyperbolic shape with reference to Sr^{+2} and CrO_4^{-2} in solution. Explain the significance of the shape of a plot of $[Sr^{+2}]$ vs. $1/[CrO_4^{-2}]$. What shape curve would one expect to obtain by graphing $[Pb^{+2}]$ vs. $[Cl^-]^2$ in illustrating the $PbCl_2$ case? In $[Pb^{+2}]$ vs. $1/[Cl^-]^2$? Try these.

2. A solution is saturated at 20 C by shaking an excess of $PbCl_2$ in pure H_2O. A 100 ml sample of clear solution is drawn off and evaporated, leaving a residue of 990.2 mg of $PbCl_2$. Calculate the molar solubility of the salt and the K_{SP}. Compare the latter with the table value.

3. Excess $Ca(OH)_2$ is shaken with pure H_2O. A 50.00 ml sample of clear, saturated solution is later withdrawn and takes 17.90 ml of 0.1400 *N* HCl to titrate its base strength completely. Calculate the K_{SP} of $Ca(OH)_2$ and compare your answer with the text value. How could one have used indicators instead of titration to arrive at the K_{SP} of $Ca(OH)_2$?

4. Mn^{+2} can be oxidized to MnO_4^- by trisodium paraperiodate, $Na_3H_2IO_6$, in the presence of $H_2SO_4 + H_3PO_4$. Whereas the color of Mn^{+2} in dilute

solutions cannot be detected, MnO_4^-, being a dark purple-red color, can be seen at concentrations as low as 0.1 part per million Mn (ppm = mg/liter).

A sample of $MnCO_3$ is shaken with pure H_2O and after the excess has settled, a sample of clear, supernatent, saturated solution is withdrawn. To this is added cond. H_2SO_4, cond. H_3PO_4, and $Na_3H_2IO_6$ and the solution is boiled. When cool, the color developed due to the oxidation of manganese(II) to manganese(VII) is visually compared with a series of known permanganate solutions prepared in the same way, and it is decided that the sample matches the 0.5 ppm Mn standard. Show that the experiment has given data which allows one to calculate the K_{SP} of $MnCO_3$. (Ans. 8.3×10^{-11})

5. (*a*) How many g of $(NH_4)_2C_2O_4$ must be added to 1 liter of solution containing 0.0050 g of $Ca(NO_3)_2$ to start precipitation of $CaC_2O_4 \cdot H_2O$? If 0.0500 g of $Sr(NO_3)_2$ were also present, which oxalate would precipitate first?

(*b*) What success would one have in attempting fractional precipitation using OH^- on a solution containing an equimolar mixture of Ca^{+2} and Sr^{+2}?

6. MX_2 is a slightly soluble salt. The ionic weight of M^{+2} is 100 and of X^- is 50. The K_{SP} is 1×10^{-12}. (*a*) Calculate the mg of each ion present in a liter of saturated solution. (*b*) How many liters would be needed to dissolve 100 g of MX_2?

7. Graph the following solubility data for PbI_2 and calculate the K_{SP} at each temperature. Explain why K_{SP} is not a constant.

Temp., °C	0	20	40	60	80	100
Solubility (g PbI_2/liter)	0.442	0.68`	1.25	1.97	3.02	4.36

8. What is the molar solubility of Ag_2CrO_4 in pure H_2O? In 0.02 *M* $AgNO_3$? In 0.02 *M* K_2CrO_4? Why aren't the last two answers the same since the common ion principle is in effect in each and the salt concentrations are the same?

9. (*a*) How many mg of Ag^+ remain unprecipitated when 500 ml of 5×10^{-5} *M* $AgNO_3$ is mixed with 500 ml of 5×10^{-4} *M* HCl?

(*b*) One has 300 mg of AgCl in a sintered glass funnel and washes it with 300 ml of H_2O. Assuming equilibrium conditions, what weight of precipitate remains? Suggest a better wash liquid considering that the residue is to be dried later and weighed in a quantitative determination.

10. A solution is made by dissolving 50 mg of $AgNO_3$ in a liter of water. About how many mg of NaCl are needed to precipitate 20 mg of AgCl from this solution?

11. What is the solubility (g/liter) of $Fe(OH)_3$ in a solution buffered at *p*H 7? *p*H 8? *p*H 6? If water is flowing through an iron pipe, should one treat the water to give it a moderately low or high *p*H to maintain a protective coating of $Fe(OH)_3$? What is the lowest *p*H at which one could theoretically precipitate $Fe(OH)_3$ from a 0.1 *M* Fe^{+3} solution?

12. A solution is 0.1 *M* in H^+, 0.01 *M* in Cd^{+2}, and 0.0001 *M* in Cu^{+2}. Which sulfide precipitates first when H_2S is bubbled in?

13. A solution contains 2 mg of Mg^{+2} per ml. How many mg of solid NH_4NO_3 must be added to 5 ml of this solution to just prevent $Mg(OH)_2$ precipitation when 3 ml of 0.04 *M* NH_4OH are later added?

14. A solution is 0.120 *M* in PO_4^{-3} and 0.055 *M* in S^{-2}. To this is slowly added solid $Pb(NO_3)_2$. (*a*) Which lead compound precipitates first? (*b*) When $[PO_4^{-3}]$ becomes 10^{-4} *M*, what is $[S^{-2}]$? (*c*) When $[S^{-2}]$ is 10^{-10} *M*, what is $[PO_4^{-3}]$?

15. If to 1 liter of 0.010 *M* NaBr is added 10.000 g of solid AgCl, what is the ratio $[Br^-]/[Cl^-]$ at equilibrium (assuming no volume changes)? Does the magnitude of the ratio suggest that one could successfully separate these silver halides by fractional precipitation?

16. Show that if one keeps 10 ml of solution, which is 0.3 *M* in H^+ and 0.01 *M* in Cu^{+2}, saturated with H_2S, a quantitative precipitation of CuS is obtained. Show by calculation that ZnS is not precipitated if the same solution also contained a $[Zn^{+2}]$ of 0.01 *M*. Calculate the final total $[H^+]$ when the $[Cu^{+2}]$ has been reduced to 10^{-10} *M*.

17. Determine what $[H^+]$ is needed from HCl to begin solution of CuS. Of ZnS. Does this calculation show that one might effect a separation between the two sulfide precipitates by $[H^+]$ control, say with a buffer solution or by using a weak acid? (Assume saturated H_2S solutions.)

18. Can one dissolve an appreciable quantity of FeS in 1 *M* HAc? What is the solubility of FeS in a buffer solution made by dissolving 8.20 g of NaAc in a liter of 1 *M* HAc? (Same assumption as 17.)

19. A solution is 0.4 *M* in Ba^{+2} and 0.15 *M* in Sr^{+2}. If solid K_2SO_4 is slowly added, and assumed to dissolve and mix immediately (*a*) At what $[SO_4^{-2}]$ does $BaSO_4$ start to precipitate? (*b*) What is the ion product $[Sr^{+2}][SO_4^{-2}]$ when condition (*a*) obtains? (*c*) What is the $[Sr^{+2}]$ when $[Ba^{+2}]$ is 10^{-9} *M*? (*d*) What is the $[Ba^{+2}]$ when two-thirds of the Sr^{+2} has precipitated? (Ans. (*a*) 3.75×10^{-9} *M*.)

20. Ten ml of solution contains 17 mg of Ag^+, 20 mg of Cu^{+2}, and is 0.20 *M* in H^+. It is kept saturated with H_2S and both metallic sulfides for practical purposes are quantitatively precipitated. Not neglecting the H^+ formed in the reactions, calculate the equilibrium concentrations of H^+, Cu^{+2}, Ag^+ and S^{-2}. (Ans. $[H^+] = 0.279$ *M*.)

21. From K_A of HNO_2 and K_{SP} of $AgNO_2$, show that *K* for $AgNO_2 + H^+ = Ag^+ + HNO_2$ has a value of about 0.27. Would you expect to dissolve much $AgNO_2$ at, for example, *p*H 5? Explain.

22. (*a*) One has a very fine water suspension of $BaSO_4$ from which he wishes to recover the solid. How would the addition of a small amount of agar gel followed by centrifuging help? How could one increase the size of the $BaSO_4$ particles so they will settle faster of their own accord?

(*b*) Iron pyrite ($FeS_2 + SiO_2$) is analyzed by dissolving FeS_2 with a mixture of $HNO_3 + Br_2$, which oxidizes sulfide sulfur to sulfate. This is then precipitated as $BaSO_4$. After the precipitate is ignited (to dry it before weighing) it invariably comes out reddish colored and one obtains results that are too high for sulfur unless a correction in technique is made near the beginning of the process. Explain what has happened and how to circumvent the difficulties so as to obtain correct analytical results.

23. If AgCl is precipitated from solution containing excess $AgNO_3$ and dried, weighed, and analyzed for silver, it is found to contain a little more than the theoretical amount of metal. With the aid of a suitable diagram, give an explanation for the experimental result.

24. (*a*) Express the colloid particle diameter range in mm, μ, mμ and A units.

(*b*) The density of Pt is 21.45 g/cc. Calculate the cm^2 area of a g cube of Pt. If this cube were reduced in size to uniform cubes, 100 mμ on a side, calculate the new surface area. If this powder were used as a *catalyst* for a reaction that took place at the catalyst's surface, by what factor would you estimate the process may be speeded up by sub-division of the solid?

25. (*Library*) (*a*) Two mechanisms of coprecipitation are *occlusion* and *mixed crystal formation*. With the aid of a textbook in quantitative analysis, describe these processes and point out how they apply to qualitative testing.

(*b*) NH_4NO_3 is frequently used as an electrolyte in aqueous washes to prevent peptization. Why is it superior to NaCl, for example, if the precipitate is to be later heated and weighed quantitatively?

26. (*Library*) Find reference to these instruments mentioned in the chapter: turbidimeter, nephelometer, and ultramicroscope. Give a schematic drawing of each, label, and briefly explain how each works. Mentally note how they are related to K_{SP} determinations. The ultra-microscope method is reputed to be the least reliable of the three. Can you suggest any reasons for its unreliability?

27. A solution is 10^{-5} M in Ag^+ and another is 0.152 M in CrO_4^{-2}. Jackson Slipshod wants to find if upon mixing equal volumes, silver chromate will precipitate ($K_{SP} = 1.9 \times 10^{-12}$). He reasons first that the solutions mutually dilute each other, so momentarily $[Ag^+] = 5 \times 10^{-6}$ M and $[CrO_4^{-2}] = 0.076$ M. Then to get the ion product, the silver concentration is doubled and squared and multiplied by the chromate concentration: $I.P. = (10 \times 10^{-6})^2(7.6 \times 10^{-2}) = 7.6 \times 10^{-12}$. Since $I.P. > K_{SP}$, Ag_2CrO_4 should come down. On actually mixing the solutions nothing happens and Jackson concludes that the table K_{SP} value was in error. What alternate explanation can you find?

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There are many colloid texts and reference books on special topics in colloid science.

9

EQUILIBRIUM
AND
WERNER IONS

Discussion in Chapter 4 showed that Werner salts are like the simpler salts in the sense that they are ionic and dissociate in aqueous solution. It was left until now, however, to point out that the complex ions themselves are capable of undergoing a second, much weaker ionization and that the chemical equilibrium principle is operative and applicable. Factors in this ionization are the ion's stability as dictated by the bond strengths, temperature, solvent, concentration, and the presence of other dissolved substances. By considering only variation in ion identity and concentrations, we are able to learn some fundamentals of these systems in a quantitative way. Equilibrium applied here is another special case of the mass action law.

Dissociation of Complex Ions

The first dissociation of a Werner compound is considered to be complete in dilute solution:

$$Cu(NH_3)_4SO_4 = Cu(NH_3)_4^{+2} + SO_4^{-2}$$

As with other strong electrolytes, the equilibrium principle is not adaptable to this. The tetrammine copper(II) ion will, however, then exhibit a second dissociation, yielding some ammonia and cupric ion in solution:

$$Cu(NH_3)_4^{+2} = Cu^{+2} + 4NH_3$$

This dissociation takes place to a small degree and since it varies in a predictable inverse ratio to the concentration of the complex, one may further develop and use the mass action concepts to aid understanding of such examples. The equilibrium constant is called the instability constant, K_{ins}, and is a measure of the ion's ability to dissociate:

$$K_{ins} = [Cu^{+2}][NH_3]^4/[Cu(NH_3)_4^{+2}]$$

It is evident that the concentration in solution of the coordinated groups for all these complexes will be an important factor in shifting equilibrium because of the many cases where 4 and 6 appear as powers.

Determination of K_{ins} Values

In Chapter 4 a number of experimental techniques were explained which have been useful in determining the formulas for complexes. After formulas have been found it is of interest to analytical chemists to evaluate the instability constants of the complex ions to see how tightly bound the complexes are and of what use one can make of this knowledge. Zinc and aluminum ions can be separated, for instance, by adding aqueous ammonia; zinc forms the soluble, stable complex $Zn(NH_3)_4^{+2}$, whereas aluminum precipitates quantitatively as $Al(OH)_3$ (hydrated). Another application in group 3 analysis is the complexing of ferric ion with phosphoric acid, so the thiocyanate-acetone test for cobalt will not be obscured by any $Fe(SCN)^{+2}$ color, etc. If instability constants are known for complexes, computations can be carried out which make these processes more meaningful.

Several simple methods have been used to find equilibrium constants for the Werner ions, and two are briefly dealt with below.

1. K_{ins} from Electrochemical Cells. Proper cell setups can relate measured voltage (which is dependent upon ion concentration) to the instability constant of the system studied. This will be illustrated in Chapter 11.

2. K_{ins} from Solubility Data. One can sometimes relate equilibrium constants that are known to an instability constant that is unknown and evaluate the latter. K_{SP} data have been helpful in this respect.

Example 9–1. A student finds that at room temp. the solub. of solid AgCl in 0.022 M NH_4OH is 10^{-3} moles/liter. Show that this is enough data for a determination of the instability constant of the diammine silver complex.

Two equilibria are involved:

$$AgCl = Ag^+ + Cl^-; \quad K_{SP} = [Ag^+][Cl^-] = 2.8 \times 10^{-10} \qquad (9\text{–}1)$$

$$Ag(NH_3)_2^+ = Ag^+ + 2NH_3; \quad K_{ins} = [Ag^+][NH_3]^2/[Ag(NH_3)_2^+] = \ ? \qquad (9\text{–}2)$$

The reaction is

$$AgCl + 2NH_3 = Ag(NH_3)_2^+ + Cl^-$$

At equil., $[Cl^-] = 10^{-3}\,M$ and $[Ag(NH_3)_2^+] = 10^{-3}\,M$ if one assumes that all 10^{-3} moles of Ag^+ are complexed. This is a valid approx. since the complexes used in anal. chem. are usually quite stable. Then $[NH_3] = 0.022 - (2)(10^{-3}) = 0.020$, since 2 NH_3's are used to complex one Ag^+. With these figures one substitutes first in equation 9–1 to find the equil. $[Ag^+]$ and then in equation 9–2 to get the instability constant:

$$[Ag^+] = 2.8 \times 10^{-10}/10^{-3} = 2.8 \times 10^{-7}\,M$$

In this homogeneous soln. there is only one silver ion concn. and it must satisfy both equations. The other concns. being known, one writes

$$K_{ins} = (2.8 \times 10^{-7})(2 \times 10^{-2})^2/10^{-3} = 11.2 \times 10^{-8} \qquad (\textit{Ans.})$$

Example 9–2. A certain soln. is $10^{-4}\,M$ in total Cd^{+2} and 0.90 M in HCl, and when this mixt. is satd. with H_2S, CdS *just* begins to ppt. Show that a discrepancy exists between these actual conditions of pptn. and the theoretical conditions. Assuming this is due to the presence of a complex, $CdCl_4^{-2}$, calc. a value for its instability constant.

From equation 7–23, we get, for satd. H_2S solns., $[H^+]^2[S^{-2}] = 1.3 \times 10^{-21}$, and the $[S^{-2}]$ in equil. with 0.90 M H^+ is calcd. to be $1.61 \times 10^{-21}\,M$. (As in the preceding chapters on equil. it is assumed that the HCl is completely dissoc.) From the K_{SP} of CdS, $[Cd^{+2}][S^{-2}] = 6.0 \times 10^{-27}$ and now knowing $[S^{-2}]$, one finds that the theoretical amount of Cd^{+2} needed to just start CdS pptn. is $3.7 \times 10^{-6}\,M$. According to the experimental evidence, however, $1 \times 10^{-4}\,M$ Cd^{+2} is actually needed.

If one postulates the existence of a tetrachlorocadmium(II) complex (since Cd^{+2} is known in other instances to coordinate four groups) then this might account for the difference between the theoretical and actual cadmium concns. needed for CdS pptn.:

$$CdCl_4^{-2} = Cd^{+2} + 4Cl^-$$

The discrepancy between the two $[Cd^{+2}]$ values must equal the tetrachloro complex concn. since that amount of cadmium is apparently tied up as metal ions unavailable for pptn. The equil. concns. are:

$[CdCl_4^{-2}] = 10^{-4} - 3.7 \times 10^{-6} \cong 9.6 \times 10^{-5}\,M$

$[Cl^-] \cong 0.90\,M$ (since little Cl^- is used in the small quantity of complex formed)

$[Cd^{+2}] = 3.7 \times 10^{-6}\,M$

The instability constant is then deducible:

$$K_{ins} = [Cd^{+2}][Cl^-]^4/[CdCl_4^{-2}] = 2.5 \times 10^{-2} \qquad (\textit{Ans.})$$

The relatively large constant shows this complex is not as stable as many that are known. Moderate dilution for example would upset the equilibrium enough to allow considerable cadmium to precipitate as the sulfide. One Cu^{+2}-Cd^{+2} separation is based on this idea; excess NaCl is shaken with the mixture, then H_2S added. Copper coordinates Cl^- quite weakly and the K_{SP} of CuS is very small, so CuS precipitates, but because $CdCl_4^{-2}$, and possibly other chloro complexes, are fairly stable (particularly in the presence of excess NaCl which forces the equilibrium toward the complex), CdS does not come down simultaneously. If the mixture is centrifuged and the centrate diluted, the equilibrium shifts to give more Cd^{+2} in solution and enough H_2S remains dissolved to now cause yellow CdS to appear—a characteristic color that is otherwise obscured by black CuS.

In calculations, one runs into difficulty if several different complexes form as $CdCl^+$ and $CdCl_3^-$. In such cases one generally does not have enough data to give more than an approximate solution to the problem.

3. ***K_{ins} from Partition Data.*** As mentioned in the section on physical equilibrium in Chapter 6, a solute distributes itself between two immiscible solvents when shaken with a mixture of them, in the ratio of its solubility in each. This ratio is called the partition, or distribution coefficient, K_D, and is established by measuring the concentration of solute in each layer by some simple means like color density matching or titration. If this equilibrium constant is previously experimentally determined and the concentration of solute in one solvent is known, then the concentration of the solute in the other solvent is simply obtained by arithmetic

$$K_D = \text{Concn. in solvent A/concn. in solvent B} \qquad (9\text{–}3)$$

This establishes a known value without the need of direct measurement, and if that solute is involved in a reaction with complex ions and means are available for finding the concentrations of other species in that solvent, one may be able to not only deduce what reaction is taking place and what complex is present, but also the instability of the complex. The general method has been useful in many investigations and qualitative separations such as those illustrated in tests 22–21, 22–34, etc.

Example 9–3. K_D for I_2 in CCl_4 and H_2O at 20° has been experimentally found to have a value of 80:

$$K_D = [I_{2(CCl_4)}]/[I_{2(aq)}] = 80 \qquad (9\text{–}4)$$

A soln. contg. a known amount of KI in water is shaken with a carbon tetrachloride soln. 0.060 M in I_2. Equil. of I_2 between the solvents is established after a time and one notices that the water layer has assumed an orange color. It is postulated that reaction takes place between I_2 and I^-, giving I_3^- to account for increased aqueous I_2 solub. and the color. In a certain expt., 0.1000 M I^- soln. is used and after being shaken with the iodine-carbon tetrachloride soln., a titration with standard sodium thiosulfate (see test 22–39) of the water layer shows that the concn. of I_3^- plus I_2 (both of which react with $S_2O_3^{-2}$ quantitatively) is 0.0028 *M*. In a later, similar expt. to gather data at different concns., when 0.080 *M* I_2 in CCl_4 was shaken with 0.1200 *M* KI aq. soln., the equil. water layer showed upon thiosulfate titration a concn. of I_3^- plus I_2 of 0.0042 *M*. From these data, easily gathered in the lab. in a few hours, one is able to prove that the postulated reaction is the correct one and he is also able to evaluate the instability constant for I_3^-.

Using the first set of data one assumes in the beginning that the CCl_4 soln. is sufficiently concd. in I_2 so that the quantity dissolving in the water will not alter the 0.06 *M* concn. much. This is a valid approx. since K_D was a comparatively large number.

$$[I_{2(aq)}] = [I_{2(CCl_4)}]/80 = 0.00075\ M$$

Since titration gave $[I_3^-] + [I_{2(aq)}] = 0.0028\ M$, the triiodide concn. can be found to be $0.0028 - 0.00075 \cong 0.002\ M$. (Notice that without the predetermined distribution constant this would not be possible, since thiosulfate titration does not differentiate between I_2 and I_3^-.) The original $[I^-]$ in the water layer is known (I^- is not sol. in CCl_4), since the original soln. was made 0.1000 *M* in I^- and from this and the triiodide value deduced above, one can find the equil. $[I^-]$.

Assuming the reaction in water to be

$$I^- + I_{2(aq)} = I_3^- \qquad (9\text{–}5)$$

one can determine the concn. of iodide remaining. Iodide was originally 0.1000 *M*, but if it reacted with some I_2 to form I_3^-, then at equil. $[I^-] + [I_3^-] = 0.1000\ M$. Since $[I_3^-] \cong 0.002\ M$, $[I^-] \cong 0.098\ M$. With the equil. concns. of all species known one can determine the instability constant of I_3^-, because its dissoc. is the opposite of its synthesis proposed in equation 9–5:

$$I_3^- = I_{2(aq)} + I^- \qquad (9\text{–}6)$$

$$K_{ins} = [I_{2(aq)}][I^-]/[I_3^-] \qquad (9\text{–}7)$$

$$= (0.00075)(0.098)/0.002 = 0.0368 \qquad (\textit{Ans.})$$

Using the second set of data mentioned above, one obtains almost the same for K_{ins}, and several other verifying experiments give the same closely checking results. One concludes from this that equation 9–5 correctly states the reaction and equation 9–6 is the statement for the complex ion dissociation. If one assumes on the other hand that the reaction was $I_2 + 2I^- = I_4^{-2}$, it is easy to show that K_{ins} is not a constant and the proposal is false.

Complex Ions and the Cu^{+2}–Cd^{+2} Separation

Further application of the type of calculations in the foregoing paragraphs is found in the copper-cadmium separations of the group 2 procedure. By one method, CN^- in excess is added to the ammoniacal solution of the metallic ions, converting $Cu(NH_3)_4^{+2}$ and $Cd(NH_3)_4^{+2}$ to $Cu(CN)_3^{-2}$ and $Cd(CN)_4^{-2}$. When H_2S is introduced into this mixture, only CdS precipitates, the instability constant of $Cd(CN)_4^{-2}$ alone being large enough to furnish sufficient metallic ion in solution for its sulfide solubility product constant to be exceeded. The K_{SP} of Cu_2S is very small itself (see Table 22–1), surprisingly enough about 10^{-22} times smaller than that of CdS, but because the K_{ins} of the tricyano copper(I) ion is also very small, Cu_2S is not precipitated, and thus separation of the two metallic ions is made. Example 9–4 shows how this is possible.

Example 9–4. A basic soln. is 10^{-2} *M* in both $Cd(CN)_4^{-2}$ and $Cu(CN)_3^{-2}$ and is also 0.1 *M* in CN^-. H_2S is bubbled in until the concn. of S^{-2} is 0.1 *M*. Show that CdS, but not Cu_2S, ppts., affording a means for the separation of metal ions.

Solving first for the cadmium concn. available from dissoc. of the complex:

$$K_{ins} = 1.4 \times 10^{-19} = [Cd^{+2}][CN^-]^4/[Cd(CN)_4^{-2}] = [Cd^{+2}](0.1)^4/10^{-2}$$

and

$$[Cd^{+2}] = 1.4 \times 10^{-17}\,M$$

The ion product $[Cd^{+2}][S^{-2}] = (1.4 \times 10^{-17})(0.1) = 1.4 \times 10^{-18}$. Since this is larger than the K_{SP} of CdS, which is 6×10^{-27}, CdS ppts. (*Ans.*)

The cuprous complex is more stable and less copper ion is available than cadmium:

$$K_{ins} = 5 \times 10^{-28} = [Cu^+][CN^-]^3/[Cu(CN)_3^{-2}] = [Cu^+](0.1)^3/10^{-2}$$

from which

$$[Cu^+] = 5 \times 10^{-27}\,M$$

The *I.P.* of cuprous sulfide = $(5 \times 10^{-27})^2(0.1) = 2.5 \times 10^{-54}$, which is smaller than the corresponding K_{SP} of 1.2×10^{-49}, so Cu_2S cannot ppt. (*Ans.*)

This and other ways of detecting these metals in the presence of each other are given in Chapter 16.

More Analytical Applications of Werner Ions

Separations of ions by complex formation and stabilization of certain oxidation states in solution are common applications of Werner ion chemistry. Two examples follow.

(1) From a mixture of chloride and iodide, only AgI is precipitated by addition of a solution containing a definite excess of NH_3 plus $Ag(NH_3)_2^+$. The K_{SP} of silver iodide being about 10^{-6} times smaller than the K_{SP} of silver chloride, it alone is exceeded and the single halide precipitates with the controlled Ag^+ concentration the complex releases to the solution.

(2) Cyanide may be determined quantitatively by titration with a standard silver nitrate solution. As long as CN^- is present, the reaction $Ag^+ + 2CN^- = Ag(CN)_2^-$ takes place. The silver complex is soluble and colorless. At the end point, however, the first excess Ag^+ gives a white turbidity due to the reaction,

$$Ag^+ + Ag(CN)_2^- = 2AgCN$$

Apropos of the first of these applications, another calculation should be illustrated.

Example 9-5. (*a*) If to a soln. 0.200 *M* in uncomplexed NH_3 and 0.020 *M* in $Ag(NH_3)_2^+$ is added an equal vol. of 0.002 *M* NaCl, will AgCl ppt.?

From the data given one can calc. the ion product of AgCl and compare it with the K_{SP} of AgCl as the condition for pptn. Each soln. dilutes the other:

$$K_{ins} = [Ag^+][NH_3]^2/[Ag(NH_3)_2^+] = 5.9 \times 10^{-8}$$
$$[Ag^+] = (5.9 \times 10^{-8})(0.010)/(0.100)^2 = 5.9 \times 10^{-8}\ M$$

Then, since $[Cl^-] = 10^{-3}\ M$, *I.P.* $= 5.9 \times 10^{-11}$, which is smaller than the K_{SP} 2.8×10^{-10}, so AgCl will not ppt. (*Ans.*)

(*b*) If instead of NaCl, 0.002 *M* NaI is added under the same conditions, can AgI form? The *I.P.* will be the same, 5.9×10^{-11}, since that part of the problem has not changed. The K_{SP} of AgI, however, is 8.5×10^{-17} and now *I.P.* $> K_{SP}$ so AgI ppts. (*Ans.*)

Something of a corollary to this problem is the following.

Example 9-6. Calc. the wt of AgBr that one can dissolve in 1 liter of 2 *M* NH_3.

Two ways will be illustrated in solving this one.

(*Method* 1.) Since the K_{SP} of AgBr is quite small, 5×10^{-13}, one may assume that little will dissolve even though the ammonia complex can form and its K_{ins} is 5.9×10^{-8}. Therefore the equil. $[NH_3] \simeq 2\ M$. The reaction being

$$AgBr + 2NH_3 = Ag(NH_3)_2^+ + Br^- \qquad (9\text{-}8)$$

it is seen that $[Br^-] \simeq [Ag(NH_3)_2^+]$ because the value of K_{ins} shows that the complex has reasonable stability and does not dissoc. to yield much free Ag^+ in soln. If these figures are substituted in the K_{SP} and K_{ins} expressions, the results are

$$K_{SP} = 5 \times 10^{-13} = [Ag^+][Br^-] = [Ag^+][Ag(NH_3)_2^+]$$
$$K_{ins} = 5.9 \times 10^{-8} = [Ag^+](2)^2/[Ag(NH_3)_2^+]$$

Solving each for $[Ag^+]$, the second equation gives

$$[Ag^+] = [Ag(NH_3)_2^+](1.5 \times 10^{-8})$$

and the first gives

$$[Ag^+] = 5 \times 10^{-13}/[Ag(NH_3)_2^+]$$

Because the soln. is homogeneous in $[Ag^+]$, these two equations are equal to each other, or $[Ag(NH_3)_2^+](1.5 \times 10^{-8}) = 5 \times 10^{-13}/[Ag(NH_3)_2^+]$. From this, one finds that the concn. of the complex is about 5.8×10^{-3} *M*. Since most of the sol. silver is in this form, this is approx. the molar solub. of AgBr in 2 *M* NH_3. The g dissolved are obtained by multiplying by 188, the mol. wt, and the salt = 1.1 g AgBr. (*Ans.*)

(*Method* 2.) If one writes the equil. constant for equation 9–8

$$K = [Ag(NH_3)_2^+][Br^-]/[NH_3]^2 \qquad (9\text{–}9)$$

he finds *K* can be evaluated in terms of the equil. constants discussed above:

$$K_{SP}/K_{ins} = [Ag^+][Br^-]/([Ag^+][NH_3]^2/[Ag(NH_3)_2^+])$$

and cancelling $[Ag^+]$ and rearranging gives equation 9–9.

$$K = K_{SP}/K_{ins} = 5 \times 10^{-13}/5.9 \times 10^{-8} = 8.5 \times 10^{-6}$$

By the same reasoning used above and having $[NH_3]$ given as 2 *M*,

$$8.5 \times 10^{-6} \cong [Ag(NH_3)_2^+]^2/(2)^2$$

from which the same answer as above is obtained.

PROBLEMS

1. Jackson P. Slipshod announces a new separation for Cu^{+2} and Cd^{+2}. "Make the solution 0.10 *M* with respect to uncomplexed NH_3 and 0.01 *M* with respect to $Cu(NH_3)_4^{+2}$ and $Cd(NH_3)_4^{+2}$. Sprinkle in enough Na_2S to make the $[S^{-2}]$ 10 ^{3} *M* momentarily. Because the K_{ins} of the Cd complex is larger than that of the Cu complex, only CdS precipitates under these conditions." Check the basis for the Slipshod approach.

2. A solution is 0.1 *M* in $[Ag(NH_3)_2^+]$ and additional NH_4OH gives the solution a *p*H of 10.0. Calculate the $[Ag^+]$.

3. Find the approximate concentrations of all species in a solution 0.1 *M* in $Ag(NH_3)_2NO_3$. (Ans. 0.1 *M* NO_3^-, 1.1×10^{-3} *M* Ag^+, 2.3×10^{-3} *M* NH_3, 0.1 *M* $Ag(NH_3)_2^+$.)

4. (*a*) What weight of AgBr can be dissolved in 100 ml of 6 *M* NH_4OH?

(*b*) What must the concentration of NH_4OH be if 1 g of AgBr is to dissolve in 100 ml.? (What is *M* of concd. NH_4OH in the lab.?)

5. If to 1 liter of the solution in problem 3 is added 1 mg of solid NaBr, will AgBr precipitate? Demonstrate with calculations.

6. How many ml of 0.05 *M* Ag^+ are needed to just complex 5 moles of CN^- as $Ag(CN)_2^-$?

7. A student has a residue of AgCl weighing 600 mg on filter paper in a funnel,

and washes it with 50 ml of 10^{-3} *M* NH_4OH solution. How many mg of AgCl are left after this treatment, assuming equilibrium was established in the process?

8. Predict whether or not:

(*a*) $Zn(CO_3)$ will dissolve in 1 M NH_4OH.

(*b*) $Hg(IO_3)_2$ will dissolve in 1 M Br^-.

9. A solution contains 0.15 moles of AgCl dissolved in 1 liter of 1 *M* NH_4OH. Tests with a sensitive reagent show the $[Ag^+]$ in the soln. is about 10^{-3} ppm (mg/liter). Show that this data leads to an approximation of the instability constant for $[Ag(NH_3)_2^+]$. (Ans. 3.0×10^{-8})

10. In Example 9–3, prove that the reaction equation is not $2I^- + I_2 = I_4^{-2}$. Explain.

11. Fifty ml of 0.1 *M* $[Ag(NH_3)_2^+]$ solution gives a white precipitate with a certain amount of NaCl. The same vol. of 0.1 *M* $[Ag(CN)_2^-]$ does not give a reaction with the same quantity of salt. Explain.

12. Could one devise an analytical separation of AgCl and AgBr on the basis of the former being more soluble in 2 *M* NH_4OH? Explain quantitatively.

13. Calculate the values for the equilibrium constants of

(*a*) $Al(OH)_3 + 6F^- = [AlF_6^{-3}] + 3\,OH^-$

(*b*) $Hg(IO_3)_2 + 4SCN^- = [Hg(SCN)_4^{-2}] + 2IO_3^-$

From the magnitudes of *K*, make qualitative statements concerning the solubility of these solids in the complexing agents. See Table 15–4 and the section on Al in Chapter 17.

14. Silver bromide has been precipitated in several flasks and a film of it still remains after soap and water washing. Rank NH_4OH, CN^-, and $S_2O_3^{-2}$ in order of decreasing effectiveness as glass cleaning solns. Explain.

15. By two methods, determine how many liters of 1 *M* NH_4OH are needed to dissolve 1.0 g of CuS by formation of tetraamine copper(II) ion.

16. In electroplating one wants the metal ion in low concentration so that plating will be slow and a hard plate will be produced, yet the solution must be heavily populated with ions so it conducts well. Explain why copper and cadmium are frequently plated from high *p*H cyanide baths. What would happen at low *p*H?

17. (*a*) One suggestion for washing off streets contaminated with radio cobalt ions is the use of dilute ammonium hydroxide. Explain.

(*b*) One "dip-type" cleaner used to remove Ag_2S from tarnished silver contained NaOH + NaCN, but was taken off the market because of its toxicity. What chemistry was behind its cleaning action?

18. You are asked to make some preliminary calculations on a reclamation process for washing unreacted AgCl from a special film using 1 *M* sodium thiosulfate. If each foot of this 35 mm film contains an average of 10.0 mg of AgCl, does it appear feasible that a liter of thiosulfate will treat several feet of film and give a solution concentrated enough in silver to make metal recovery easy?

19. In a student experiment it is found that 1.00 ml of 3.00 *M* NH_4OH just dissolves 230 mg of Ag_2CrO_4. Given the K_{SP} of that salt (*a*) find the equilibrium

$[NH_3]$, $[Ag(NH_3)_2^+]$, and $[CrO_4^{-2}]$ and (*b*) from the data, find K_{ins} for the complex. (Ans. (*a*) 0.228, 1.386, 0.693).

20. Solve the problem of Example 9–3 using the second set of data given there and compare answers.

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(Also see list at the end of Chapter 4)

10

EQUILIBRIUM AND HYDROLYSIS

The term hydrolysis is loosely applied to any reaction in which water is split or is otherwise a reactant. As used here, *hydrolysis will be taken to mean the reaction between water and salts to produce weak acids and/or weak bases.* Thus reactions of the type shown in equation 10–1 will not be considered, but those illustrated by equation 10–2 will be

$$4H_2O + 3Fe \overset{\Delta}{=} Fe_3O_4 + 4H_2 \qquad (10\text{–}1)$$

$$H_2O + NO_2^- = HNO_2 + OH^- \qquad (10\text{–}2)$$

The hydrolysis process is reversible and usually only a few per cent complete unless the products formed are very weak electrolytes. Again the mass action principle is operative and the methods of problem solving given in the previous four chapters will be used again. The equilibrium constant for the hydrolysis reactions is another limiting case of the general equilibrium constant and will be called the *hydrolysis constant* and abbreviated, K_H.

Determination of K_H

Hydrolysis constants are found experimentally by means that have been described in earlier chapters on equilibria. These procedures include (*a*) *measurement of solution* pH, which will be shown to bear a simple relationship to K_H (*b*) *conductivity data,* which includes evaluation of the individual contribution to total conductivity by each species present to find the equilibrium concentrations (this is not always easy to do), and (*c*) *partition measurements*, from which one may again get equilibrium information. Some of these methods will be explained or illustrated with problems.

Hydrolysis of Neutral Salts of Strong Acids and Strong Bases

Neutral* alkali and alkaline earth salts of HCl, HBr, HI, $HClO_4$, HNO_3, and H_2SO_4 are the main types considered under this heading. Possible reaction, taking KNO_3 as a typical salt, is

$$K^+ + NO_3^- + H_2O = K^+ + OH^- + H^+ + NO_3^- \qquad (10\text{–}3)$$

But since KOH is a strong base the ions composing it are not prone to combine in solution and the same can be said about the strong acid HNO_3. Therefore the dissociation of water is unaffected, since the salt ions do not react with either H^+ or OH^-. According to the discussion on water in Chapter 6, this means that the pH of such solutions will be 7 since H^+ and OH^- are produced in equal numbers and

$$[H^+][OH^-] = 1 \times 10^{-14} = K_W \qquad (10\text{–}4)$$

Neutral (strong) salts thus do not hydrolyze since they cannot shift the water equilibrium by a demand for hydrogen or hydroxyl ions.

Hydrolysis of Salts of Monvalent Weak Bases and Strong Acids

The only common weak base for purposes here is ammonium hydroxide and a typical example of a weak base-strong acid salt is NH_4NO_3. This gives ammonium and nitrate ions in solution, but only NH_4^+ is capable of reaction with water (*hydrolysis*) since it is a derivative of a weak electrolyte. The reactions are:

$$NH_4^+ + NO_3^- + H_2O = NH_4OH + H^+ + NO_3^- \qquad (10\text{–}5)$$

or

$$NH_4^+ + H_2O = NH_4OH + H^+\dagger \qquad (10\text{–}6)$$

The equilibrium expression in equation 10–6 will not include water, as its concentration is regarded as unchanging, so the hydrolysis constant becomes

$$K_H = [NH_4OH][H^+]/[NH_4^+] \qquad (10\text{–}7)$$

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* A *neutral salt* implies here a strong acid-strong base derivative giving a solution pH of 7. *Acid salts* like $NaHSO_4$ give acidic aqueous solutions.

† This can also be written

$$\begin{array}{c} NH_4^+ + H_2O \;=\; NH_3 + H_3O^+ \\ \text{Acid 1} + \text{base 2} = \text{Base 1} + \text{acid 2} \end{array} \qquad (10\text{–}10)$$

to show the role of H_2O in functioning as a Brönsted base. This representation of hydrolysis equations will not be used for the reasons given in the footnote on p. 86 though it is to be understood that the bases NH_3 and H_2O compete for the proton.

K_H is related to K_W and K_B, since by multiplying both numerator and denominator by $[OH^-]$ (a method used before in example 8–7), one obtains

$$K_H = [NH_4OH][H^+][OH^-]/[NH_4^+][OH^-] \qquad (10\text{–}8)$$

which can be regrouped:

$$K_H = [H^+][OH^-] \cdot [NH_4OH]/[NH_4^+][OH^-] \qquad (10\text{–}9)$$

The first part is K_W, the water constant, and the second is $1/K_B$, the reciprocal of the ionization constant of the weak base. Substituting these known quantities into equation 10–7, one obtains a general equation for this type salt.

$$\boldsymbol{K_H = K_W/K_B} \qquad \mathbf{(10\text{–}11)}$$

From equation 10–6 it can be seen that since one ammonium hydroxide is formed for each proton $[NH_4OH] = [H^+]$. Further, the salt in solution is 100% ionic and if each ion directly derived from it is considered to be always capable of independent action, then for monovalent ions [salt] = [each ion]. If one assumes that hydrolysis is only a few per cent complete, as it is with usual dilutions of most salts, then the original salt concentration will not change much due to reaction of the cation with water, so

$$K_H \cong [H^+]^2/[NH_4^+], \qquad \text{or } [H^+] \cong (K_H[NH_4^+])^{\frac{1}{2}}$$

If c is the molar concentration of the cation, a general formula can be developed for finding the hydrogen ion concentration of a solution of a salt whose cation is derived from a weak base:

$$[H^+] \cong (K_H \cdot c)^{\frac{1}{2}} \cong [(K_W/K_B)c]^{\frac{1}{2}} \qquad \mathbf{(10\text{–}12)}$$

The $[H^+]$ varies directly with the square root of the concentration of salt but inversely with the square root of the ionization constant of the weak base. The simple relationships between pH, c, and K_H immediately suggest that constants of this type are determinable by merely measuring solution pH and vice versa.

Example 10–1. 50 ml of 0.2 M HNO_3 are titrated with 50 ml of 0.2 M NH_4OH. Calculate the $[H^+]$ and pH at the equivalence point. What indicator would one use? What is the % hydrol. of NH_4^+ in the final soln.?

At the end point one has a soln. 0.1 M in NH_4^+, since NH_4NO_3 is the product formed and the reacting solns. dil. each other. From (10–12):

$$[H^+] \cong [(1 \times 10^{-14}/1.8 \times 10^{-5})(0.1)]^{\frac{1}{2}} \cong 7.5 \times 10^{-6}\,M \qquad (\textit{Ans.})$$

From the definition of pH in Chapter 6

$$pH = -\log[H^+] = \log 10^6 - \log 7.5 \cong 5.1 \qquad (\textit{Ans.})$$

From Appendix A17, one notes that bromcresol green and methyl red have ranges which include *p*H 5.1. (*Ans.*)

The degree of hydrol. is that fract. of the salt ion that has reacted with water. The percent of hydrol. is 100 times that. The amount of NH_4^+ hydrol. is equal to the amount of H^+ formed, therefore

$$(7.5 \times 10^{-6}/0.1)(100\%) = 7.5 \times 10^{-3}\% \text{ hydrol.} \qquad (Ans.)$$

Hydrolysis of Salts of Monovalent Weak Acids and Strong Bases

Salts of this type are formed by reaction of alkali and alkaline earth bases with the weak acids listed in Appendix A20. The remarks and procedures in the section just previous will apply again, with a few modifications.

KAc, potassium acetate, is a weak acid-strong base salt. K^+ does not react with H_2O, as shown in equation 10–3. The Ac^-, however, does hydrolyze because the product, HAc, is a weak acid. The reactions are:

$$K^+ + Ac^- + H_2O = K^+ + HAc + OH^-$$

or

$$Ac^- + H_2O = HAc + OH^- \qquad (10\text{–}13)$$

and the hydrolysis constant is

$$K_H = [HAc][OH^-]/[Ac^-] \qquad (10\text{–}14)$$

Again K_H is related to equilibrium constants of the substances present, in this instance to K_W, and K_A. By multiplying the right side of equation 10–14 by the factor $[H^+]/[H^+]$ and separating the result into two parts one gets:

$$K_H = [H^+][OH^-][HAc]/[H^+][Ac^-]$$

The first product is recognized as K_W, the water constant, and the second as $1/K_A$, the reciprocal of the weak acid's ionization constant. Substitution gives

$$K_H = K_W/K_A \qquad \mathbf{(10\text{–}15)}$$

From equation 10–13 it can be seen that $[HAc] \simeq [OH^-]$ since these are produced in mole for mole ratio. If hydrolysis proceeds only slightly, as is the general rule, then $[Ac^-]$ will be about the same at equilibrium as it was initially and

$$K_H \cong [OH^-]^2/[Ac^-] \qquad \text{or } [OH^-] \cong (K_H[Ac^-])^{\frac{1}{2}}$$

If again c represents the molar concentration of the ion hydrolyzing (this time the anion), then

$$[OH^-] \cong (K_H \cdot c)^{\frac{1}{2}} \cong [(K_W/K_A)c]^{\frac{1}{2}} \qquad (10\text{–}16)$$

or, solving for $[H^+]$ which is more frequently desired,

$$[OH^-] = K_W/[H^+] \cong [(K_W/K_A)c]^{\frac{1}{2}}$$

from which by squaring both sides, rearranging, and solving for $[H^+]$ one gets

$$[H^+] \cong (K_W K_A/c)^{\frac{1}{2}} \tag{10–17}$$

The acidity of these solutions thus varies directly with the square root of the ionization constant of the acid and inversely with the square root of the salt concentration.

By using equation 10–17 the following tables were prepared to show these trends.

TABLE 10–1. *p*H OF VARIOUS NaAc SOLUTIONS

NaAc *M*	*p*H
0.5	9.2
0.2	9.0
0.1	8.9
0.01	8.4

TABLE 10–2. *p*H OF 0.1 *M* SOLUTIONS OF VARIOUS Na^+ SALTS OF WEAK ACIDS

Na^+ Salt	K_A of Weak Acid	*p*H of 0.1 *M* Solutions
$NaClO_2$	1.1×10^{-2}	7.48
NaOCN	2.0×10^{-4}	8.35
NaOCl	3.2×10^{-8}	10.35
NaCN	4.0×10^{-10}	11.20

Why Hydrolysis Stops

One may wonder why the hydrolysis reaction usually stops far short of 100% conversion. Considering cyanide ion as a typical example, the three equilibria concerned are,

(*a*) $H_2O = H^+ + OH^-$
(*b*) $H_2O + CN^- = HCN + OH^-$
(*c*) $HCN = H^+ + CN^-$

As (*b*) proceeds to the right, H^+ is used from H_2O to make HCN. This means that (*a*) is displaced toward the right to furnish the H^+ for (*b*) and maintain the water equilibrium. Both (*a*) and (*b*) produce OH^-, however, whose increased concentration keeps (*b*) from going far by the common ion effect. The equilibrium $[H^+]$ satisfies both K_W for (*a*) and K_A for (*c*). It is thus the build up of OH^- in this instance (and build up of H^+ in the case of salts of weak bases and strong acids) that acts to limit the extent of hydrolysis. If the acid formed is exceedingly little dissociated, the equilibrium $[H^+]$ will be very small, so $[OH^-]$ can be large and hydrolysis will approach a maximum. Such is demonstrated in the section on sulfides.

Hydrolysis of Salts of Monovalent Weak Acids and Weak Bases

This is a more complex situation than those already presented, since both cation and anion hydrolyze. Two cases will be described.

1. Hydrolysis if $K_A \cong K_B$. If the ionization constants of the weak acid and weak base that are formed are about equal, derivation of a formula for finding $[H^+]$ is easy. Ammonium acetate is a standard example of this case since $K_A \cong K_B \cong 1.8 \times 10^{-5}$.

$$H_2O + NH_4^+ + Ac^- = HAc + NH_4OH \qquad (10\text{–}18)$$
$$\text{Acid 1} + \text{base 2} = \text{Acid 2} + \text{base 1}$$

The hydrolysis constant for equation 10–18 is

$$K_H = [HAc][NH_4OH]/[NH_4^+][Ac^-] \qquad (10\text{–}19)$$

If the right side of equation 10–19 is multiplied by the factors $[H^+]/[H^+]$ and $[OH^-]/[OH^-]$, the terms can be separated into three products whose values are known:

$$K_H = ([HAc]/[H^+][Ac^-])([NH_4OH]/[NH_4^+][OH^-])([H^+][OH^-])$$
$$= (1/K_A)(1/K_B)(K_W) \text{ or}$$
$$\mathbf{K_H = K_W/K_AK_B} \qquad \mathbf{(10\text{–}20)}$$

The $[H^+]$ in such solutions may be found as follows. If in equation 10–18 we let $x = [HAc] = [NH_4OH]$, since the weak acid and base form in equimolar quantities, then if c is the original molar concentration of the salt, $c - x$ will be the quantity of salt ions at equilibrium:

$$H_2O + \underset{c-x}{NH_4^+} + \underset{c-x}{Ac^-} = \underset{x}{HAc} + \underset{x}{NH_4OH}$$

and

$$K_H = x \cdot x/(c - x)(c - x) \text{ or}$$
$$x/(c - x) = K_H^{\frac{1}{2}} \qquad (10\text{–}21)$$

The H^+ in the solution comes from HAc,

$$K_A = [H^+][Ac^-]/[HAc]$$

and solving for $[H^+]$ in terms of c and x, one gets

$$[H^+] = K_A(x/c - x)$$

This is simplified by relating the term in the parenthesis to equation 10–21 giving

$$[H^+] = K_AK_H^{\frac{1}{2}} \qquad (10\text{–}22)$$

and relating K_H to the system's individual equalibrium constants by equation 10–20, the final statement is

$$[H^+] = (K_W K_A/K_B)^{\frac{1}{2}} \qquad (10\text{–}23)$$

Thus for salts of this type, the acidity is a direct function of the square root of the acid constant and an inverse function of the square root of the base constant. By solving for $[OH^-]$ in similar sequence one obtains

$$[OH^-] = K_B K_H^{\frac{1}{2}} = (K_W K_B/K_A)^{\frac{1}{2}} \qquad (10\text{–}24)$$

Inspection of equation 10–23 brings forth several useful ideas:

(*a*) The *p*H is independent of solution concentration. Term *c* is absent.

(*b*) If $K_A = K_B$, $[H^+] = K_W^{\frac{1}{2}} = [OH^-] = 10^{-7}\ M$, and the solution *p*H = 7.00

(*c*) If $K_A > K_B$, *p*H < 7

(*d*) If $K_A < K_B$, *p*H > 7

2. *Hydrolysis if $K_A \neq K_B$.* Equations 10–23 and 10–24 were derived for the case in which the two salt ions hydrolyze in equal amounts because $K_A \cong K_B$. A more general case is one in which the ion constants are not equal, as ammonium metaborate, NH_4BO_2; $K_B = 1.8 \times 10^{-5}$, $K_A = 6.0 \times 10^{-10}$. Borate ion is expected to hydrolyze more than ammonium ion because it results in formation of a weaker electrolyte.

$$H_2O + NH_4^+ + BO_2^- = HBO_2 + NH_4OH \qquad (10\text{–}25)$$

This can lead to a fairly complex calculation in which three simultaneous equations are needed to find three unknowns, $[H^+]$, $[HBO_2]$, and $[NH_4OH]$. The problem is simplified, however, by the fact that as BO_2^- hydrolyzes, $H_2O + BO_2^- = HBO_2 + OH^-$, it produces hydroxyl ions that are used by ammonium ions, $NH_4^+ + OH^- = NH_4OH$. The latter reaction causes both NH_4^+ and BO_2^- to hydrolyze more than would otherwise be possible and the net reaction is essentially only that shown in equation 10-25 with $[NH_4OH] \cong [HBO_2]$. This effect is more significant than differences in ionization constants of the weak acid and base, and equation 10–23 can be used again.

A typical problem follows.

Example 10 2. HQ is a weak monoprotic organic acid that has just been synthesized. When NH_3 is added and the soln. concd., the pure ammonium salt NH_4Q crystallizes. A 0.10 *M* soln. of the salt is found to have a *p*H of 9.20 by *p*H meter measurement. Calculate the ioniz. const. K_A for HQ.

One assumes that equation 10–23 can be used with its previously stated approximations. Substitution of $6.3 \times 10^{-10}\,M$ H^+ (which corresponds to a pH of 9.2), 1×10^{-14} for K_W and 1.8×10^{-5} for K_B, one gets

$$6.3 \times 10^{-10} = (1 \times 10^{-14} K_A / 1.8 \times 10^{-5})^{\frac{1}{2}}$$

Squaring both sides and solving for K_A gives 7.2×10^{-10} (*Ans.*)
Thus HQ is an acid similar to HCN in strength.

Hydrolysis of Salts of Polyprotic Acids

Included in this category are salts like Na_2CO_3, $NaHCO_3$, Na_2S, NaHS, Na_3PO_4, NaH_2PO_4, Na_2HPO_4, $NaHSO_4$, etc. Problems concerning them can be difficult to solve since several simultaneous reactions of ionization and hydrolysis take place. Such calculations are considered in quantitative analysis and only a few easier examples will be illustrated.

1. ***Bisulfates.*** The bisulfate cases are not as complicated as they first appear because the acid strength of HSO_4^- dominates the reactions. For example, if one wishes to find the pH of a solution of ammonium bisulfate, the reactions are

$$NH_4^+ + H_2O = NH_4OH + H^+ \text{ and}$$
$$HSO_4^- = H^+ + SO_4^{-2}$$

K_A for HSO_4^- is 1.2×10^{-2}, which means that the dissociation of bisulfate is considerable. The prime effect of H^+ from this source is to send the NH_4^+ hydrolysis reaction to the left by the common ion principle. This actually occurs to such a degree that NH_4^+ hydrolysis is considered negligible and the pH is simply calculated as in example 7–11.

2. ***Carbonates.*** These cases are more involved since several sets of equations must be carried.

(*a*) *Dissociations*

$$1.\ H_2CO_3 = H^+ + HCO_3^- \tag{10-26}$$
$$2.\ HCO_3^- = H^+ + CO_3^{-2} \tag{10-27}$$

(*b*) *Ionization constants*

$$K_{A\text{-}1} = [H^+][HCO_3^-]/[H_2CO_3] = 4.16 \times 10^{-7} \tag{10-28}$$
$$K_{A\text{-}2} = [H^+][CO_3^{-2}]/[HCO_3^-] = 4.84 \times 10^{-11} \tag{10-29}$$

(*c*) *Hydrolyses*

$$1.\ HCO_3^- + H_2O = H_2CO_3 + OH^- \tag{10-30}$$
$$2.\ CO_3^{-2} + H_2O = HCO_3^- + OH^- \tag{10-31}$$

(*d*) *Hydrolysis constants*

$$K_{H\text{-}1} = [H_2CO_3][OH^-]/[HCO_3^-] = K_W/K_{A\text{-}1} \tag{10-32}$$
$$K_{H\text{-}2} = [HCO_3^-][OH^-]/[CO_3^{-2}] = K_W/K_{A\text{-}2} \tag{10-33}$$

Equation 10–31 is the dominant force among the reactions. This means that CO_3^{-2} is the ion which hydrolyzes more than any other and K_{H-2} will be larger than K_{H-1}. Equation 10–33, therefore, is the most important one in the calculation of the acid or base strength of the solution. Letting c = molar concentration of the salt $\cong [CO_3^{-2}]$ at equilibrium, then it has already been shown how the following could be derived:

$$[OH^-] = [(K_W/K_{A-2})c]^{\frac{1}{2}}$$

$$[H^+] = (K_W K_{A-2}/c)^{\frac{1}{2}} \qquad \mathbf{(10\text{–}34)}$$

*3. **Bicarbonates.*** The HCO_3^- ion is ampholytic and so is capable of giving or accepting protons:

$$HCO_3^- + OH^- = CO_3^{-2} + H_2O \quad \text{(acts as acid)} \qquad (10\text{–}35)$$

$$HCO_3^- + H_2O = H_2CO_3 + OH^- \quad \text{(acts as base)} \qquad (10\text{–}36)$$

The $[OH^-]$ at equilibrium will be the difference between that produced in equation 10–36 and that used in equation 10–35. The quantity produced is equal to $[H_2CO_3]$ (since OH^- and H_2CO_3 are formed mole for mole in equation 10–36 and the quantity used is equal to $[CO_3^{-2}]$ (since for every mole of OH^- disappearing in equation 10–35 a mole of CO_3^{-2} is formed), so one may write

$$[OH^-] = [H_2CO_3] - [CO_3^{-2}] \qquad (10\text{–}37)$$

To evaluate this one refers to equations 10–28 and 10–29, which relate the carbonic acid and carbonate concentrations to terms that are known, and equation 10–37 becomes

$$[OH^-] = ([H^+][HCO_3^-]/K_{A-1}) - (K_{A-2}[HCO_3^-]/[H^+]) \qquad (10\text{–}38)$$

At equilibrium $[HCO_3^-]$ is about the same as it was originally when the bicarbonate salt solution was prepared, and this term is again called c. Using the identity $[OH^-] = K_W/[H^+]$ and solving equation 10–38 for the hydrogen ion concentration gives

$$[H^+] = [(K_W K_{A-1}/c) + K_{A-1}K_{A-2}]^{\frac{1}{2}} \qquad (10\text{–}39)$$

If c is not too small, $K_W K_{A-1}/c$ becomes insignificant and the formula for usual problem solving is reduced to

$$[H^+] = (K_{A-1}K_{A-2})^{\frac{1}{2}} \qquad \mathbf{(10\text{–}40)}$$

*4. **Dihydrogen Orthophosphates and Monohydrogen Orthophosphates.*** By derivations similar to those above it can be shown that for solutions of salts like NaH_2PO_4, the hydrogen ion concentration is shown by equation 10–40 and for solutions of salts like Na_2HPO_4, the hydrogen ion concentration is given by

$$[H^+] = (K_{A-2}K_{A-3})^{\frac{1}{2}} \qquad \mathbf{(10\text{–}41)}$$

where the K's are respectively the second and third ionization constants of orthophosphoric acid, H_3PO_4. It is again noteworthy that pH is independent of concentration and this is true for the usual range of laboratory concentrations, say between 1 and 10^{-3} M, as one can prove from actual measurements.

Example 10–3. The pH of a 0.10 M soln. of Sorensen's salt, KH_2PO_4, is found to be 4.66 using the pH meter. Show that equation 10–40, which takes cognizance of the ampholytic character of $H_2PO_4^-$ is the correct interpretation of this case, whereas equation 10–17, which was derived for simple anion hydrol. only, does not account for the experimental data.

Two reactions take place, hydrol. and dissoc.

$$H_2PO_4^- + H_2O = H_3PO_4 + OH^-$$

$$H_2PO_4^- = H^+ + HPO_4^{-2}$$

Using equation 10–40 and the table values for the first two ioniz. constants, both reactions are taken into consideration:

$$[H^+] = [(7.5 \times 10^{-3})(6.2 \times 10^{-8})]^{\frac{1}{2}} = 2.2 \times 10^{-5}\ M$$

from which pH = 4.7, in good agreement with the measured value. (*Ans.*)

Using equation 10–17 and $K_{A\text{-}1}$

$$[H^+] = [(1 \times 10^{-14})(7.5 \times 10^{-3})/0.10]^{\frac{1}{2}} = 2.7 \times 10^{-8}\ M$$

from which pH = 7.6, which shows that one oversimplified if he assumed that equation 10–17 could be used indiscriminately. (*Ans.*)

5. *Sulfides.* These salts are important for at least two reasons: the first being that because $K_{A\text{-}1}$ for H_2S is so small, hydrolysis uniquely approaches 100%, and the second, that since sulfides are so common in qualitative testing it is logical to study their behavior from as many viewpoints as possible.

The sulfide ion from a salt like Na_2S will react with water to give a basic solution containing bisulfide ions which hydrolyze further to give hydrogen sulfide and more hydroxyl ions:

$$\mathbf{1.}\quad \mathbf{S^{-2} + H_2O = HS^- + OH^-} \qquad \mathbf{(10\text{–}42)}$$

$$2.\quad HS^- + H_2O = H_2S_{(aq)} + OH^- \qquad (10\text{–}43)$$

If we evaluate the hydrolysis constant for each step,

$$K_{H\text{-}1} = [HS^-][OH^-]/[S^{-2}] = K_W/K_{A\text{-}2} = \mathbf{0.077} \qquad \mathbf{(10\text{–}44)}$$

$$K_{H\text{-}2} = [H_2S][OH^-]/[HS^-] = K_W/K_{A\text{-}1} = 1.0 \times 10^{-7} \qquad (10\text{–}45)$$

The magnitude of $K_{H\text{-}1}$ is evidence that equation 10–42 is the important reaction, and since $K_{H\text{-}2}$ is insignificant by comparison, *it is permissible to calculate the* pH *of sulfide salt solutions via equation* 10–44 *alone.*

Example 10–4. Calculate the degree of hydrol. and *p*H of 0.1 *M* K_2S.

Since from the magnitude of K_{H-1} we suspect extensive hydrol. it is not wise to use equation 10–17, which applies only when hydrol. is low. If α is the degree of hydrol. then the equil. concns. are

$$\underset{0.1\,(1-\alpha)}{S^{-2}} + H_2O \rightleftharpoons \underset{0.1\alpha}{HS^-} + \underset{0.1\alpha}{OH^-}$$

If α is large, $(1 - \alpha) \neq 1$, and equation 10–44 becomes,

$$K_{H-1} = 0.077 = (0.1\,\alpha)(0.1\,\alpha)/0.1(1 - \alpha) = 0.1\,\alpha^2/1 - \alpha \qquad (10\text{–}46)$$

Solving the quadratic gives $\alpha = 0.57$. (*Ans.*) If one takes equation 10–43 also into account, the hydrol. is better than 57% complete!

From this, $[OH^-] \cong (0.1)(0.57) = 0.057\ M$, corresponding to a *p*H of almost 12.8! (*Ans.*)

Hydrolysis and Sulfide Solubility

The fact that sulfide ion hydrolysis is always extensive has a pronounced effect upon the solubility of difficultly soluble metallic sulfides. The products of hydrolysis are often complex and exact problem solving is not attempted. For a metal sulfide, MS, the solution may contain species like $M(H_2O)_2(H_2S)_2^{+2}$, $M(H_2O)_2(HS)_2$, $M(OH)_2 \cdot MS$, MH_2SHS^+, etc. If the sulfide is quite soluble, its solutions are almost as basic as NaOH solutions of comparable molarity, and hydroxides as well as sulfides and mixed compounds such as M(OH)SH have been shown to be present. Occasionally the hydroxide of a metal or its hydrolysis products formed in basic solution are less soluble than its sulfide, so they form instead of the sulfide when S^{-2} is added. Despite the possibility of nonstoichiometric reactions, one can make some reasonable estimates concerning the effect of sulfide hydrolysis upon the solubility of sulfides.

Example 10–5. Calculate the solub. of FeS, first from K_{SP} alone, then by correcting for S^{-2} hydrol.

The first reaction to consider is

$$FeS = \underset{x}{Fe^{+2}} + \underset{x}{S^{-2}}$$

$$K_{SP} = 4 \times 10^{-17} = x \cdot x, \text{ and } x = 6.3 \times 10^{-9}\ M$$

$$= [Fe^{+2}] = [S^{-2}] = \text{molar solub. of FeS} \quad (\textit{Ans.})$$

However, S^{-2} is reacting with water which displaces both the following and the preceding reactions to the right, meaning that more FeS than calcd. goes into soln.:

$$S^{-2} + H_2O = HS^+ + OH^-$$

K_{H-1} for this process has been shown in equation 10–44 to have a value of 0.077. The $[S^{-2}]$ from the calcn. just performed is 6.3×10^{-9}, and since one can assume it to be about 60% hydrol., the $[OH^-]$ should be $\simeq 3.6 \times 10^{-9}\ M$. This value is lower, however, than that contributed by pure water, namely $10^{-7}\ M$, and is negligible compared with it. One may conclude that the soln. pH will be close to 7 and use $10^{-7}\ M\ OH^-$ for further calcn.:

$$K_{H-1} = 0.077 = [HS^-](10^{-7})/[S^{-2}]$$
$$[S^{-2}] = [HS^-](1.3 \times 10^{-6})$$

This sulfide concn. is in equil. with solid FeS and the hydrol. process as well. Substituting into the K_{SP} expression $[Fe^{+2}]$ can be found:

$$K_{SP} = 4 \times 10^{-17} = [Fe^{+2}][HS^-](1.3 \times 10^{-6})$$

FeS originally dissolved to give $[Fe^{+2}] = [S^{-2}]$, but since most of the sulfide hydrol. yielding bisulfide, at equil. $[Fe^{+2}] \simeq [HS^-]$, which we will let be equal to y:

$$K_{SP} = 4 \times 10^{-17} = y \cdot y(1.3 \times 10^{-6})$$

And from this, y, which is the $[Fe^{+2}]$ and also the molar solub. of FeS, is $5.6 \times 10^{-6}\ M$. (*Ans.*)

The solubility is thus greater than originally found by a factor of over 1000 and is actually even more than that since the further hydrolysis by HS^- was not considered nor was the possibility of hydrolysis of the metal ion, a subject treated briefly below.

The last equation can be generalized for very slightly soluble sulfides of the type MS in which the first sulfide hydrolysis step is the important one:

$$\text{Molar solubility of MS} = [M^{+2}] \cong [HS^-] = (K_{SP}/1.3 \times 10^{-6})^{\frac{1}{2}} \qquad (10\text{–}47)$$

Hydrolysis of Metallic Ions

Metallic ions in solution are more or less hydrated (Table 4–1) and may react with the water molecules closely associated with them. This effect was neglected in the calculations of the preceding paragraphs. Again, however, probably only the first hydrolysis step is important. Ferrous ion may react as follows:

$$Fe^{+2} + 6H_2O = Fe(H_2O)_6^{+2} = Fe(H_2O)_5OH^+ + H^+ \qquad (10\text{–}48)$$

The last three substances are in equilibrium involving two equations, one being the water equilibrium, the other expressing the base strength of the pentaaquohydroxy iron(II) ion:

$$H_2O = H^+ + OH^-$$
$$Fe(H_2O)_5OH^+ + H_2O = Fe(H_2O)_6^{+2} + OH^- \qquad (10\text{–}49)$$

From K_B for equation 10–49, and K_W, one is able to evaluate K_H for equation 10–48 by referring to equation 10–11:

$$K_H = K_W/K_B = [Fe(H_2O)_5OH^+][H^+]/[Fe(H_2O)_6^{+2}] \qquad (10\text{–}50)$$

Inspection of equations 10–48 and 10–50 shows that K_H is also K_A for $Fe(H_2O)_6^{+2}$. (Why?) Generally speaking not much is done with calculations of this type because data for determining the extent of hydration of ions in solution and equilibrium constants for their reactions are difficult to obtain. A method for approximating some values is shown in the next example.

Example 10–6. A 0.1 M soln. of $FeCl_2$ is prepd. and the pH, as ascertained with a pH meter, is 5.50. Show that K_B for equation 10–49 and K_H from equation 10–50 can be approximated.

If $pH = 5.50$, then $[H^+] = 3.2 \times 10^{-6}\ M \cong [Fe(H_2O)_5OH^+]$, since these ions are formed in equimolar quantity. If one assumes that equation 10–48 does not proceed far (pH is not too low) then the final and initial concns. of the hexaaquo iron(II) ion will be about the same or, at equil., $[Fe(H_2O)_6^{+2}] \cong 0.1\ M$. From equation 10–50

$$K_H = 1 \times 10^{-14}/K_B \cong (3.2 \times 10^{-6})(3.2 \times 10^{-6})/0.1$$

from which $K_H \cong 10^{-10}$ and $K_B \cong 10^{-4}$. (*Ans.*)

The low magnitude of K_H shows that the increase in solubility of FeS over that calculated from the K_{SP} depends much more upon the hydrolysis of S^{-2} than the hydrolysis of Fe^{+2}.

Some Industrial Applications of Hydrolysis

There are a number of valuable hydrolysis applications used in chemical industry, and chemical engineers have improved processes by applying equilibrium principles to their study. In the organic field these include the saponification of fats to make soap and glycerine, of starches to make sugars, of unsaturated hydrocarbons to make oxygenated products, and of sulfonates and halides to give hydroxylated derivatives. Inorganic examples include the hydrolysis of aluminum sulfate giving aluminum hydroxide, which clarifies water as it settles, and cheap detergent additives like Na_2SiO_3, Na_3PO_4, $Na_2CO_3 \cdot 10H_2O$, and $Na_2B_4O_7 \cdot 10H_2O$, whose alkalinity due to hydrolysis aids in removing grease.

PROBLEMS

1. Calculate the pH of 0.3 M solutions of KCl, NH_4Cl, $NaNO_2$, and NH_4NO_2.
2. Calculate the pH of 0.2 M solutions of Na_2S, Na_2HPO_4 NaH_2PO_4, Na_2CO_3, $NaHCO_3$, and $NaHSO_4$.
3. Calculate the solubility of ZnS from K_{SP} data alone, then by also considering sulfide hydrolysis. Explain the reason for the difference.
4. A solution is 0.01 M in Zn^{+2} and finely powdered K_2S is sprinkled in.

Assuming rapid solution and mixing, does $Zn(OH)_2$ or ZnS precipitate first? See Table 17–6.

5. Calculate the pH of 0.04 M K_2HPO_4 by simple hydrolysis treatment, then by equation 10–41. Explain the reason for the difference.

6. Explain as fully as you can this statement: "Beryllium ion is quite strongly hydrolyzed, hence it is impossible to prepare Be salts of weak acids, such as $Be(CN)_2$."

7. A 0.1 M solution of NaOCl is tested with a few drops of thymolphthalein and the color produced is a very faint blue (before NaOCl bleaches the indicator). Show that this simple experiment allows one to approximate K_A for HClO.

8. The pH of MAc is 6.0. Find K_B for the soluble weak base, MOH.

9. 0.8 M NaAc is about 0.005% hydrolyzed. Use this fact to calculate the solution's pH.

10. One has a weak acid that is known to be one of these: HAc, HClO, HF, or HNO_2. The pH of an 0.1 M solution of its ammonium salt is 6.3. Which acid is it?

11. Look over the discussion of fluoride ion in Chapter 22 and note the two equilibria given there. What effect will the second one have on a calculation concerning F^- hydrolysis? Explain.

12. A piece of zinc is placed in a hot Na_3PO_4 solution. It soon becomes covered with bubbles that are continuously being produced and expelled. When this gas is analyzed it is found to burn with oxygen to form only water. Explain with equations.

13. (*a*) Explain this statement: "evidence that HX is a weak acid is the observation that a dilute solution of its potassium salt is basic."

(*b*) It is observed that any dilution of KBr has a pH of 7.00, as has any dilution of NH_4Ac. Explain each case and point out differences that exist between them despite the fact that both salts have the same pH.

(*c*) $CaCO_3$ added to a solution of $FeCl_3$ causes $Fe(OH)_3$ to precipitate. Explain.

14. One has 1 M aqueous solutions of high purity NaCN, Na_2CO_3, Na_2S, and NaAc. Over two of the solutions very distinct odors are noted. Explain fully with the aid of equations and any quantitative data needed.

15. Explain why MgS cannot be dissolved and recrystallized from water. How could one prepare MgS?

16. Explain with equations how hydrolysis of both cation and anion affect the solubility of $FePO_4$.

17. Add two more columns to Tables 10–1 and 10–2 for % hydrolysis and K_H. Calculate these values. How do they vary with concentration and K_A?

18. (*a*) The pH of 0.2 M $Zn(NO_3)_2$ solution is found to be about 5.0. Find a value of K_H for

$$[Zn(H_2O)_4^{+2}] = [Zn(H_2O)_3OH^+] + H^+$$

(*b*) The pH of 0.1 M aluminum nitrate solution is 2.90. Calculate a value for the hydrolysis constant (assume only the first step is important) of

$$[Al(H_2O)_6^{+3}] = H^+ + [Al(H_2O)_5OH^{+2}] \quad (\textit{Ans.}\ (b)\ 1.6 \times 10^{-5})$$

19. Give a derivation of equation 10–34 using specific ions from equations 10–31 and 10–33.

20. Show in a stepwise derivation that equation 10–39 is applicable to finding $[H^+]$ in NaH_2PO_4 solutions.

21. The hydrolysis constant for the first hydrolytic reaction of $(Cu(H_2O)_4^{+2}]$ is about 10^{-10}. Calculate the *p*H of 0.1 *M* $CuBr_2$.

22. If α = degree of hydrolysis and c = molar concentration of the salt, prove the following:

(*a*) For NaAc, $\alpha = (K_W/K_A \cdot c)^{\frac{1}{2}}$

(*b*) For NH_4Cl, $\alpha = (K_W/K_B \cdot c)^{\frac{1}{2}}$

23. Show: (*a*) For NaAc, $pOH = -\frac{1}{2}\log(K_W \cdot c/K_A)$

(*b*) For NH_4Cl, $pH = -\frac{1}{2}\log(K_W \cdot c/K_B)$

24. Jackson Slipshod is watching a student in the quantitative analysis laboratory titrate a vinegar sample with standard NaOH. After thinking about it a few minutes J.S. announces that no accuracy is possible, since as NaAc forms it produces more titratable HAc by hydrolysis, therefore, one can never reach the end point and hence the only practical titrations are those between strong acids and strong bases. Has J.S. revolutionized thinking in this field?

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11

EQUILIBRIUM AND REDOX: ELECTROCHEMICAL CELLS

In Chapter 1, *oxidation* was described as a process of electron loss and *reduction* as a process of electron gain. The oxidizing agent was defined as the substance gaining electrons and the reducing agent as the one donating electrons. In the first chemistry course one usually has an experiment to perform in which various metals are put in acids, and in solutions of each others' ions, to determine by evidence of reaction the relative ability of the metals to be oxidized (dissolved) or reduced (plated out). An "*activity series*" of metals is then arranged with the most active reductant at the top, the least active reductant at the bottom, and hydrogen somewhere between. In other words, a rough measure of ability to give and take electrons was effected. It should be possible with more subtle methods to make these and other redox relationships quantitative, so that one has data upon which to predict both the feasibility of reactions in unfamiliar mixtures and the extent to which the processes might go. These methods are known.

Standard State, the H-Electrode and E° Values

Measurements are made on properly constituted *electrochemical cells* (Fig. 11–1) with reduction going on in one compartment and oxidation going on in the other. An electrode is in each compartment, and each is connected in an external circuit through a *potentiometer* or sensitive *volt meter* that gives the difference in *potential* (also called *voltage*, *electromotive force*, or simply *emf*) between the two electrodes. This difference is a measure of the combined abilities of the reductant at one electrode (in one *half cell*) to give electrons (which travel through the external circuit) and the oxidant, which takes electrons at the other electrode (other half cell). It is necessary to compile data on such oxidations and reductions under definite reference conditions. These conditions of ionic concentration, gas pressure, and temperature are called *standard state*, and for purposes here will mean ions at unit molarity, gases at 1 atmosphere pressure,* and a temperature of 25 C.

A *redox reaction* is made up of two *half reactions*. Thus, with iron and acid

$$\mathrm{Fe} + 2\mathrm{H}^+ = \mathrm{Fe}^{+2} + H_2$$

the *over-all reaction* can be thought of as the sum of two half reactions. Iron metal is oxidized, gives electrons, and is the reductant:

$$\mathrm{Fe} = \mathrm{Fe}^{+2} + 2e^-$$

Hydrogen ions are reduced, take electrons and act as the oxidant:

$$2e^- + 2\mathrm{H}^+ = H_2$$

It has not been possible to accurately evaluate *absolute potentials* of half cells so they have all been referred to a *standard reference electrode* and their potentials compared to it. Since the whole cell voltage is the difference of the two half cell potentials, only relative potential values need be used in calculations anyhow. The reference electrode is the so called *standard hydrogen electrode* and it is arbitrarily assigned zero potential. That is, for this reaction,

$$H_2 = 2\mathrm{H}^+ + 2e^-$$

the *standard state voltage*, E°, is 0.00 volts. Any other half cell at standard state when coupled with the standard hydrogen cell will have a potential different from this reference cell. Since all conditions are standard and the H-cell contribution to the measured whole cell voltage is zero, then the experimentally measured voltage is E° for the other half cell. In this way appendix Table A18 was developed. (Some values, not experimentally obtainable, were calculated by thermodynamical methods.)

The H-cell consists of a solution of HCl containing H^+ at *unit activity*† into which is placed a *platinum electrode* coated with finely divided platinum

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* In thermodynamics the more exact measurements use unit *activity* of ions (molal concentrations corrected for interionic attractions), and unit *fugacity* for gases (pressures corrected for gas law imperfections). No attempt will be made to include these refinements.

† This is 1.2 molar HCl in which, due to interionic forces, H^+ has an effective concentration of only 1 *M*. Omitting the activity correction for simplicity, we will consider the solution to be simply 1 *M* in both HCl and H^+.

called *platinum black*. H_2 gas at 1 atm. pressure bubbles over this catalytically active surface.

Some First Considerations in Setting Up Cells

If one hooks up a hydrogen half cell with a half cell containing a copper electrode dipping into a 1 *M* cupric sulfate solution, and the two electrodes are connected by wires through a sensitive voltmeter, the voltmeter will record the whole cell potential. The laboratory set up might resemble the accompanying figure.

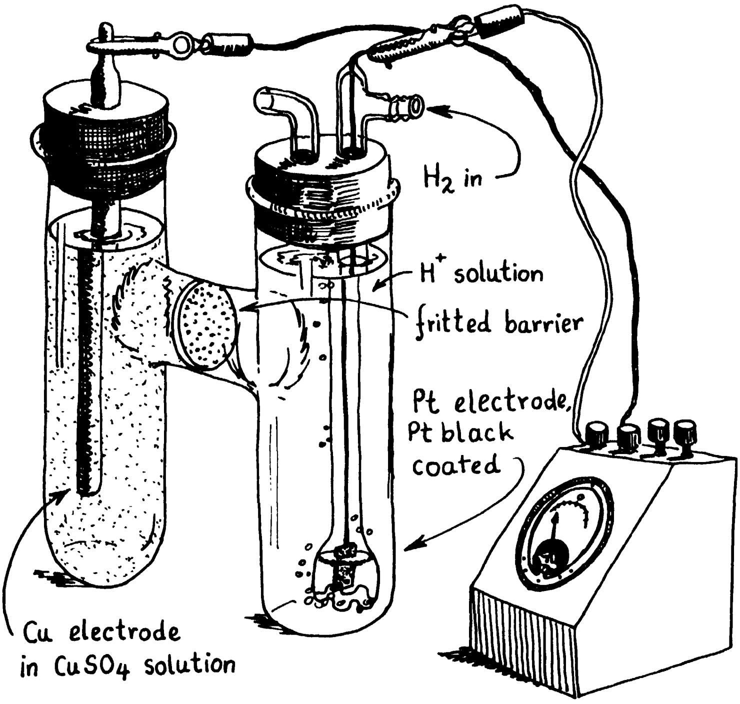

FIG. 11–1. An electrochemical cell consisting of a H_2–H^+ half cell and a Cu–Cu^{+2} half cell.

The cell compartments are separated by a fritted glass disk that permits only slow mixing of the solutions, although ions can travel through this barrier. With all concentrations at standard state, the initial voltage developed is — 0.34 volts* and one has determined the $E°$ value for the

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* The convention for signs will be discussed in later paragraphs.

copper half cell. If after running for a period of time, samples are withdrawn from each compartment and analyzed, it is found that $[H^+]$ has increased and $[Cu^{+2}]$ decreased. The half cell reactions must have been

$$H_2 = 2H^+ + 2e^- \qquad (11\text{–}1)$$

$$2e^- + Cu^{+2} = Cu \qquad (11\text{–}2)$$

Adding these gives the over-all or whole cell reaction:

$$H_2 + Cu^{+2} + 2e^- = Cu + 2H^+ + 2e^-$$

From reactions in equations 11–1 and 11–2 one notes that electrons are furnished by the hydrogen half cell, since increase in acidity also means production of electrons, and electrons are used by the copper half cell. Thus H_2 is oxidized by the oxidizing agent, Cu^{+2}, and Cu^{+2} is reduced by the reducing agent, H_2. It will be characteristic of all cells described to be *reversible*.

One convention adopted here is that *the electric current in the external circuit is considered to be a stream of electrons, and since electrons are negative, they are attracted by the positive electrode and repelled by the negative electrode.* Across the wire in this cell, electrons travel from the Pt (−) electrode to the Cu (+) electrode. The convention to be followed with regard to naming the electrodes will be this: *the anode is the electrode at which oxidation takes place* (Pt, in this case) and *the cathode is the electrode at which reduction occurs* (Cu, here). In this cell, if electrons are leaving the hydrogen side and hydrogen ions are appearing, then negative ions (SO_4^{-2} in this example) must migrate through the permeable barrier from the other compartment. Electrical neutrality is simultaneously maintained in the copper half cell since as copper ions plate out, the excess of negative sulfate ions leave for the other side.

If ions are not free to move through a barrier separating the cell compartments no current will flow because of the internal resistance. This can be demonstrated by putting the half cells in two beakers. If a wire connects the electrodes, no reaction is noted. If a U-shaped tube filled with a concentrated solution of an inert electrolyte like KCl is inverted to connect the half cells with a *salt bridge* that can furnish cations or anions on demand, current flows. If the apparatus of Fig. 11–1 were modified in this way Cl^- would go to the hydrogen side and K^+ would go to the copper side to balance the ionic changes brought on by electron movement.

It is not convenient to draw pictures of cells for each discussion so abbreviated notation is used. The cell above may be represented as

$$\mathbf{Pt},\ H^+(1\ M),\ H_2\ (1\ \text{atm})||Cu^{+2}\ (1\ M),\ \mathbf{Cu}$$

The left side indicates that a platinum electrode is in contact with 1 molar hydrogen ions and hydrogen gas at 1 atmosphere pressure. Commas are used to separate different phases. The two vertical lines signify a contact between the two cells, as described above, which goes under the general name of a *liquid junction.* The right-hand side shows the other half cell written in reverse order, cupric ions at 1 molar concentration and a copper metal electrode.

Types of Half Cells

Many different redox reactions have been studied and some elaborate laboratory methods used, but only four types of half cells are important.

(1) A metallic element electrode in contact with a solution of its ions. This was illustrated above with **Cu,** Cu^{+2}.

(2) An inert metallic element electrode in contact with a nonmetal and a solution of the latter's ions. This was also illustrated with **Pt,** H_2, and H^+.

(3) An inert metallic element electrode in contact with a solution containing both the ions of a reduced and an oxidized state of some element. An example of this is a platinum electrode dipping into a solution containing both cupric and cuprous ions: **Pt,** Cu^{+2}, Cu^+.

(4) A metallic element electrode in contact with a mixture of a slightly soluble salt of that metal and a solution of common anion: **Ag, AgCl,** Cl^-.

One may also classify cells according to those with liquid junctions (usually a salt bridge) and those without liquid junctions. The latter operate with a common electrolyte in both compartments. Those cells with liquid junctions in refined treatment involve calculations for voltage loss due to different ionic mobilities, resulting in a resistance at the junctions, but as the losses are in the order of 10^{-2} volts or less they will not be mentioned further.

Oxidation Potential Conventions

Tables of half-cell reactions and potentials are given in Appendixes A18 and A19. The organization and conventions of this compilation are listed below.

(1) Each half-cell equation is written with the reduced form on the left side and the oxidized form and electron(s) on the right. This means that each is written as an oxidation, hence the name "Table of Standard Oxidation Potentials".

(2) Standard state for our purposes will mean ions at 1 molar concentration, gases at 1 atmosphere pressure, and a temperature of 25 C. Voltage developed under these conditions is the E° value.

(3) If the reduced state in a certain half reaction in acid solution is

better able to give electrons than is H_2 in the standard hydrogen half cell, then that half cell is a better reductant than H_2 and will be listed above H. The most powerful reducing agent (Li) is at the top of the table and poorer ones listed in order under it. The E° values for their reactions to proceed as written are positive. Thus the reaction $Li = Li^+ + e^-$ has more tendency to occur than $H_2 = 2H^+ + 2e^-$.

(4) If the oxidized state of a given half reaction is better able to take electrons than is H^+, then it is a better oxidizing agent than H^+ and will be listed beneath H in the table. The strongest one is at the bottom. The E° values for their reactions to proceed as written are negative since they tend to go in the reverse direction. For example, from the half reaction, $2F^- = F_2 + 2e^-$, the large negative E° value means that F_2 is a much better oxidant than H^+, so if the fluorine and hydrogen half cells were coupled, the cell reaction would be $H_2 + F_2 = 2H^+ + 2F^-$.

Conventions and Steps in emf Calculations

Once the table of oxidation potentials is established, one has available a condensed collection of data from which he can predict the feasibility of literally thousands of redox reactions, calculate the voltage developed by the various combinations, determine their equilibrium constants, and find other values of both theoretical and practical interest. The following steps in solving typical problems involving the reaction equation and theoretical emf of the whole cell at standard state are helpful.

(1) A whole redox reaction is made up of two half reactions. Some of the latter are given in Tables A18 and A19. The two half reactions involved in the problem are copied from the table as they appear there. The form always is *Reduced state = Oxidized state + electron(s)*, E°.

(2) It is obvious that the two half reactions comprising the whole redox reaction under examination cannot proceed from left to right as copied from the table because both are given as oxidations and one must be a reduction.

To determine the direction in which each half reaction proceeds, so that their addition will give the correct overall redox reaction, one inspects the E° values he has copied from the tables. The half cell with the larger E°, regardless of sign, will be the one that dictates the reaction direction since its larger E° indicates superior driving force for electron transfer. When one determines in which direction that half-cell reaction proceeds, he knows that the direction of the other half cell is the opposite.

(3) We will follow the convention that a positive voltage indicates a spontaneous reaction, and if one is talking about a redox reaction that takes place, he then automatically means E° for the overall reaction is positive. Since the overall E° is found by addition of the half cell E°'s,

it follows that one will always arrange for the half cell with the larger E° to go in a direction in which the sign of E° is positive. All half reactions and E° signs are reversible.*

(4) Consequently if the half cell with the larger value has a negative sign on E° as copied from the table, one reverses the reaction direction and the sign. If on the other hand that reaction has a positive E° as copied from the table, it proceeds spontaneously from left to right as written. Once this direction is determined, the other half reaction goes in the opposite direction, since one half reaction must produce electrons and the other must use electrons. Reversing any half reaction from that given in the tables automatically reverses the sign of E°.

Another way of thinking about this is as follows. Of the two half reactions as copied from the table, the one that is more positive, or less negative, will be the one that is proceeding as written, since by our conventions it will be spontaneous compared to the other half cell. The latter is reversed together with its potential. This is equivalent to the stepwise reasoning given above.

(5) If different numbers of electrons appear in the two half reactions, the reactions are mutually balanced by multiplying all chemical terms by minimum integers to give the same number of electrons in each half cell. *This multiplication does not affect E° values* since they still refer to substance at unit activity.

(6) After determining the electron balance, the direction of each half reaction, and the sign of the E°'s the two reactions are added to give the over-all cell reaction and the E°'s are algebraically added to give E°_{1-2}, *the over-all cell voltage at standard state for half cells* 1 *and* 2. This is the initial theoretical voltage (the actual may be smaller due to internal cell resistances) and the combined equation is the spontaneous reaction that takes place at that time. Since the larger E° value was by these conventions made positive, E°_{1-2} *will always be positive* and a positive emf will signify spontaneous reaction. One has no way of predicting, however, how fast this reaction will proceed, what catalyst might be needed, or how long it takes to attain equilibrium; but one can say that a positive E°_{1-2} means that the reaction is thermodynamically feasible. Qualitatively, a large E°_{1-2} means that a reaction will probably proceed rapidly and will continue nearly to completion; a small E°_{1-2} signifies the opposite.

(7) Since both of the half reactions in a given problem are written as oxidations, but one must be changed to a reduction to get the spontaneous over-all reaction (and since the change of a half reaction's direction means a change in sign of E°), it follows that (*a*) if the E°'s have the same sign as copied from the table, E°_{1-2} will be their difference, and (*b*) if the E°'s

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* A few listed are only theoretically reversible, but this will not affect our calculations.

have different signs in the table, E°_{1-2} will be their sum. E°_{1-2}will be positive in either case.

Some Simple emf Problems

A few examples of determining the over-all reaction equation and emf at standard state are given in order to illustrate the preceding general directions.

Example 11–1. For a cell consisting of a nickel bar in a 1 *M* $NiSO_4$ soln. and a zinc bar in 1 *M* $ZnSO_4$, find the spontaneous redox reaction and the theoretical cell voltage at stand. state.

From Table A18 the half reactions are:

$$\begin{array}{ll} Zn = Zn^{+2} + 2e^- & E^\circ = 0.76 \\ Ni = Ni^{+2} + 2e^- & E^\circ = 0.25 \end{array}$$

Both E°'s are positive, which means that both half reactions are spontaneous as written. Zinc metal, however, with its larger potential is a better red. agent than is nickel metal, and so electrons will leave the zinc electrode, as zinc metal goes into soln. and will travel to the nickel electrode where nickel ions are forced to accept them and nickel metal plates out. The zinc reaction dictates the direction of the cell reaction, and, since as written it goes left to right with a + E°, the entire nickel reaction is reversed including the E° sign. Addn. gives the overall reaction and voltage:

$$\begin{array}{rll} Zn \rightleftharpoons Zn^{+2} + 2e^- & E^\circ = 0.76 & \\ \text{Rev.}\ \ (Ni \leftrightharpoons Ni^{+2} + 2e^- & \underline{E^\circ = -0.25)} & \\ \hline Zn + Ni^{+2} + 2e^- = Zn^{+2} + Ni + 2e^- & E^\circ_{1-2} = 0.51 & (\mathit{Ans.}) \end{array}$$

This reaction proceeds if the electrodes are connected until equilibrium is established, and the voltage would gradually decrease to zero. One can deduce further that, since electrons leave zinc, that electrode must be negative, and, since an oxidation is taking place there, it is the anode. Electrons go to the positive nickel cathode where a reduction takes place. Since $[Zn^{+2}]$ is increasing in the zinc side, SO_4^{-2} must migrate from the nickel side to maintain electrical neutrality. For each SO_4^{-2} leaving, however, one Ni^{+2} is being reduced to nickel metal, and so there is ionic balance in the nickel compartment.

Example 11–2. One wishes to devise a test for iodide by ox. $2I^-$ to I_2, since the appearance of the brown color of iodine (or its dark-blue reaction product if starch is present) would be good visual evidence of a positive test. Would nitric acid (in going to NO + H_2O) be a feasible ox. agent to produce iodine with all substances at stand. state?

The half reactions from appendix A18 are:

$$\begin{array}{ll} 2I^- = I_2 + 2e^- & E^\circ = -0.54 \\ NO + 2H_2O = 4H^+ + NO_3^- + 3e^- & E^\circ = -0.96 \end{array}$$

Since both E°'s are negative it means that neither reaction tends to go as written but that both are spontaneous in proceeding from right to left. The stronger, as indicated by the larger E° value, is the reaction in which nitrate reacts as an oxidant by using electrons, and this is the reaction that will be spontaneous. Because our convention is to make the E° of the spontaneous reaction positive, the nitrate reaction will go in a reverse direction to that written in the table, and its E° will then be positive. The iodide reaction is forced to go as written, since NO_3^- is a stronger ox. agent than I_2. The least common multiple of the numbers of electrons in the half reactions is 6, so the iodide equation is multiplied by 3 and the nitrate equation by 2 to obtain electron balance. E° values are not multiplied. Addn. then gives the over-all reaction (in which the electrons cancel) as well as its voltage at stand. state. Since E°_{1-2} is of moderate magnitude, and is positive for the combined spontaneous reaction as written, one may answer the problem's question that it is feasible at these concns. to oxidize iodide to iodine with nitric acid:

$$\begin{array}{rl}
6I^- \rightleftharpoons 3I_2 + 6e^- & E^\circ = -0.54 \\
\text{Rev. } (2NO + 4H_2O \leftrightharpoons 8H^+ + 2NO_3^- + 6e^- & E^\circ = 0.96) \\
\hline
6I^- + 8H^+ + 2NO_3 = 3I_2 + 2NO + 4H_2O & E^\circ_{1-2} = 0.42 \quad (\textit{Ans.})
\end{array}$$

Example 11–3. One wishes to devise a test for formic acid, HCO_2H, which is known to give bubbles of CO_2 when oxidized in acid soln. Will hydrogen peroxide, in being reduced to water, be strong enough to do this in 1 M H^+ soln. at stand. state? What potential could theoretically be developed?

The half reactions from Table A18 are

$$\begin{array}{rl}
HCO_2H_{(aq)}{}^* = CO_2 + 2H^+ + 2e^- & E^\circ = 0.20 \\
2H_2O = H_2O_2 + 2H^+ + 2e^- & E^\circ = -1.77
\end{array}$$

The larger E° value is from the hydrogen peroxide half cell so it will be spontaneous in the direction in which E° is positive, namely the reverse of that given in the table and copied above. This means that with H_2O_2 taking electrons in its role as oxidizing agent, HCO_2H must give electrons as a reducing agent and its reaction goes as written:

$$\begin{array}{rl}
HCO_2H_{(aq)} \rightleftharpoons CO_2 + 2H^+ + 2e^- & E^\circ = 0.20 \\
\text{Rev. } (2H_2O \leftrightharpoons H_2O_2 + 2H^+ + 2e^- & E^\circ = 1.77) \\
\hline
HCO_2H_{(aq)} + H_2O_2 = 2H_2O + CO_2 & E^\circ_{1-2} = 1.97 \quad (\textit{Ans.})
\end{array}$$

The large E°_{1-2} shows that the reaction oxidizing the acid would be quantitative.

The Calomel Electrode

While the hydrogen electrode is the zero potential standard it is an experimentally aggravating device to use. The platinum black surface must be uniform, clean, and continually resaturated with H_2. Its use is

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* (aq) means an aqueous solution of the substance, to differentiate it from its anhydrous form.

limited to solutions that do not contain substances that are reduced by H_2 or oxidized by H^+. Volatile substances like CO_2 must also not be a part of the reaction, since they are removed with the H_2 excess. Even at best, the H-electrode may be erratic and slow in its response.

For these reasons, other standard reference electrodes have been developed. One of the best is the *normal calomel electrode* which gets its name from the common name for Hg_2Cl_2, calomel, and also contains 1 *M* KCl and mercury metal. These electrodes are easy to prepare and give repetitive results. The reaction is,

$$2Hg + 2Cl^- = Hg_2Cl_2 + 2e^- \qquad E^\circ = -\,0.28$$

A typical design is shown in Fig. 11–2.

The Nernst Equation and Equilibrium Constants

Reactions and cell emf's so far considered have been for processes at standard state. The question naturally arises as to what happens at other concentrations and temperatures? A formula developed in 1889 by *W. Nernst* supplies the relationships:

$$E_{\text{cell}} = E^\circ_{1-2} - (1.98 \times 10^{-4}T/n) \log Q \qquad (11\text{–}3)$$

E_{cell} = the emf of the whole cell at conditions other than standard, E°_{1-2} = emf of the whole cell at standard state as already illustrated, T = the absolute temperature at which the cell operates, n = the number of electrons involved in either the oxidation or reduction when the half cells are mutually balanced, and Q = the product of molar concentrations (more accurately, activities) of reaction products divided by the product of molar concentrations of reactants, each term raised to a power corresponding to its coefficient in the balanced over-all equation. Thus Q has the form of the equilibrium constant of the reaction, but the terms are usually for experimental conditions, not equilibrium conditions. If the temperature is 25 C,

$$\mathbf{E_{\text{cell}} = E^\circ_{1-2} - (0.059/n) \log Q} \qquad \mathbf{(11\text{–}4)}$$

All calculations henceforth will be made for 25° unless otherwise specified.

If the terms comprising Q are equilibrium concentrations, then $Q = K$, the equilibrium constant. At equilibrium, however, there is no net electron or ion transfer, so the cell voltage is $E_{\text{cell}} = 0$ and the Nernst equation can be solved for the equilibrium constant:

$$0 = E^\circ_{1-2} - (0.059/n) \log K$$

so

$$E^\circ_{1-2} = (0.059/n) \log K \qquad (11\text{–}5)$$

and

$$\log K = nE^\circ_{1-2}/0.059 \qquad (11\text{-}6)$$

therefore

$$K = 10^{17nE^\circ_{1-2}} \qquad \mathbf{(11\text{-}7)}$$

By proper combination of half cells and the measurement of concentrations and whole cell voltage, many equilibrium constants of interest like K_{SP}, K_H, K_A, K_B, and K_{ins} have been determined. Knowing these constants, the chemist can use equation 11–6 in reverse fashion to determine equilibrium concentrations, such as [H$^+$] (therefore the *p*H of an unknown solution) or the quantities of other ions left after reactions, and also to see whether or not redox reactions are at least theoretically quantitative.

Example 11–4. In the Reinsch test described in Chapter 16, one displaces "heavy metals" from soln. by using a superior reducing agent, copper metal. A copper wire is placed in a small amount of 10^{-3} *M* Hg^{+2} soln. Calculate *K* for the reaction and the equil. [Hg^{+2}]. From this information comment on the test sensitivity.

The half reactions to look up from Table A18 will be those concerning Cu—Cu^{+2} and Hg—Hg^{+2}, and when written and the mercury reaction and its E° sign reversed, we have:

$$\begin{array}{rl}
\mathrm{Cu} \rightleftarrows \mathrm{Cu}^{+2} + 2e^- & E^\circ = -0.34 \\
\underline{\text{Rev. }(\mathrm{Hg} \leftrightarrows \mathrm{Hg}^{+2} + 2e^-} & \underline{E^\circ = 0.85)} \\
\mathrm{Cu} + \mathrm{Hg}^{+2} = \mathrm{Cu}^{+2} + \mathrm{Hg} & E^\circ_{1-2} = 0.51
\end{array}$$

The desired reaction, that is, displacement of the heavy metal by copper metal, is the spontaneous one, proceeding with a respectable voltage.

K is calculated using equation 11–7:

$$K = [\mathrm{Cu}^{+2}]/[\mathrm{Hg}^{+2}] = 10^{(17)(2)(0.51)} = 2.0 \times 10^{17} \qquad (\textit{Ans.})$$

As explained in the discussion on K_{SP} in Chapter 8, the concns. of solids are regarded as constants and do not appear. Since *K* is large, we may assume the reaction is quant. and that almost all the Hg has been reduced, making the equil. [Cu^{+2}] $\simeq 10^{-3}$ *M* (since 1 Cu^{+2} if formed for every Hg^{+2} disappearing and 10^{-3} *M* was the orig. [Hg^{+2}]). Therefore,

$$K = [\mathrm{Cu}^{+2}]/[\mathrm{Hg}^{+2}] = 2.0 \times 10^{17} = 10^{-3}/[\mathrm{Hg}^{+2}]$$

from which [Hg^{+2}] at equil. = 5.0×10^{-21} *M* (*Ans.*)
The reduction of Hg^{+2} is essentially complete, and the test is a sensitive one, capable of detecting as little mercury for which one can visibly find displacement evidence.

Deductions from the Magnitude of E°_{1-2}

If E°_{1-2} of a particular cell is near zero volts by virtue of selection of half cells whose spontaneous reaction potentials are about alike, the standard state concentrations are close to those of equilibrium. Relatively minor concentration changes can, by the mass action effect, cause the spontaneous reaction to be the reverse of the one originally found. This is the case when E_{cell} comes out to be negative. On the other hand, if E°_{1-2} is large, then K is large and there is no likelihood of equilibrium conditions being reached until some concentrations become vanishingly small.

Electrochemical Determination of *p*H

One way of finding the *p*H of a solution is to couple a calomel and a hydrogen cell as shown in Fig. 11-2.

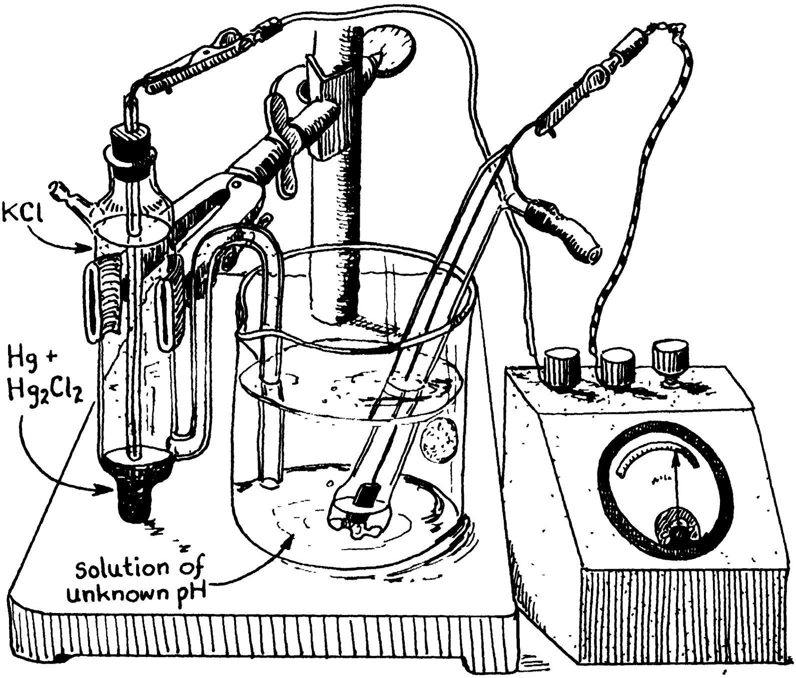


FIG. 11-2. A calomel-hydrogen electrode system for finding *p*H.

The cell data is

$$\text{Rev. }(2\text{Hg} + 2\text{Cl}^- \leftrightharpoons \text{Hg}_2\text{Cl}_2 + 2e^- \qquad E^\circ = 0.28)$$

$$\frac{H_2 \rightleftharpoons 2\text{H}^+ + 2e^-}{H_2 + \text{Hg}_2\text{Cl}_2 = 2\text{Hg} + 2\text{Cl}^- + 2\text{H}^+} \qquad \frac{E^\circ = 0.00}{E^\circ_{1-2} = 0.28}$$

If everything but $[H^+]$ (the solution's unknown acid strength) is at standard state, then Q simply is $[H^+]^2$. The Nernst equation then is

$$E_{cell} = 0.28 - (0.059/2)\log[H^+]^2$$

which reduces to

$$E_{cell} = 0.28 + 0.059\,pH \qquad (11\text{-}8)$$

or

$$pH = 17(E_{cell} - 0.28) \qquad (11\text{-}9)$$

This means that if one measures the experimental cell voltage, the solution's pH is found in one simple calculation. If the solution contains a weak acid such as HY at known concentration c, the pH can be converted to $[H^+]$, which will be equal to $[Y^-]$ and the ionization constant follows since all other terms are known in $K_A = [H^+][Y^-]/c$. See example 7-5.

Electrochemical Determination of K_{SP} and K_{ins}

Correct construction can result in a cell for which the observed cell voltage is a measure of the solubility of a slightly soluble salt or of the dissociation of a complex ion. This is done by arranging the other cell components to be solids or ions at standard state, so they conveniently cancel from the calculations.

One can also calculate equilibrium constants from E° values given in Table A18 without making any lab measurements. This is illustrated in example 11-8. See also problems 7 and 8 on p. 186.

Example 11-5. Calculate the instability constant of $Ag(S_2O_3)_2^{-3}$ from data given in Table A18.

Since

$$K_{ins} = [Ag^+][S_2O_3^{-2}]^2/[Ag(S_2O_3)_2^{-3}]$$

the cell data selected must include these three ions. The two half reactions which do this are

$$\begin{array}{ll} \text{Rev. }(Ag \rightleftharpoons Ag^+ + e^- & E^\circ = +0.80) \\ \underline{Ag + 2S_2O_3^{-2} \rightleftharpoons Ag(S_2O_3)_2^{-3} + e^-} & \underline{E^\circ = -0.01} \\ Ag^+ + Ag + 2S_2O_3^{-2} = Ag + Ag(S_2O_3)_2^{-3} & E^\circ_{1-2} = \quad 0.79 \end{array}$$

The solid Ag terms are constant, so

$$Q = [Ag(S_2O_3)_2^{-3}]/[Ag^+][S_2O_3^{-2}]^2 = 1/K_{ins}$$

At equil. E_{cell} is zero so the Nernst equation is

$$0 = 0.79 - (0.059/1)\log(1/K_{ins}) = 0.79 + 0.059\log K_{ins}$$

from which we get an answer checking with the value from Table 15-1:

$$K_{ins} = 10^{-13.4} = 4 \times 10^{-14} \qquad (Ans.)$$

Equilibrium Constants for Redox Half Reactions

By methods already given, one can calculate the equilibrium constant associated with each of the half reactions given in the tables. It is but a simple step further to combine any two of them to get K_{eq} for a whole reaction.

Example 11–6. One has the cell Pb, $Pb^{+2}||Cu^{+2}$, Cu. Find K for each side, and K_{eq} for the spontaneous over-all reaction.

From Table A18 we copy

$$\mathrm{Pb} = \mathrm{Pb}^{+2} + 2e^- \qquad E^\circ = 0.126$$
$$\mathrm{Cu} = \mathrm{Cu}^{+2} + 2e^- \qquad E^\circ = -0.337$$

By equation **11-7**, the equil. const. for the Pb half reaction is

$$K_{\mathrm{Pb}} = [\mathrm{Pb}^{+2}]/[\mathrm{Pb}] = [\mathrm{Pb}^{+2}] = 10^{(2)(17)(0.126)} = 1.95 \times 10^4$$

and for the Cu reaction is $K_{\mathrm{Cu}} = [\mathrm{Cu}^{+2}]/[\mathrm{Cu}] = [\mathrm{Cu}^{+2}] = 10^{(2)(17)(-0.337)}$
$= 3.55 \times 10^{-12}$ (*Ans.*)

If one now combines the two half reactions from Table A18 as shown in previous problems, he finds the spontaneous reaction and over-all voltage is

$$\mathrm{Cu}^{+2} + \mathrm{Pb} = \mathrm{Pb}^{+2} + \mathrm{Cu} \qquad E^\circ_{1-2} = 0.463$$

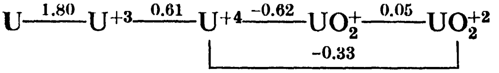
and the equil. const. is $[\mathrm{Pb}^{+2}]/[\mathrm{Cu}^{+2}]$. But these values were just calcd., so $K_{eq} = 1.95 \times 10^4/3.55 \times 10^{-12} = 5.50 \times 10^{15}$ (*Ans.*)

The result can be checked by the method used to find K_{eq} in previous problems.

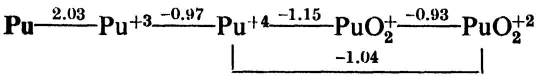
Potential Diagrams

Speculation on reaction feasibilities can be facilitated by what are known as *potential diagrams*. These are condensed versions of half-cell data that summarize potentials and valence states of a given element. By means of the diagrams one can quickly see how interconversions among the valence states can be effected. In addition, if one knows something of the chemistry of these states, he has an excellent summary of the element's chemistry.

Suppose we are interested in devising a separation between uranium and plutonium, and cell study in acid solution has given us data to construct the following diagrams. (Reading right to left, the E° values are reversed.)



$$\mathrm{U}\overset{1.80}{\text{———}}\mathrm{U}^{+3}\overset{0.61}{\text{———}}\underbrace{\mathrm{U}^{+4}\overset{-0.62}{\text{———}}\mathrm{UO}_2^{+}\overset{0.05}{\text{———}}\mathrm{UO}_2^{+2}}_{-0.33}$$



$$\mathrm{Pu}\overset{2.03}{\text{———}}\mathrm{Pu}^{+3}\overset{-0.97}{\text{———}}\underbrace{\mathrm{Pu}^{+4}\overset{-1.15}{\text{———}}\mathrm{PuO}_2^{+}\overset{-0.93}{\text{———}}\mathrm{PuO}_2^{+2}}_{-1.04}$$

Two separation paths seem worth investigating. Given a solution of U^{+3} and Pu^{+3}, a very mild oxidizing agent can oxidize $U^{+3} \rightarrow U^{+4}$, a spontaneous reaction anyhow, whereas Pu^{+3} does not go to Pu^{+4} because its large negative potential means it is difficult to oxidize to the + 4 state. If an anion, X^-, is then added, such that UX_4 is say insoluble, volatile, or perhaps extractable in some immiscible solvent, while PuX_3 is not, separation can be made.

Another route is from a solution containing U^{+4} and Pu^{+4}. The uranium is not difficult to oxidize to UO_2^{+2}, whereas the large –1.04 value for the conversion $Pu^{+4} \rightarrow PuO_2^{+2}$, precludes the latter happening simultaneously with a properly selected oxidant. The resulting solution contains only UO_2^{+2} and Pu^{+4} now, and as above, a precipitant, etc. is then sought.

Some Practical Applications

The discussion thus far has concerned theoretical electrochemistry as used by chemists for a quantitative approach to redox reactions. The same principles apply wherever electrochemical phenomena are found.

1. Electrolysis. In a cell in which electrolysis is taking place, electrode polarity is dictated by an external source of potential, such as a battery of the type already described. The battery can be thought of as an electron "pump," causing an electron deficiency at the electrolysis cell's anode and an electron excess at the cathode. In the electrolysis cell, positive ions, therefore, move toward the negative cathode and may gain electrons and be neutralized, as $Cu^{+2} + 2e^- = Cu$. Negative ions move toward the positive anode and may give up electrons and be neutralized, as $2Br^- = Br_2 + 2e^-$. Thus, electrons do not move through the solution but electrical conduction occurs by ionic migration.

Two principles governing electrodepositions were discovered by *M. Faraday* in 1834, and are known as *Faraday's Laws*:

(*a*) The weight of a substance produced at an electrode is directly proportional to the quantity of electricity passing through the cell.

(*b*) Identical numbers of equivalents of different substances can be liberated at electrodes by the passage of a given quantity of electricity.

The quantity of electricity liberating a gram equivalent weight is called a *faraday*. It is 6.02×10^{23} electrons (Avogadro's number) and equals 96,500 coulombs. A coulomb is that quantity of electricity which passes a given point in a conductor in one second when the current is one ampere. Thus $C = It$, where C is coulombs, t is time in seconds, and I is current in amperes. The equivalent weight of an ionic substance undergoing reaction at an electrode is the ionic weight divided by the number of electrons per ion needed for its oxidation or reduction. A faraday could therefore plate out 107.88/1 grams of silver, 63.54/2 grams of copper, and 26.98/3 grams of aluminum.

Example 11-7. Find the lbs of Mg and the s.c. ft^3 of Cl_2 produced by electrolysis of a molten $MgCl_2$ bath using 100 amps for 1 hr. (see Mg, Chapter 19).

The electrode reactions are:

$$Mg^{+2} + 2e^- = Mg \qquad \text{(cathode)}$$

$$2Cl^- = Cl_2 + 2e^- \qquad \text{(anode)}$$

Thus the equiv. wts are Mg/2 = 12.2 and $Cl_2/2 = 35.5$. The number of coulombs is (100 amp)(3600 sec) = 3.6×10^5, and the number of faradays is $3.6 \times 10^5/9.65 \times 10^4 = 3.74$. Since one faraday deposits a g equiv. wt and since 454 g = 1 lb, the lbs produced will be (3.74)(12.2)/454 = 0.100 lb of Mg (*Ans.*) and (3.74)(35.5)/454 = 0.293 lb of Cl_2. A lb mol. wt of any gas at s.c. occupies about 359 ft^3, so the vol. produced is (0.293)(359)/71.0 = 1.48 ft^3 of Cl_2. (*Ans.*)

Industrial electrochemistry includes preparation and/or purification of metals by reduction from aqueous solution (Cu from $CuSO_4$) and from molten salt baths (Al from $Al_2O_3 + Na_3AlF_6$), as well as preparation of chemicals by oxidation ($H_2S_2O_8$ from $H_2SO_4 + H_2O$, $KMnO_4$ from K_2MnO_4, etc.).

2. Corrosion via electrochemical mechanisms. The analyst is sometimes asked to analyze corrosion products as a means of determining how to protect metals. Diagnosis is complicated by the possible presence of several paths by which electrochemical deterioration can occur.

(*a*) *Galvanic cells.* Two dissimilar metals in contact with each other and a solution constitute a short-circuited cell of the type given in the first part of this chapter. As one example, a brass fitting on an iron water pipe sets up the reaction **Fe** + Cu^{+2} = Fe^{+2} + **Cu**, as determined by the oxidation potentials. Air oxidation and hydrolysis of Fe^{+3} gives a precipitate of $Fe(OH)_3$, further displacing the reaction to the right.

Galvanizing and cadmium plating and the use of attached anodes of Mg are ways in which the same principle is used to protect iron at the expense of sacrificial metals. Under nonlaboratory conditions, such as a tank buried in moist soil, a ship in salt water, or new alloys in use, the usual metal activity series and table values of oxidation potentials are often of little value, and the experimenter must determine the characteristics of each new situation.

(*b*) *Concentration cells.* These are usually systems in which the same type of electrodes are in contact with a solution of varying composition; for example, an iron well casing penetrating two salt water pools of different concentration.

Metal ions go into solution with the aid of a force called *solution* *pressure* and are opposed from doing so by the force of *osmotic pressure* manifested by ions already in solution. Although these pressures are difficult to measure, one may use their concept to explain that in the more concentrated solution, the high osmotic pressure hinders further ionic production, hence the metal corrodes more in the more *dilute* solution.

(*c*) *Differential temperature and differential strain cells.* A high temperature accelerates ionic movement and gas release and speeds corrosion. Corrosion is also favored in areas in which metal is strained, as nonannealed areas and where stresses develop in use.

(*d*) *Differential aeration cells.* These cells often consist of a metal in contact with two solutions differing only in quantity of dissolved air, and it may be surprising to learn that corrosion primarily takes place in the solution containing the *lesser* oxygen concentration. Consider trying to dissolve copper in hydrochloric acid:

$$\begin{array}{rl}
\text{Rev. } (\text{Cu} \leftrightharpoons \text{Cu}^{+2} + 2e^- & E^\circ = 0.34) \\
H_2 \rightarrow 2\text{H}^+ + 2e^- & E^\circ = 0.00 \\
\hline
\text{Cu}^{+2} + H^2 = 2\text{H}^+ + \text{Cu} & E^\circ_{1-2} = 0.34
\end{array}$$

One calculates the equilibrium constant to be

$$K = [\text{H}^+]^2/[\text{Cu}^{+2}]\cdot p_{\text{H}_2} = 3.6 \times 10^{11}$$

The tendency for copper metal to reduce protons and form hydrogen gas is therefore slight, but since this is an equilibrium process one may assume that a thin film of H_2 forms on the Cu to establish early equilibrium. The copper is said to be insulated by the H_2 or is *polarized.* If oxygen is readily available to depolarize the electrode by reaction with the hydrogen, an electron deficiency is imminent on metal where the oxygen concentration is high. This exerts an electron demand on areas which are not depolarized so the latter give up electrons, become anodic, and metal dissolves there. By this mechanism, corrosion is prevalent in that part of the system containing comparatively little oxygen. Water systems are mechanically de-oxygenated by vacuum, or chemically, using Na_2SO_3, $NaNO_2$, or hydrazine hydrate, $(NH_2)_2 \cdot H_2O$.

(*e*) *Impressed current cells.* An outside source of current such as a leak from dc machinery may force electrons to flow away from a metal surface such as a pipe, causing metal to deteriorate at that point. Water or water plus dissolved oxygen is the recipient of electrons, the former giving $OH^- + H_2$ as products, the latter giving only OH^-. Ferric hydroxide is the final product and its deposition may or may not yield a protective coating to the metal surface. Repairing or shielding machinery to minimize current leaks stops this corrosion in its first step.

PROBLEMS

1. For each reaction calculate (*a*) the spontaneous standard state reaction equation (*b*) E°_{1-2} (*c*) the direction of electron flow in the external circuit (*d*) the polarity of the electrodes (*e*) K:

(1) $Cd + 2H^+ = H_2 + Cd^{+2}$
(2) $Sn + 2H^+ = H_2 + Sn^{+2}$
(3) $Cd^{+2} + Sn = Sn^{+2} + Cd$
(4) $Cl_2 + 2I^- = I_2 + 2Cl^-$
(5) $O_2 + 4H^+ + 4Cr^{+2} = 4Cr^{+3} + 2H_2O$

2. Calculate the items given in problem 1 for each of the indicated cells at standard state:

(1) Pt, Fe^{+2}, Fe^{+3} || H_2, H^+, Pt
(2) Fe, Fe^{+2} || Cd^{+2}, Cd
(3) Mg, Mg^{+2} || Br^-, $Br_{2(aq)}$, Pt
(4) Ag, Ag^+ || Pb^{+2}, Pb
(5) Pt, Sn^{+2}, Sn^{+4} || Cu^{+2}, Cu^+, Pt

3. The Daniell cell consists of a copper bar in a solution of cupric sulfate and a zinc bar in a solution of zinc sulfate. (*a*) Draw a picture of the cell. Calculate: (*b*) E°_{1-2} (*c*) K (*d*) E_{cell} if $[Cu^{+2}] = 10^{-4}\ M$ and $[Zn^{+2}] = 2\ M$ (*e*) E_{cell} if $[Cu^{+2}] = 3\ M$ and $[Zn^{+2}] = 10^{-6}\ M$ (*f*) E_{cell} if $[Cu^{+2}] = 4\ M$ and $[Zn^{+2}] = 4\ M$. What will be the effect if to the cell at standard state one adds: (*g*) H_2S to the copper side? (*h*) NH_4OH to the zinc side? (*i*) heat to raise the temperature from 25 to 50 C? (*j*) an equal excess of NH_4OH to both sides?

4. (*a*) Why does $E_{cell} = 0$ at equilibrium?
(*b*) Why does E_{cell} change with concentration changes?
(*c*) What is meant by standard state?
(*d*) Why does $Q = K$ at equilibrium?
(*e*) Which cell would theoretically give the greatest emf at standard state? Which the least?

5. One has the cell Pt, H_2 (1 atm.), H^+ (M)||H^+ (?), H_2 (1 atm.), Pt and experimentally finds $E_{cell} = 0.21$. Find [H^+ ?] and pH.

6. A calomel cell and a hydrogen cell are coupled. All substances are at standard state except the acid solution, which consists of 0.1 M HZ, a weak acid. The measured cell voltage is 0.575. Calculate (*a*) pH (*b*) K_A for HZ. (*Ans.* (*a*) 5.0 (*b*) 10^{-9}).

7. Find the K_{SP} of AgBr from

$$Ag + Br^- = AgBr + e^- \qquad E^\circ = -0.06$$
$$Ag = Ag^+ + e^- \qquad E^\circ = -0.80$$

8. Find the K_{SP} of $PbCl_2$ from the proper E° values.

9. Find in Table A18 one example of each of the four types of half cells mentioned early in this chapter. Choose examples not previously discussed.

10. Find the spontaneous reactions and *K*'s to support your answers for the following.

(*a*) It is stated in the group 3 cation discussion that some FeS may form when H_2S is added to acidified Fe^{+3} solution due to the reducing effect of H_2S on ferric iron. Does this reaction appear to be quantitative?

(*b*) Will a spiral of silver wire wrapped around an iron pipe in moist soil keep the iron from corroding?

(*c*) Will Fe^{+3} be reduced to Fe^{+2} by iron metal?

(*d*) It is reported that one can test for ozone by bubbling it through an acidic Mn^{+2} solution, whereupon purple MnO_4^- is formed. Is this feasible?

11. One has the two cells shown in Fig. 11-3. In each set up, tell which end of the iron horseshoe corrodes more rapidly and why.

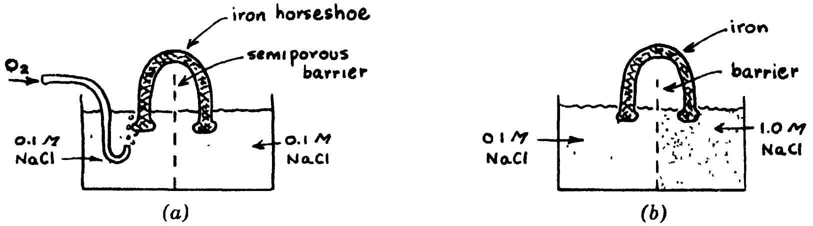


FIG. 11-3. Two schematic experimental corrosion cells.

12. (*a*) On the basis of hydrogen depolarization, explain why Cu dissolves in HNO_3 yet H_2 is not given off. Why does Cu dissolve in HCl + H_2O_2 but not in HCl or H_2O_2 alone?

(*b*) It is observed that a ship rusts badly at several spots well below the water line, where air is not readily available. Explain.

13. Balance the following half reactions and obtain the over-all reaction. Will this reaction proceed furthest at low or high *p*H (neglecting possible side reactions)?

$$Mn^{+2} + H_2O = MnO_4^- + H^+ + e^-$$

$$H_2O_2 = H^+ + O_2 + e^-$$

14. Draw a simple diagram to illustrate one practical example of each of the five types of cells mentioned in the section on corrosion. Indicate where corrosion takes place and the electron flow in each.

15. Suppose you are working on an atomic energy program and are given some strips of neptunium for the determination of E° for

$$Np = Np^{+2} + 2e^-$$

Discounting handling problems due to its radioactivity, draw a set up you might use and explain.

16. A man has a large gold dental bridge in his mouth. He touches it with an aluminum spoon and experiences what he describes as an electric shock. Explain.

17. From the reactions

$$\mathrm{Ag} + 2\mathrm{NH_3} = \mathrm{Ag(NH_3)_2^+} + e^- \qquad E^\circ = -0.373$$
$$\mathrm{Ag} = \mathrm{Ag^+} + e^- \qquad E^\circ = -0.799,$$

show that K_{ins} for diammine silver(I) ion is about 6×10^{-8}.

18. Show by calculation of the spontaneous reaction and K that magnesium will act as an anode and protect lead from corrosion. If these metals were in a laboratory cell with $[\mathrm{Pb^{+2}}]$ and $[\mathrm{Mg^{+2}}]$ initially 0.1 M, calculate the equilibrium lead ion concentration.

19. In organic qualitative analysis, one matches an unknown with a known sample as proof of their similarity by means of a *mixed melting point.* This entails intimately mixing the samples and slowly heating the mixture. A pure compound melts over a short range (1 C), whereas a mixture (except eutectics) melts over a wide range. In somewhat analogous fashion the following is suggested as a qualitative testing method for metallic samples: "Connect the known metal and unknown metal to the terminals of a milliameter and immerse the metals in dilute sulfuric acid solution." Explain what one would observe and why.

20. J. P. Slipshod describes the electrolysis of aqueous sodium chloride using Pt electrodes this way: "$\mathrm{Cl^-}$ goes to the anode, takes electrons, and becomes $\mathrm{Cl_2}$ gas which reacts with $\mathrm{H_2O}$ forming HClO. $\mathrm{Na^+}$ goes to the cathode and changes to Na atoms which immediately react with $\mathrm{H_2O}$ giving NaOH + $\mathrm{H_2}$." What is your version of this process?

21. A large excess of neutral $\mathrm{CuSO_4}$ solution is electrolyzed at Pt electrodes for 15 minutes, using 3 amperes. The anode reaction is $2\mathrm{H_2O} = 4\mathrm{H^+} + \mathrm{O_2} + 4e^-$. Find (*a*) the number of faradays and coulombs used (*b*) g of Cu and liters of $\mathrm{O_2}$ produced, (*c*) g equivalents of $\mathrm{H^+}$ produced (*d*) final solution *p*H.

22. A silver coulometer contains Ag electrodes in an $\mathrm{AgNO_3}$ solution. Electricity is passed through the cell and the weight of Ag gained by the cathode or lost by the anode is determined and used to calculate the quantity of electricity involved. If after 10.0 minutes, 1.3416 g of Ag are lost by the anode, what was the current strength in amperes? (*Ans.* 2.0 amp)

23. You are asked to go to the laboratory and, using simple equipment, to determine the number of coulombs in a faraday. Explain your method and include a labelled drawing of the experimental setup.

24. Recalculate K for each of the reactions in problem 1 using the method of Example 11-6.

25. Which will fail sooner in use and why: copper plates riveted together with iron rivets or iron plates riveted together with copper rivets?

26. Given the following hypothetical potential diagram for metal M, in acid media.

$$\mathrm{M} \xrightarrow{0.3} \mathrm{M^{+2}} \xrightarrow{0.4} \mathrm{M^{+4}} \xrightarrow{0.8} \mathrm{MO^{+3}} \xrightarrow{-1.5} \mathrm{MO_4^{-2}}$$

Explain how one can deduce these conclusions: (*a*) M dissolves in dilute acids, releasing H_2. (*b*) M^{+2} tends to disproportionate. (*c*) MO_4^{-2} is an oxidant similar to permanganate in strength. (*d*) Br_2 is powerful enough to oxidize M^{+4} to MO^{+3}. (*e*) Addition of metallic M to a Cu^{+2} solution yields a mixture of Cu and M^{+4}.

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12

ORGANIC REAGENTS FOR QUALITATIVE ANALYSIS

Fifty years ago, the chemical analyst had only a modest number of tools at his disposal. A man with some knowledge of chemical reactions, a small supply of chemicals and glassware, a few books, and a chemical balance was equipped about as well as the next chemist for the performance of chemical analyses. This is not true today. Although much of the fundamental theory of analytical separations is the same, the number of methods and their sensitivity has increased greatly. Two important fields where advancement has been most fruitful are *instrumentation* and the use of *organic reagents*. The analyst should know something of these developments, their application, and potentiality. Scarcely an issue of an analytical journal appears now without a majority of articles on these two topics. While the manipulation of instruments is reserved for more advanced study, a little familiarity with organic analytical reagents is desirable at this time, since the use of several of them will be described in the laboratory directions.

Advantages of Organic Reagents

1. They can be more specific than conventional reagents. Because of this property they can frequently be used to detect a single type of ion in a complex mixture. The time may soon be at hand when enough is known about organic reagents and enough of them are available so that a relative novice may run qualitative analyses with their use alone and circumvent more laborious inorganic separations and tests. This prospect particularly appeals to students.

2. They can be more sensitive. Classical semimicro-methods of qualitative analysis will usually not detect much less than 100 gammas ($1000\gamma = 1$ mg) of a substance under specific test conditions, although a few are better than that. Organic reagents, on the other hand, are capable of detecting absolute amounts of desired substances below 10γ and in certain cases, as little as $10^{-3}\gamma$. This rivals the spectrograph as a means of detecting traces of metals. Concentrationwise, one expresses the quantities usually as γ/ml = mg/liter = parts per million (ppm), and concentration limits of many tests using organic compounds are well below 1 ppm. The sensitivity of these methods is due to the formation of a highly colored material which is discernible at low concentration, or to the production of a precipitate which, due to the size of the organic molecules involved, has a molecular weight several times that of the substance whose presence it indicates. If large samples are available for concentration, then almost no lower limit may be put on the percentage of a constituent that can be found.

3. They can be adapted to *quantitative* analysis. The organic precipitates are generally insoluble in water at a given *p*H and may be separated, dried, and weighed. Those reactions giving colored, soluble products frequently show a regular change in color intensity with concentration of the substance under test and so are adaptable to accurate comparison with colors representing known concentrations. This is the basic idea in that branch of the science called *colorimetry*. The color matching may be done visually or by use of instruments like the *colorimeter* or *spectrophotometer* designed for the purpose. Many thousands of methods in colorimetry have been reported and are used daily in clinical laboratories, hospitals, etc., where production with accuracy is stressed. Some examples are given of this in the preliminary laboratory exercises and in the special experiments. (See special experiment 3.)

Disadvantages of Organic Reagents

1. The application of organic compounds is still somewhat new and many structures of products and mechanisms of reactions are not known. This makes discussion of tests limited and always gives an uncertain feeling, since one does not know what factors must be regulated. As with any new reactions, interferences are not always known and may not have been studied or reported. And from the teacher-student viewpoint, little chemistry is to be taught unless fairly definite concepts are dealt with and these are lacking in some empirical tests.

2. Organic reagents are many times not too stable toward certain solvents, *p*H, oxidizing and reducing agents, and temperature changes. They may, under these influences, be destroyed or render false colors

and/or precipitates. For this reason, along with the unknown sample, one should always run a known and a blank sample to check the reagent itself. Some reagents must be made just prior to use because of their sensitivity, particularly toward air oxidation.

3. The sensitivity of the reagents may be so great that extraordinary precautions are needed to insure their proper functioning and because of the time involved, other tests may be preferable. Sometimes the useful color range is in the order 0–2 ppm, and for quantity estimation great sample dilution is necessary. There are reagents, for instance, that readily detect copper in water condensed in copper tubing, give vivid tests for zinc from galvanized pipes, and show metallic impurities in filter paper. They are too sensitive for student purposes.

Kinds of Reagents

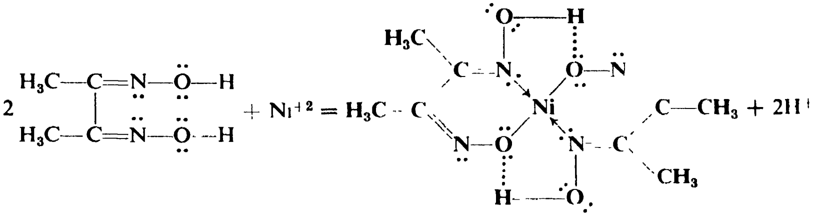
A number of classifications of organic analytical reagents are possible. The four given below are based upon mode of reaction with the test ions. Laboratory exercises are later described using each reagent.

The organic chemist needs to write *structural* rather than *molecular* formulas for the compounds he describes because the latter are not adequate. This simply means that dots are used to show unshared electrons, lines indicate covalent bonds, and the important elements in organic chemistry are then given as $-\overset{|}{\underset{|}{\mathrm{C}}}-$, H—, $:\overset{|}{\underset{\cdot\cdot}{\mathrm{O}}}-$, $-\overset{|}{\underset{\cdot\cdot}{\mathrm{N}}}-$, and $:\overset{|}{\underset{\cdot\cdot}{\mathrm{S}}}-$. About 800,000 organic compounds are known. This means there are approximately three times as many carbon compounds known as compounds of the other 100 elements. The diversity is due to the ability of carbon atoms to form strong covalent bonds not only with other kinds of atoms, but also with themselves, thus building up molecules containing chains and rings of atoms in great variety. In addition, carbon-carbon covalent bonds may be single, double, and triple as related in Chapter 3.

Type A. The reagent forms a chelate, or inner complex, with the substance being tested due to the presence and proximity of groups capable of coordination. The resulting substance is either colored or insoluble or both.

Chelates have been described in Chapter 4. When the electron donating atoms O, N, and/or S are part of the organic compound and 5- and 6-membered rings can form by incorporating the inorganic ion as part of an expanded structure, chelation may occur. The increase in molecular weight usually means a decrease in solubility.

1. Dimethylglyoxime for Ni^{+2}.

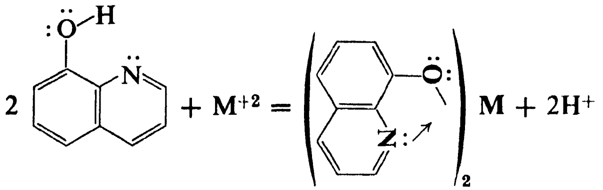


The chelate is not appreciably water-soluble and is red colored. It has the possibility of closing four rings by application of three bond types: covalent (lines), coordinate (arrows), and hydrogen (dots). The hydrogen bonds are weak, but the four links to Ni are strong, and the chelate is stable. The test will detect 0.3 ppm Ni^{+2}. See cation test, 17–11.

2. Dithizone (diphenylthiocarbazone) for Heavy Metals. This reagent can be used as a *screening agent* for solutions suspected of containing any of these heavy metal ions: Bi^{+3}, Cd^{+2}, Co^{+2}, Cu^{+}, Cu^{+2}, Au^{+}, In^{+3}, Fe^{+2}, Pb^{+2}, Mn^{+2}, Hg_2^{+2}, Hg^{+2}, Ni^{+2}, Pd^{+2}, Pt^{+2}, Ag^{+}, Tl^{+}, Tl^{+3}, Sn^{+2}, and Zn^{+2}. If under specified experimental conditions a color does not develop, then these ions may automatically be considered to be absent in significant quantities, since the test is quite sensitive. By carrying the reagent in a water-immiscible solvent like $CHCl_3$, one may carry out extractions (and hence concentration) of these ions from aqueous solution. By comparison to colors developed with solutions of known concentration, the method is adaptable to quantitative analysis. The structure of the chelate is similar to the one in the preceding example. The concentration limit of the test is in the order of 0.002 ppm for Zn^{+2} and 0.05 for Pb^{+2}. See special experiment 10.

3. Quinalizarin, Carmine, and Benzoin for Boron. The first two reagents give color reactions with borates as described in anion test 22–26. The solvent used is concentrated H_2SO_4. The chelate formed when benzoin and borate react in alcoholic solution is fluorescent under ultraviolet light. See special experiment 8. All these methods are capable of detecting 0.2 ppm of boron.

4. 8-Hydroxyquinoline (Oxine) for Several +2 and +3 Metals. This reagent is well known in quantitative analysis, used for example as a precipitating agent for Mg^{+2} and Al^{+3} in light alloy analysis. It also gives bulky precipitates under proper conditions with Mn^{+2}, Zn^{+2}, Cd^{+2}, Co^{+2}, Pb^{+2}, Cu^{+2}, Fe^{+3}, Cr^{+3}, Ga^{+3}, and some others, about twenty-five in all. As in previous discussion, the proximity of electron-donating groups makes ring formation by chelation possible. With divalent metals (illustrated below) two oxine molecules are coordinated, and with trivalent metals, three. This greatly increases the molecular weight of the product over the original ionic weight of the metal ion, giving a large volume of precipitate from a comparatively small amount of metal tested. See special experiments 6 and 8.



This ring system means a carbon atom is at each corner and hydrogen atoms are attached wherever needed to complete the structure with four valence bonds on each carbon. The molecular formula is C_9H_7ON.

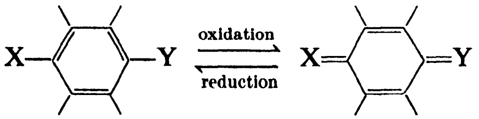
5. ***Zirconyl Alizarinate for*** F^-. This test in a sense is the opposite of the four cases above, in that the disappearance of a colored chelate indicates a positive reaction. A chelate formed between zirconium and the organic reagent, alizarin, is somewhat weakly constituted and in the presence of fluoride is destroyed, accompanied by a color change from red to yellow. A stronger zirconium-fluoride complex is formed. By visual observation alone, the test will detect 0.1 ppm F^-. See anion test 22–27 and special experiment 3.

6. ***α-Nitroso-β-naphthol for*** Co^{+2}. A coordination compound is formed in HAc solution which has a characteristic red color. The test is good in the presence of 100 times as much Ni^{+2} as Co^{+2}, which is valuable since these ions occur together in group 3 analysis. The concentration limit is about 2 ppm Co^{+2}. See test 17–12.

7. ***Sodium Diethyl Dithiocarbamate for*** Cu^{+2}. In NH_4OH solution this reagent gives yellow to brown colors with cupric ions in the range 0.02–5 ppm Cu^{+2}, and with more concentrated copper solutions gives brown precipitates. The reagent also is used to detect certain other metal ions (see references) but is most sensitive for copper. See test 16–8.

Type B. The reagent and the substance under test are involved in oxidation-reduction, the reagent changing in characteristics, usually color.

Redox is most often associated with bond rearrangement in rings. The structural changes are from a *benzenoid* (reduced form) ring to a *quinoid* (oxidized form) ring and vice versa:



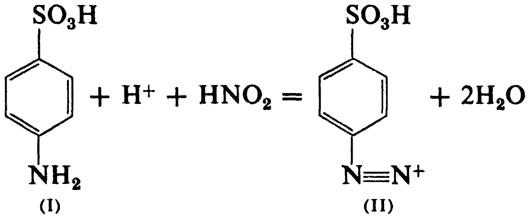
The presence of electron-donating groups (X and Y) such as —OH and —NH_2 facilitates the reaction. All *quinones* are colored.

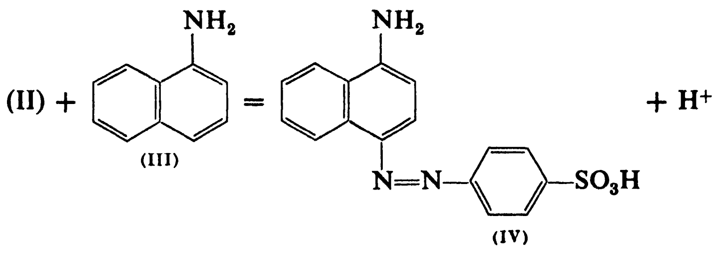
8. Benzidine for Certain Oxidizing Agents. A number of oxidants like MnO_2, PbO_2, NO_2^-, NO_3^-, and some biological substances give this test. The reagent is converted from a colorless to a deep blue solution (benzidine blue) containing some of the benzidine in the quinoid form. About 1 ppm of the oxidants will give the test. See test 22–18 and special experiment 7.

9. Rhodamine-B for Antimony. In the presence of the reagent and nitrite ion, Sb^{III} is oxidized to Sb^{V}. The latter then oxidizes the reagent, which gives a color change. This test is good to about 10 ppm of antimony. Tin, which occurs with antimony in cation group 2B does not interfere. See test 16–12.

10. Malachite Green for SO_3^{-2}. As described in test 22–10, this reagent is used to detect SO_3^{-2} in the presence of $S_2O_3^{-2}$, although sulfides, polysulfides, and some other reducing agents give the same reaction. A positive test is the bleaching of the green color as the dye is reduced to its colorless (leuco) form with concentrations of sulfite greater than 20 ppm.

11. The Diazo Reaction for Nitrite. In acid solution, nitrite is in the form of a weak acid HNO_2, which oxidizes aromatic primary amines to diazonium salts: $ArNH_2 + HNO_2 \rightarrow Ar—N{\equiv}N^+$. The salts are capable of reacting (coupling) with other aromatic molecules to produce azo compounds whose colors are detectable at low concentration. If sulfanilic acid (I) is diazotized (II) and coupled with α-naphthylamine (III), a visible color develops with any concentration of nitrite greater than 0.01 ppm. The result is synthesis of a red dye (IV). See anions, test 22–5.



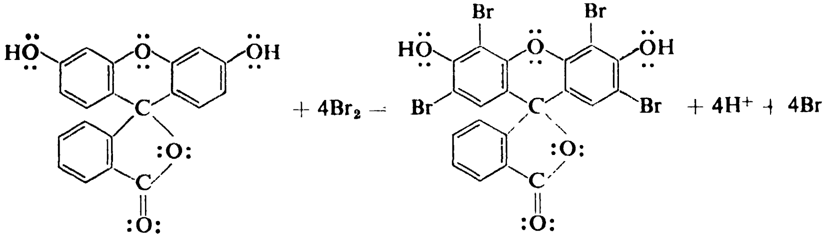


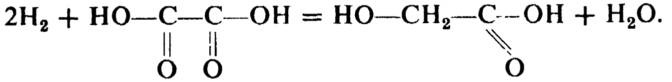
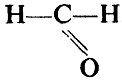
12. Orthotolidine for Cl_2. A yellow to red color is obtained with the reagent and free chlorine. Other strong oxidizing agents interfere. Again the colorless form of the reagent is benzenoid and becomes quinoid upon oxidation. The method is employed quantitatively to check chlorine in swimming pools, disinfecting baths, etc., using permanent color standards prepared from color matching K_2CrO_4 and $K_2Cr_2O_7$ solutions. As little as 0.01 ppm Cl_2 is detectable. See special experiment 6.

Type C. The reagent and the substance under test react to give a compound by direct synthesis without chelation or redox.

13. Fluorescein for Br^-. The yellow dye fluorescein is converted to the red tetrabromo derivative, eosin, when a bromide is oxidized to give Br_2 and the latter brominates the dye. The test is adaptable to detection of this halide in the presence of other halides and thiocyanate, which are interferences in most other methods. See test 22–35.

The concentration limit is about 40 ppm Br^-.

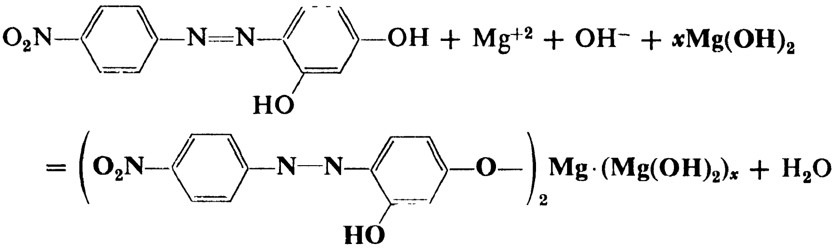


14. Resorcinol for $C_2O_4^{-2}$. In dilute H_2SO_4, oxalates are in the form of oxalic acid and that is reducible with Mg to glycolic (hydroxyacetic) acid:  $2H_2 + \mathrm{HO{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}OH} = \mathrm{HO{-}CH_2{-}\underset{\underset{O}{\diagdown\!\diagdown}}{C}{-}OH} + H_2O$. When resorcinol in concentrated H_2SO_4 is added, glycolic acid is converted to formaldehyde,  $\mathrm{H{-}\underset{\underset{O}{\diagdown\!\diagdown}}{C}{-}H}$, and it gradually reacts with the resorcinol and air to form a blue colored two-ring quinone. This procedure will indicate oxalate at a concentration of about 150 ppm. See anions, test 22–32.

Type D. The reagent forms a colored adsorption complex ("lake") with the inorganic substance being tested.

Hydrated oxides like $Al(OH)_3$ have a large surface area and *adsorb* substances strongly. When some organic compounds are adsorbed, they change structure and color. These so-called lakes are colloidal at low concentrations and appear as colored solutions rather than as colored precipitates. The bonding involved is not definitely known, but there may be some chemical reaction, as shown in the example below.

15. Paranitrobenzeneazoresorcinol for Mg^{+2}. With strong bases, Mg^{+2} gives $Mg(OH)_2$. The surface of this gel adsorbs the reagent, which changes color from red to blue. The product given in the equation below is hypothetical. The test will detect Mg^{+2} at a concentration of 10 ppm, although similar gelatinous precipitates may also give a positive reaction. It may be used as a spot test with a group 4 and 5 mixture. See cation test 19–2.



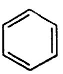
16. Aluminon (Aurin Tricarboxylic Acid) for Al^{+3}. This test may be carried out in slightly acidic solutions where interference due to other hydroxide-forming metals is decreased. Hydrous SiO_2 does not give the test. The yellowish reagent solution gives a red color upon adsorption with $Al(OH)_3$. Reaction is probably similar to that pictured above. The test will detect 0.3 ppm Al^{+3} although in such dilute solution, $Al(OH)_3$ is invisible. When a large quantity of $Al(OH)_3$ is formed in the presence of the reagent and the mixture centrifuged, the color of the precipitate is bright red.

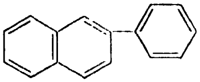
PROBLEMS

1. (*Library*) A number of reagents have been described without accompanying reaction equations. Find reference to these, copy the equations, and in each point out the features that classify the reaction according to the four divisions given in this chapter.

2. You are asked to select some organic compounds that might react with inorganic ions as described here. Which of the following do you think have possibilities? Why?

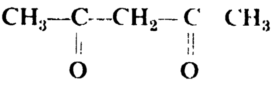
(*a*) $CH_3—CH_2—CH_3$

(*b*)


(*c*)


(*d*) $HS—CH_2—CH_2—NH_2$

(*e*) CH_3OH

(*f*)


$$CH_3—\underset{\|}{\underset{O}{C}}—CH_2—\underset{\|}{\underset{O}{C}}\ CH_3$$

(*g*) CH_2F_2

3. (*Library*) The symbol R— is used in organic chemistry to denote a hydrocarbon segment or radical, as CH_3—, C_5H_{11}—, etc. From reference works and using R as necessary, show formulas for the general alcohol, ether, aldehyde, ketone, carboxylic acid, acid anhydride, amide, amine, nitrite, and sulfonic acid.

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3. Organic Reagents Symposium, *Anal. Chem.*, **21**, 1298 (1949). '(General)
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13

MINERALS, METALS, AND CRYSTALS

Metallurgy is a broad field which will be surveyed here under its two main subdivisions: *process metallurgy*, which is concerned with the extraction of metals from their natural sources and subsequent refinement, and *physical metallurgy*, which deals with metal combinations, micro structures, and prediction of behavior in use. Metallurgy is a very old art (viz. "The Bronze Age"), but a newcomer among the sciences. Since a good portion of the qualitative analysis course is concerned with metal analysis, and because about 80 of the 101 elements now known are metals, a brief survey of metals, minerals, and alloys is needed to increase the analyst's viewpoint and understanding of his own specialty.

PROCESS METALLURGY

Sources of Metals

Metals are obtained from two sources: the earth's crust and the ocean. Although only Mg is commercially extracted from the latter, its potentialities are being further explored as the earth's supply is rapidly dwindling and as atomic power promises to give cheap energy for the evaporation of sea water. In examining Table 13–1 it must be kept in mind that the figures are averages and that only concentrated ore deposits, which are relatively rare, are economically feasible for exploitation. Thus, titanium and aulminium are spectrographically found in almost all rocks and clays, but recovering them from low-grade ores is at this time only a laboratory exercise.

TABLE 13-1. AVERAGE COMPOSITIONS OF THE EARTH'S CRUST AND THE OCEAN

(*a*) Elements In The Earth's Crust

Element	Per Cent by Weight	Element	Per Cent by Weight	Element	Per Cent by Weight
O	46.43	H	0.127	Ni	0.019
Si	27.77	Mn	0.096	Sr	0.018
Al	8.13	F	0.077	Li	0.003
Fe	5.12	Cl	0.055	Cu	0.002
Ca	3.63	S	0.052	Ce	0.0015
Na	2.85	Ba	0.048	Other rare earths	0.0034
K	2.60	Cr	0.037	Be	0.001
Mg	2.09	Zr	0.028	Co	0.001
Ti	0.629	C	0.027	U	0.0004
P	0.130	V	0.021	All others	0.0041

(*b*) Elements In Sea Water

Element	Parts per Million	Element	Parts per Million	Element	Parts per Million
Cl	18,980	Rb	0.2	U	0.0015
Na	10,561	Li	0.1	Mo	0.0005
Mg	1 272	P	0.001–0.10	Th	0.0005
S	884	Ba	0.05	Ce	0.0004
Ca	400	I	0.05	Ag	0.0003
K	380	As	0.01–0.02	V	0.0003
Br	65	Fe	0.002–0.02	La	0.0003
C	28	Mn	0.001–0.01	Y	0.0003
Sr	13	Cu	0.001–0.01	Ni	0.0001
B	4.6	Zn	0.005	Sc	0.00004
Si	0.02–4.0	Pb	0.004	Hg	0.00003
F	1.4	Se	0.004	Au	0.000006
N	0.01–0.7	Cs	0.002	Ra	$0.2\text{–}3 \times 10^{-10}$
Al	0.5				

Minerals and Ores

Minerals or *ores* are naturally occurring free metals or chemical combinations of metals with other elements. Mixtures of minerals are called rocks. Ores are found in a few places in the earth in sufficient concentration to warrant extraction. The mineral is first *mined*, commonly by digging or washing out with water. In most cases it is not of sufficient purity to be sent directly to chemical processing, so it first must undergo *ore dressing*, a term applied to any preliminary purification. This rids the useful portion of surrounding *matrix* or *gangue*, and the concentration process is known as ore *beneficiation*. These methods must be cheap, rapid, and simple because of the large tonnages to be handled daily. Matrix material finds use as gravel in road building, fills, etc.

Beneficiation Methods

(*a*) *Magnetic separations* are used for some iron and other magnetic ores. The rock is crushed so that a minimum of matrix is carried along.

(*b*) *Water or acid leaching* processes may be used to selectively dissolve either ore or gangue. Low-grade copper (oxide) ore, for example, is handled in this way; H_2SO_4 dissolves the oxide, giving a cupric sulfate solution.

(*c*) *Specific gravity separations* are conducted on a small scale by the gold panner, or on a large scale in tanks where crushed minerals are separated from matrix by floating one or the other off and allowing the rest to settle. The *flotation* process is a modification of this in which finely crushed ore called *pulp* is mixed with water, soap, an oil, and air. The froth produced preferentially wets certain ore components, usually the more dense mineral itself and floats it off, leaving the worthless matrix behind. The recovery of the process is good and *tailings* left from previous less efficient beneficiation processes have been reworked profitably.

(*d*) *Other chemical separations* besides acid leaching are used in some special cases. One example of this is the Dow process for winning magnesium from sea water. Calcined oyster shells (CaO) are added to the water, precipitating $Mg(OH)_2$. This is filtered off, dissolved in HCl, and evaporated giving $MgCl_2 \cdot H_2O$. A great concentration of magnesium has obviously been effected.

Reductions

After beneficiation, the dressed ore is ready for *reduction* to the free metal if it does not occur *native* (free) as an original mineral. At least one chemical reaction is necessary.

(*a*) *Pyrometallurgy* is characterized by being a high temperature process. If the metal is sufficiently low in the activity series to be native, it is simply melted away from the less *fusible* gangue. If the metal oxide is the mineral, or the metal has been roasted previously to the oxide, carbon (*coke*) is the usual reducing agent. If easier, the gangue may be made fusible (lower melting) by adding a *flux* to it, and the metal is separated from this liquid at high temperature. Matrixes are often *silicaceous* (SiO_2) or *limestone* ($CaCO_3$) types. At high temperature, silica is acidic and CaO (from calcium carbonate decomposition) is basic, and they neutralize each other to form fusible calcium silicate glass slags. Thus if one wishes to fuse a silica matrix like quartz, he uses a basic flux like limestone, and vice versa. In the furnace both metal reduction and slag formation take place with the slag rising to the top and the molten metal being tapped off the bottom. The following is typical:

$$\underset{\text{Reducing agent}}{\mathrm{C}} + \underset{\text{mineral}}{\mathrm{Fe_2O_3}} + \underset{\text{matrix}}{\mathrm{SiO_2}} + \underset{\text{flux}}{\mathrm{CaCO_3}} \xrightarrow{\Delta} \underset{\text{Molten slag}}{\mathrm{CaSiO_3}} + \underset{\text{gases}}{CO + CO_2} + \underset{\text{molten metal}}{\mathrm{Fe}}$$

Furnace linings must be able to withstand the temperatures and reactions, and they are gradually dissolved as slag although *refractory* (high melting) oxides like Al_2O_3 and Cr_2O_3 are used. The role of carbon in these reactions is most important since it is the principal reducing agent:

$$\mathrm{C} + CO_2 \overset{\Delta}{=} 2CO$$

Carbon monoxide can also work as a reductant but excess carbon is needed to prevent CO_2 from reoxidizing metal:

$$CO_2 + \mathrm{Fe} \overset{\Delta}{=} \mathrm{FeO} + CO$$

(*b*) *Hydrometallurgy* processes are run at ordinary temperatures in aqueous solution. Minerals containing more noble metals are dissolved in acid or with complexing compounds and the metals are displaced by adding cheaper, more active metals. For example, NaCN dissolves Ag and Au as cyano complexes which are decomposed when powdered zinc is added:

$$2\mathrm{Ag(CN)_2^-} + \mathrm{Zn} = 2\mathrm{Ag} + \mathrm{Zn(CN)_4^{-2}}$$

Another example is one already mentioned wherein copper oxide, while still in ore pockets, is leached from an inert matrix with acid. The acid is allowed to react underground for some time, then pumped up to tanks where scrap iron ("tin" cans) is added to displace copper. Tons of cans are collected daily in large cities and magnetically separated from other refuse for this purpose.

(*c*) *Electrometallurgy* is the process in which metals are electroplated from aqueous solutions at ordinary temperature or from anhydrous molten salt solutions at high temperature. An example of the latter is the electrolysis of magnesium chloride in the final step of the Dow process to produce magnesium metal and chlorine. Similar methods to obtain aluminum (Hall process) and alkali metals (Downs cell) are described with the chemistry of those elements in later chapters.

(*d*) *Aluminothermy* or the *Goldschmidt process* is used on oxides which for one reason or another (as carbide formation) are not satisfactorily reduced with carbon. The powdered oxide is mixed with fine aluminum particles and heated. Enough heat is liberated as Al_2O_3 forms to give molten metal as the main product:

$$Cr_2O_3 + 2Al = Al_2O_3 + 2Cr$$

(*e*) *Special methods* are described for some of the refractory metals in Chapter 20. Because of their high melting points, ordinary procedures for metal recovery and general metallurgy do not work. Their high temperature applications have nevertheless centered a great weight of recent metallurgical research on metals like Be, Ti, Zr, Hf, V, Cb, Ta, Cr, Mo, and W. The radioactive metals of the actinide series and other active wastes of the atomic energy operations also present major difficulties in handling because of the radiation and newness of the field. For example, the Hanford works for plutonium separation were built on the basis of micro experimentation with a mass of Pu practically invisible to the naked eye—a scale-up of an unprecedented 10^{10} times.

Refining

When the metals have been obtained in semipure form by one of the above processes, they may find use as such or be further refined.

(1) *Electrolytic refining* is as described under electrometallurgy, p. 202, although here a semipure metal is used as the anode, a pure bar or plate of the same is the cathode, and a solution of one of its salts is the electrolyte. In this way copper of purity better than 99.9% is produced. For very high melting metals like Ti, W, etc., sintered bars are melted by electrical resistance in special crucibles under vacuum or in an inert atmosphere (see Chapter 20).

(2) *Distillation and sublimation* are used on metals such as Hg, Zn, and As, which are volatile. The vapor is condensed and may be redistilled or resublimed to give products almost 100% pure.

(3) *Smelting* at high temperatures is needed to purify many metals. Fluxes and degasifying materials are added to lower the melting temperature, float off impurities, and keep gases from dissolving, which might otherwise embrittle the metal. Aluminum, for example, is added to remove O_2 and give a fine grain structure in steel.

Mineral Types and Their General Treatment

Which methods of metallurgy one uses will be determined by all the factors involved, from ore type to availability of flux materials and energy for reductions. Of the common mineral types, five are worthy of mention:

(*a*) *Oxide minerals* are usually reduced with coke (e.g., Fe_2O_3, CuO). Some noncarbon-reducible oxides are those of Ca, Sr, Ba, and Al (Table 1–1), and in addition, Cr, Mn, and some other transition metal oxides cannot be treated well in this way because they dissolve carbon and form very hard, brittle carbides. Their oxides may be reduced by aluminothermy or special methods.

(*b*) *Volatile metals* are distilled. As an example, in the Pidgeon process for magnesium, finely divided ferrosilicon is pressed into briquettes with roasted dolomitic limestone and heated in evacuated retorts at 1150 C. The magnesium collects in large crystalline masses at the cool end of the reactor.

$$\mathrm{FeSi} + \mathrm{CaO} + \mathrm{MgO} \xrightarrow{\Delta} \mathrm{Fe_2O_3} + \mathrm{CaSiO_3} + Mg$$

(*c*) *Carbonate minerals are calcined* (roasted) and treated as above:

$$\mathrm{MgCO_3} \overset{\Delta}{=} \mathrm{MgO} + CO_2$$

(*d*) *Sulfide minerals* are roasted in air to convert them to the oxides whose handling is described above; SO_2 as a by-product can be converted to SO_3 and H_2SO_4. Industrial processes are typified by utilization of everything of value in the operation.

(*e*) *Miscellaneous minerals* handling includes electrolysis and hydrometallurgy as previously described.

The relatively small number of *important mineral types* is a consequence of the comparative abundance of the elements and their chemical combinations at high temperature when the earth was in process of formation. Seven types cover most of the cases:

(*a*) *Native* (*free*)*:* Ag, Au, Pt, Pd, Cu, Hg, Bi, Sb, As. As expected, the easily reduced metals, low in the replacement series (Table 1–1), are the ones forming unstable and few compounds.

(*b*) *Oxides:* Fe, Sn, Mn, Al, Cu, Zn, Ti, U, Zr. The same metals will of course burn in air to give these oxides.

(*c*) *Sulfides:* Fe, Cu, Zn, Ni, Co, Sb, Pb, Cd, Hg, Mo, V. Familiar metals are from group 2 and 3 cations.

(*d*) *Sulfates:* Pb, Ba, Ca, Sr. The same sulfates are used to separate and identify these metals in qualitative tests.

(*e*) *Carbonates:* Ca, Mg, Sr, Ba, Fe, Cu, Zn, Pb. The first four may be precipitated with $(NH_4)_2CO_3$ in cation group 4. The others form sulfides, in previous separations, that are more insoluble than their carbonates.

(*f*) *Halides:* Na, K, Mg, Ag. The first three occur in natural brines and the ocean.

(*g*) *Silicates:* K, Li, Al, Be. The metals are not reasily recovered.

PHYSICAL METALLURGY

Metal Characteristics

No sharp dividing line separates metals from nonmetals, and borderline cases will have some chemical and physical attributes of both types of element. It is helpful, however, to have in mind the most obvious differences before further elaboration on the metallic state.

(a) Physical Properties of Metals. 1. *High luster.* Metals reflect visible light well although reflectance varies considerably with the wavelength of incident radiation. In a finely divided state many metals appear black, but in massive form they are silvery, with the exception of Cu and Au. Use is made of metallic *reflectivity* in mirrors and reflectors. Silver reflects 95% of the visible light falling on it, platinum 65%, and copper (one of the poorest) only 55%.

2. *High electric conductivity.* The conductivity varies with different metals and for a given metal is inversely proportional to temperature. Bismuth and mercury are not especially good electric conductors; silver, the best, is about sixty times better than mercury. Metals, with their low electrical resistance, are used in wires, bus bars, etc., where good conduction is needed, while nonmetals, with high resistances, are used as *insulators.* Electric conductivity involves electron movement without metallic decomposition. Some metals like Hg, Sn, and Pb exhibit super electrical conducitivity at temperatures in the range 0–10° A, current flowing for long periods after a potential across them is removed, due to exceptionally low electrical resistance.

3. *High heat conductivity.** The order is roughly parallel to that of electrical conductivity trends. The generally high melting points and good heat conductivities make metals useful in all types of heat exchange equipment from cooking pots to condensers, radiators, and boilers. Nonmetals are insulators.

4. *High density.* Compared with other substances, metals are usually more dense. Some exceptions occur with the lighter metals, but, lower in the periodic table where metallic properties are pronounced, densities are high. Alloys containing large amounts of dense elements have high densities also, of course.

5. *High strength.* Mechanical strength of materials is measured and expressed in various ways. The *ultimate tensile strength,* for example, is

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* The relation between heat and electric conductivities has been studied. The Law of Wiedemann and Franz gives a simple relationship which approximately describes many cases:

$$\text{Thermal conduct.} \times 10^8/\text{Electrical conduct.} \quad KT$$

where T is the absolute temperature and K is approximately a constant.

defined as the axial load per unit of cross-sectional area (pounds per square inch, psi) needed to rupture a prismatic test specimen in a machine designed for the purpose. Other measures of strength express characteristics of elasticity, creep, crack resistance, etc.

6. *High hardness.* Hardness is defined as resistance to *permanent deformation* by indentation, as measured on standard machines which indent the metal surface with a diamond or hard-alloy stylus under given loading. The test results are expressed in arbitrary units deriving their names from the machines used: *Brinnel*, *Rockwell*, *Vickers*, etc. (For geologist's hardness measure, find library reference to Mohs' scale.) Although some light nonmetallic elements and their compounds are hard, such as diamond, silicon carbide, and boron nitride, the metals are more generally typified by high hardness.

7. *High deformability.* This is manifested in two ways: ability to be hammered into thin sheets (*malleability*), and ability to be drawn into fine wires (*ductility*). A few metals like Pb, Bi, and Sb are poor in this respect but most are superior to nonmetals. Metals are thus said to be capable of plastic flow with large elastic limits. *The combination of high yield strength and great capacity for plastic deformation is the most important mechanical characteristic of metals.*

8. *High melting and boiling points.* There are nonmetallic materials like graphite and silicon carbide that are refractory; that is, they retain their shape and original composition at high temperatures. However, it is more characteristic of metals than nonmetals to have high melting and boiling points, but even the melting and boiling points of metals are scattered on the temperature scale between the extremes of mercury and tungsten. High temperature applications of metals as in jet aircraft have brought new demands on metallurgists to develop alloys with refractory properties, and attention is automatically directed to the transition metals that have low creep at high temperature.

9. *Crystalline.* All metals are typified by being crystalline, and most of their space lattices are simple (see the section on **metal structures,** p. 211). Alloys are crystalline also and may have simple or complex lattices.

(b) Chemical Properties of Metals. 1. *Metals usually form the cation of a chemical compound* and during formation from the elements became *positive ions* by electron loss and act as *reducing agents.* Metals appear not infrequently in the anion also, as $Zn(OH)_4^{-2}$, AsS_2^-, $Fe(CN)_6^{-4}$, etc.

2. *Metals form oxides that give basic reactions.* Thus, dissolving calcium oxide in water gives the base calcium hydroxide or dissolving it in acid gives a salt. Exceptions to this are amphoteric oxides like ZnO which dissolve in either acid or base, showing that they can act as weak

bases or acids, and some higher valent oxides like Mn_2O_7, which give weakly acidic reactions.

3. *Metals replace hydrogen in acids.* See Table 1–1.
4. *Metals have low electronegativity values* although a few nonmetals like H also have a strong tendency to form positive ions. See Fig. 3–14.

The above properties are best demonstrated by elements in the lower left portion of the periodic table.

Metallic Valence

The binding forces in metals interest engineers as well as chemists, and explanation of metallic bonds has contributed to general understanding in both their fields.

The first theory of the metallic bond is due primarily to the work of *Drude*, *Losenty*, and *Lorentz* at the beginning of this century. They proposed that metal atoms be thought of as spheres vibrating about points in a crystal lattice, and surrounded by clouds of moving electrons belonging to no particular atoms. This condition is brought about by each atom tending to give electrons because of the electropositive character of metals. The metal structure is one of positive centers arranged in regular geometric pattern through the interstices of which move free electrons, the whole bonded together by attraction of the oppositely charged bodies. The theory was successful in explaining many metallic properties. Thus, high electric and heat conductance is due to readily mobile, energy-carrying electrons, and opacity is due to loosely held electrons of various energies absorbing and re-emitting light of all visible wavelengths. Since atomic vibration is directly proportional to temperature, it is expected that high temperature will hinder electron movement because vibrating atomic centers will scatter the electron wave front. Electric conductance in metals is therefore inversely proportional to temperature. Electrical resistance approaches zero and conductivity approaches infinity near absolute zero. Alloys as cast have a disordered atomic structure and the conductivity is usually lower than that of the pure metals. Heat treatment will allow the atoms to move into a more ordered pattern with better conductivity and some heat treatment results are followed by such measurement.

Nonmetals generally are oppositely constituted. In substances like SiO_2, electrons are tightly held in formal covalent bonds, and, not being capable of movement, are not available to conduct heat or light or to intercept radiations; they are therefore insulators and are transparent. There are also some borderline substances called *semiconductors* which conduct under certain conditions. These and nonconductors become conducting if energy put into them is sufficient to break bonds and produce unattached electrons. In this way silicon and germanium crystals become conducting upon heating to moderate temperatures, and even diamond is a conductor under high energy ray bombardment. This is the principle behind "*crystal counters*"—devices used to detect and measure radiation. Electrons thus loosened move under applied voltage and constitute an electrical current. The bond robbed of an electron now is a positive "hole" in the structure and electrons will drift toward it, creating holes where they depart and giving the effect not only of moving electrons but of oppositely moving (positive) holes which also contribute to conductance. These ideas have been refined by application of the quantum theory by *Fermi*, *Sommerfeld*, and *Dirac*, but are beyond the scope of this text.

Metal atoms are capable of forming many types of bonds, and electrons resonate among various positions. This not only helps explain stability and conductivity but also ductility and malleability.

When a metal ingot is rolled into a sheet, bonds are broken as atoms are moved away from each other, and this can result in fracturing a crystalline substance. Metals, however, are not dependent on single sets of bond types, distances, and angles, and reformation of bonds among new neighboring atoms gives a sheet about as well knit electronically as the original ingot. Metals toward the bottom of the periodic table are best capable of deformation, since they have only small energy differences between possible bonding levels and bonds break and form with little change in total energy.

For bonding, each atom must have unpaired electrons to donate to the bonds and empty orbitals in which to accomodate accepted electrons. The maximum number of covalent bonds is limited in elements on the left side of the periodic table by too few electrons, and on the right by too few empty orbitals. Thus it is that maximum covalence occurs in elements in the middle of the periodic table with a resultant maximum density.

Ferromagnetism

Ferromagnetism is related to electron structure. It is a property of Fe, Co, and Ni, the three elements which are strongly drawn into magnetic fields and exhibit lasting magnetism after being withdrawn. It is postulated that in these metals there exist *domains of magnetism* which feature groups of atoms showing electronic displacement in single directions. Under magnetic field influence, the domains themselves align, and their magnetic effects reinforce each other. If the metal is then withdrawn from the field, it remains magnetized until heated or severely deformed, whereupon the domains return to a random orientation and magnetism is destroyed.

Conditions for domain existence appear to include both unfilled orbitals and a particular internuclear distance, and the three elements mentioned above are the only one having both. From its position in the periodic table, electron arrangement, and atomic radius, one suspects manganese might be ferromagnetic, but apparently the nucleii are a little too close together. It is interesting to note that certain Mn alloys containing nonmagnetic elements such as Cu, are ferromagnetic, presumably because now the Mn atoms are displaced to the proper distances.

Crystal Chemistry

Obviously if one knew the arrangement of atoms in a metallic crystal he would be in an excellent position to understand many chemical and physical properties of all metals and crystalline materials. It is also evident, however, that because of the minuteness of individual atoms, ordinary methods of measurement will be to no avail.

The discovery of X-rays occurred 17 years before *M. von Laué*, in 1912, conceived of a use for them in crystal measurements. It was known that parallel lines (a *diffraction grating*) ruled on a surface would scatter (diffract) visible light incident upon them if the distance between lines was in the range of the wavelengths of light. It was Laué's idea that if one assumed crystals to be built up of parallel layers of atoms as close together as X-ray wavelengths, perhaps such planes within crystals might act as diffraction gratings for X-rays. The experiment was tried by *Friedrich* and *Knipping*, who exposed a thin, cubical crystal of ZnS to X-rays. They obtained a photograph showing spots in an arrangement having cubical symmetry. Since their X-ray tube simultaneously produced X-rays of many wavelengths, all crystal planes of high atomic population, although various distances apart, were shown present by having diffracted radiation of some wavelength. Mathematical translation of the photo pattern is capable of giving the angles between planes and hence the shape of the structural unit, though not its dimensions. This *unit cell* is visualized as containing enough atoms to describe its symmetry, and, if repeated in three dimensions many times, will yield the visible crystal. The crystal's external form thus depends upon internal atomic arrangement.

The following year, *W. H. Bragg* and his son, *W. L. Bragg*, began experiments to find whether or not crystal planes might *reflect* X-rays. Since X-rays are not significantly bent upon passing through matter (as is visible light), they should penetrate and reflect without distortion, thus making accurate measurements on reflectance angles within crystals possible if monochromatic rays are used. This was proved by the Braggs, and from the geometry of the setup they showed that knowledge of these angles allows calculation of interatomic distances. The relationship is stated by the *Bragg equation* (derived in many physics texts):

$$n\lambda = 2d \sin \theta \tag{13-1}$$

Theta is the angle of incidence and reflection of monochromatic X-rays having wavelength λ. As θ is increased from 0 C, a progression of angles is found at which reflection reinforcement from successive parallel sheets of atoms takes place. These positions are called the order of reflection and correspond to $n = 1, 2, 3 \cdots$ etc. At other angles reflection interference takes place because reflected rays are out of phase. Term d is the distance between planes. Since each crystalline material has its own atomic arrangement and atomic dimensions, each gives a different series of θ values for which the Bragg equation is satisfied. These may be compared with values obtained by measurements on known substances, and unknowns can be identified.

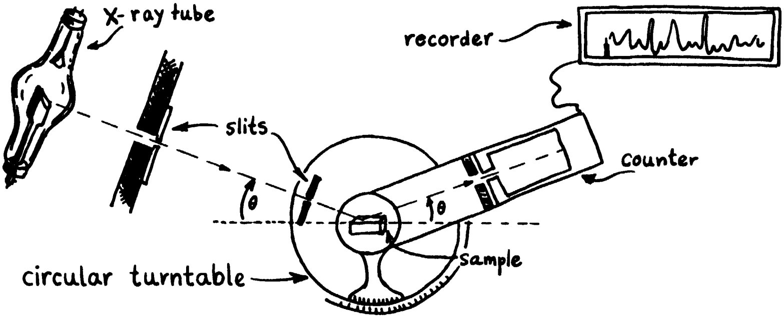

FIG. 13-1. A recording X-ray spectrometer. As the crystal is rotated, θ changes, reflection reaches the counter, and the pen traces a graph characteristic of the sample's internal arrangement.

Structure determination from Bragg data begins by computing interplanar distance ratios once d values are found. The ratios are then compared to ratios calculated for probable geometrical arrangements of atoms until, by trial and error (or more recently by automatic punch card machines which sort out data), a fit is obtained.

A simple two-dimensional analogy is as follows. Suppose someone has arranged many marbles on a table in a regular repeating pattern and covered it with a sheet of cardboard. You are then asked to find what the arrangement is, based only on whatever measurements you can make as you squint down the rows of marbles from various positions around the edge of the table. By means of a ruler, interrow distances can be found and ratios of these distances can be calculated by choosing one row as a reference. The ratios are then compared to those calculated by geometry for different marble arrangements drawn on paper. The pattern that fits the ratios is assumed to be the correct one. When this process is applied to a three-dimensional pattern containing several different sizes of atoms, it is considerably more complicated.

Metal Structures

Of the many possible geometrical patterns metal atoms might assume upon crystallization from a melt, only three are common. These are high-symmetry types where maximum coordination is possible; i.e., a given atom is within bonding distance of a maximum number of other atoms. Such structures are expected to make bond resonance easy, stability high, and be dense and hard; all general characteristics of metals.

If the atoms are imagined as spheres, there are two types of *closest packing* of spheres: *cubic closest* and *hexagonal closest packing* (both of which have 12-coordination), and a third structure called *body centered*, in which a given atom has eight near neighbors and six others only a little more distant, giving 14-coordination. X-ray analysis of metals shows these three *space lattices* are the usual ones.

1. Cubic closest packing. This may be thought of as an expanded simple cubic lattice with six additional atoms—one in each face of the cube. For this reason it is called a *face-centered cubic lattice.* As seen in Fig. 13-2, the unit cell, each atom may form 12 bonds of about equal length. Metals crystallizing in this pattern are Ca, Sr, Al, Sc, La, Ce, Th, U, Fe, Co, Rh, In, Ni, Pd, Pt, Cu, Ag, Au, Tl, and Pb.

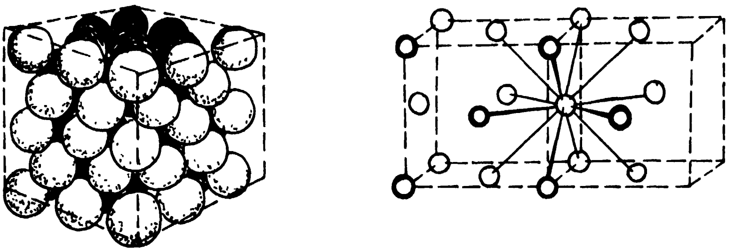

FIG. 13-2. Two views of cubic closest packing which gives the face centered cubical lattice. Twelve-coordination is demonstrated in the right-hand figure.

2. Hexagonal Closest Packing. The unit cell plus four atoms to illustrate 12-coordination is shown in Fig. 13-3. It is to be noted that atomic population is greater along the basal planes than in other directions.

Compressibility is least and electric conductance greatest in these planes. Slippage of sheets of atoms may occur under stress along the same planes but is resisted in other directions. The cubic lattice above, on the other hand, has four equivalent planes of high atomic population, and, due to this, metals of the close packed cubical structure are usually most ductile and malleable. Metals having the hexagonal lattice are Be, Mg, V, Ti, Hf, Re, Ru, Os, Zn, Cd, Pr, Nd, and Er.

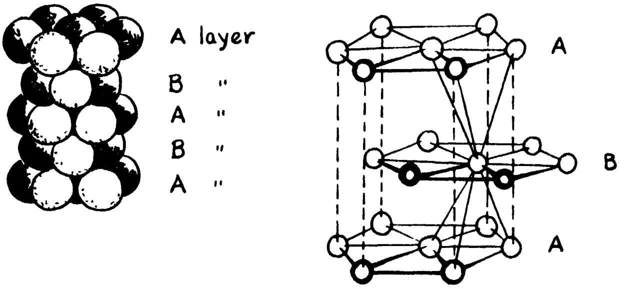

FIG. 13-3. Two views of hexagonal closest packing showing 12-coordination. Compare these to Fig. 13-2. Note alternate arrangement of planes.

3. ***Body-centered cubic.*** This lattice is not as tightly packed as the other two. A given atom has eight atoms equidistant from it and six others 15% further removed with which it may also form bonds, so the coordination number is said to be 14. Selecting the atom in the center for reference, its eight nearest neighbors are at the corners of the cubic

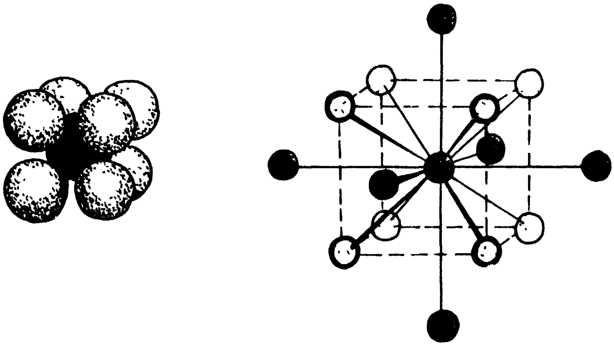

FIG. 13-4. The body-centered cubic lattice. The right-hand figure demonstrates the 14-coordination. Body-centered atoms are shaded darkly for contrast.

lattice and the six others are the body-centered atoms of the six adjacent cubes. Metals crystallizing in this form are Li, Na, K, Rb, Cs, Zr, V, Cb, Ta, Cr, Mo, W, U, and Fe.

It will be noted that several metals are capable of crystallizing in more than one of these three common lattices and the *polymorphism* (several forms) of some include rarer lattices as well.

PROBLEMS

1. Why are minerals commonly the oxides, sulfides, carbonates, and silicates of metals rather than say, acetates, nitrates, and perchlorates?

2. J. P. Slipshod reasons that increasing temperature should increase the kinetic energy of electrons and so make metals better electric conductors at high temperatures than at low temperatures. J.P.'s Uncle Frisbee argues, on the other hand, that electrons are too small and bound too tightly to be affected by heat, so electric conductance should be temperature independent. Comment on these opinions.

3. (*Library*) From data to supplement tables in this book, plot atomic numbers (abscissa) vs. melting points of the elements. Repeat for numbers vs. densities. In a few sentences summarize the trends. List the extreme values from both compilations to emphasize the spread.

4. (*Library*) For each of these metals, give briefly the main minerals, metallurgy, alloys, properties of the metals, valence states, and commercial uses of a few important compounds and alloys: (*a*) Ce (*b*) Pd (*c*) Ga (*d*) Ge (*e*) Th.

5. Early work on crystals was done by *E. Mitcherlich*, who announced in 1819 his *rule of isomorphism*. This states that compounds of similar chemical formula, such as $KH_2PO_4 \cdot H_2O$ and $KH_2AsO_4 \cdot H_2O$, often form crystals with the same external form. Show how the concept clarifies this problem: metal x forms a sulfate isomorphous with zinc sulfate heptahydrate, containing 19.81% x. Find the atomic wt of x. (Ans. 54.9).

6. Consider a simple unit cube of a metallic element comprising eight atoms. If that cube is completely surrounded and its atoms shared by bonding to similar structures on all sides (*a*) how many atoms may be said to exclusively belong to the reference cube? (*b*) If the side of the cube is 3.40 A and the density is 8.00 g/cc, what is the element's atomic wt? (Ans. (*b*) 188)

7. Certain planes of atoms in a crystal are known to be 2.80×10^{-8} cm apart. Second-order X-ray reflection is found to occur at an angle of 12°50′. Show that one can find the wavelength of the X-rays.

8. (*Library*) (*a*) Copy the structures of diamond and graphite and describe how these explain the radically different properties of the two allotropic forms of carbon.

The lubricating ability of layer lattice materials like graphite and MoS_2 has been attributed to slippage of sheets of atoms, made possible by relatively long, and hence weak, bonds between sheets. More recently it has been postulated that air molecules adsorbed between the sheets weaken the intersheet bonds and the sheets slide on these air "cushions." In one experiment, ordinary graphite was heated in an evacuated chamber, then tested as a lubricant. It was found to be abrasive. Explain how the experiment bolsters one of the above theories.

(*b*) It is known that when potassium metal is heated with graphite, the metal is absorbed, forming a red compound, C_8K, and a dark-blue compound, $C_{16}K$. X-ray measurement shows that the distance between carbons in the layers is the same as before but the distance between layers has increased. Postulate structures with rough sketches.

9. (*Library*) Find reference to (*a*) electron diffraction (*b*) neutron diffraction (*c*) powder method of *P. J. W. Debye* and *P. Scherrer*, and (*d*) goniometer of *W. H. Wollaston*. Sketch the device inferred in each and give brief qualitative statements concerning operation and use.

10. From Table 13–1 (*b*) Calculate the number of pounds of gold in a cubic mile of sea water. ($D = 63.86$ lb./ft^3). How many tons of Mg could be recovered in that volume of water?

11. In metallurgical processes, explain why sodium carbonate is a basic flux and borax is an acidic flux, yet both give basic reactions in water. Give specific examples.

12. The following are high-temperature metallurgical reactions. Give the balanced equations.

(*a*) Carbon monoxide reacts with antimonous oxide, producing antimony metal and carbon dioxide.

(*b*) Silica reacts with calcium orthophosphate and coke to give calcium metasilicate, phosphorous, and carbon monoxide.

(*c*) Ferrous metasilicate is fused with calcium carbonate, producing iron(II) oxide, calcium metasilicate, and carbon dioxide.

(*d*) Boric oxide and cuprous oxide are heated with air in an oxidizing flame and copper(II) metaborate is the product.

(*e*) Potassium carbonate, bismuthous sulfide, and oxygen react to form potassium bismuthate, potassium sulfate, and carbon dioxide.

(*f*) Manganese dioxide plus potassium hydroxide yields potassium manganate.

(*g*) Ferrous chromite, oxygen, and sodium carbonate fused together give iron(III) oxide, sodium chromate, and carbon dioxide.

(*h*) Manganese heptoxide fused with plumbous oxide yields lead(II) permanganate.

(*i*) Fusion of lead(II) sulfide, potassium nitrate, and calcium oxide produces a mixture of calcium sulfate, potassium nitrite, and calcium plumbate.

(*j*) Sodium metaphosphate and manganous oxide give a single product, sodium manganese(II) orthophosphate, upon fusion.

13. A certain compound of elements X and Y crystallizes in the body-centered cubic lattice. X atoms occupy the body-centered positions while Y atoms form the corners of the cube. J. Slipshod reasons that the simplest formula must be XY_8, but the sharpies in class conclude it is XY. Explain.

14. Consider three separate structures consisting of rigid equivalent spheres

2 Angstrom units in diameter and representing atoms in cubic symmetry. Consider further that imaginary lines connect *centers* of spheres at the corners of the cubes. Structure *A* is simple cubic, *B* is body-centered, and *C* is face-centered. (*a*) Add up the whole spheres and fractions of spheres contained within the cubes described by the imaginary lines for each structure. (*b*) Find the volumes of the cubes within the imaginary line boundaries. (*c*) Find the volumes of total sphere material within each cube. (*d*) By comparing the last two answers, determine very approximately what fraction of each cube is occupied by spheres. (Ans. (*d*) *A*, $\frac{1}{2}$ *B*, $\frac{2}{3}$ *C*, $\frac{3}{4}$)

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There are many excellent periodicals, texts, and reference books on general and specific metallurgy. Publications from The American Society for Metals are especially recommended. In addition, trade literature from the large metal companies give the very recent developments and industrial applications. These include organizations like U.S. Steel, Allegheny-Ludlum Steel, Aluminum Company of America, American Brass, Westinghouse, General Electric, Bridgeport Brass, Chase Brass, Bell Telephone, Reynolds Metals, International Nickel, Crucible Steel, Bethlehem Steel, Haynes Stellite, Jones and Laughlin Steel, Norton, Republic Steel, Revere Copper and Brass, Ryerson and Son, etc. References to specific metals are given at the ends of Chapters 15, 16, 17, 18, 19, and 20.

14

ORIENTATION FOR THE LABORATORY WORK

Semimicro laboratory methods are less expensive than macro ones as well as being more rapid, but, because of the small quantities of materials handled, good technique is mandatory. For example, a speck of rust from the ring stand or wire gauze may pass as an unnoticed contamination if one is working with a 20-ml sample, but it gives a strong test for iron if the sample volume is only 10 drops. It is incumbent upon the good student, therefore, to know and follow the procedures carefully and to organize his work neatly with clean equipment and pure reagents. By contrast, the sloppy, impatient operator who "borrows" neighbors' chemicals, seldom cleans any glassware, makes illegible notes on scraps of paper, and looks at the lab directions for the first time as he runs the unknown sample can expect only uncertain analytical results.

Apparatus

The suggested standard complement of locker equipment is listed in appendix Tables A4–8. The following items, if not present, should be made, as their use is described in later procedures.

*1. **Four Dropping Pipets (Syringes) and Calibrations.*** These pipets are in addition to two (machine made) droppers supplied with the regular apparatus. Two may be made from 6-mm tubing and two from 8-mm tubing. Steps in this preparation are illustrated below. A piece of tubing is cut about 8 in. long and heated in the middle by holding the ends and rotating it in the flame of a burner equipped with a wing top.

When pliable, the tube is held vertically and stretched (1) as the operator sights down through the tube to keep it straight. When cool, it is cut in two at some convenient point in the narrow section and the tips fire polished (2) to give fine openings. A lip is turned on the big end (3) by heating it and manipulating the glass with the end of a file or a sharpened carbon rod (as salvaged from small batteries). The lip may be reheated to plastic workability and turned over more by rotating it on a charcoal block so that its shape is convenient to hold a rubber bulb. Finally the pipet is calibrated, with the aid of a small cylinder, to deliver some commonly used volume of water like 1.0 or 0.5 ml and a label is pasted on or a file mark made to indicate the calibration (4). All labels meant to be permanent must be sealed with a coat or two of label varnish or paraffin (dissolved in benzene). The final length of the glass portion should be about 2.5 4.5 in.

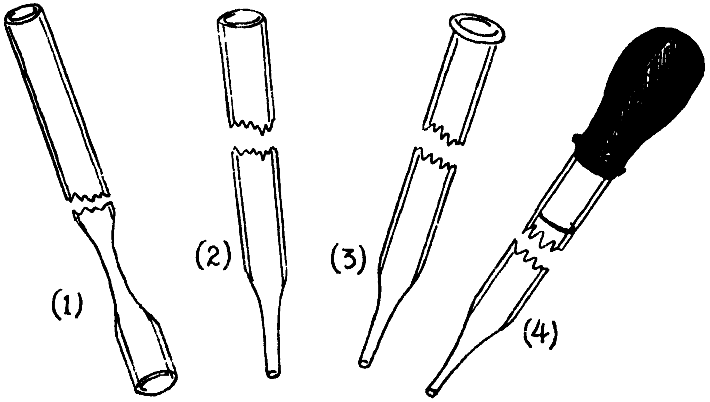


FIG. 14-1. Operations in making droppers.

For ordinary machine-made droppers, tips are fairly uniform at 3 mm O.D. and 2 mm I.D., and these droppers can be used most handily for dropwise measurements. The cautious student may wish to calibrate one or two machine droppers, as time allows, or the following table can be used. Tip diameter and surface tension, density and temperature of the liquid are the factors governing the size of drops delivered.

2. ***Three Stirring Rods.*** These may be made from 4-mm tubing by melting both ends shut or from 4-mm rod as described below. The rods may have different end shapes for special jobs and should be measured for length using the containers in which they will be employed. One rod will

TABLE 14–1. APPROXIMATE DROPWISE MEASUREMENTS FOR MACHINE MADE DROPPERS (3-mm. O.D. Tips)

Solution	Drops per Milliliter	Milliliters per Drop
H_2O	20	0.050
Dilute H_2O solutions	20	0.050
Concentrated HCl	22	0.046
Concentrated HNO_3	33	0.030
Concentrated H_2SO_4	41	0.024
Glacial HAc	47	0.021
6 *M* NaOH or NH_4OH	18	0.055
Concentrated NH_4OH	19	0.052

be needed with a blunt end for crushing solids in spot plate holes (1), another may have a cane shape for stirring and resting in 4-in. test tubes (2), and a third may be made to fit the 20-ml beakers (3). The only thing to remember is to make them long enough so they can be used in hot and corrosive solutions without danger to the fingers, yet not so long that they will make the containers top heavy and subject to tipping.

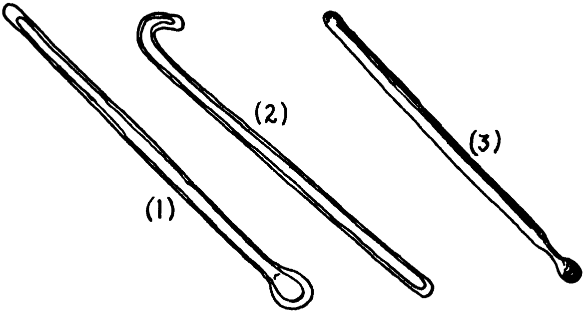


FIG. 14–2. Stirring rods with different shapes.

3. ***Student Reagent Bottles.*** Bottles in the student locker which contain the chemical supply must be labeled legibly and completely, and a protective lacquer used over the paper. Before and after filling from stock bottles, all labels should be checked and of course droppers should never be interchanged. Dropping-bottle droppers are fairly uniform and calibration of one or two will correlate drop and milliliter measurements. Concentrated NH_4OH should not be stored in the locker with concentrated acids as everything soon becomes coated with ammonium salts. The same applies to NH_4OH solutions unless this is occasionally unavoidable, and such solutions are to be well stoppered. Acids, including acid-containing

reagents and H_2O_2, should be put in glass-stoppered bottles because they cause rubber deterioration.

4. H_2S Generator. Although directions in this text are given primarily on the assumption that an aqueous 8% solution of thioacetamide will be used as an H_2S source, H_2S gas as such can be produced in a generator and conducted to the container where precipitation is to be made. Many schools have their own design for the H_2S generator and only a simple one is sketched here. If a set up similar to this is employed, the student will have to make a number of *capillary delivery tubes* because they become contaminated with sulfides that are difficult to remove. The cartridge in Fig. 14–3 contains the commercially available product "Aitch-tu-ess," or a self prepared mixture of sulfur, paraffin, and asbestos, either of which when heated gives H_2S gas. If a cylinder of H_2S or a Kipp generator is employed, a scrubbing bottle should be in the line between source and sample.

In putting glass tubing through holes in stoppers one should lubricate it with a little glycerine then wash off the excess with water. As an added precaution, tubing may be held through several folds of a towel to minimize danger of cutting one's self in case of breakage.

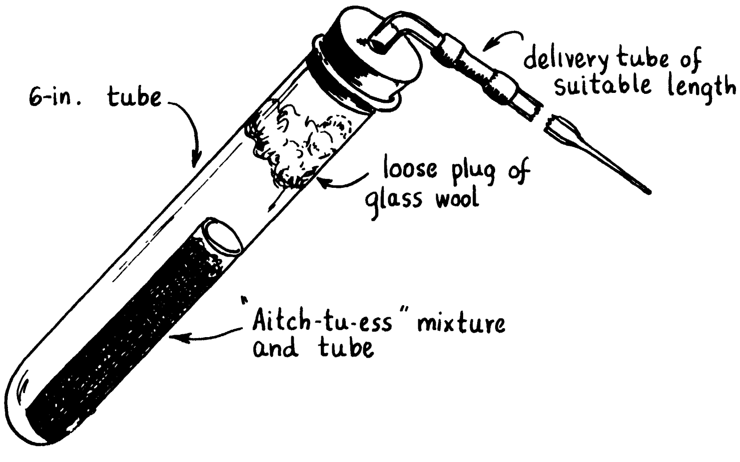


Fig. 14–3. One type of student H_2S generator.

5. Gutzeit-Fleitmann Apparatus. These tests are further described in Chapter 16 under **arsenic** and **antimony**. A piece of 8-mm tubing is heated and drawn as described in section 1 above, this time to produce a tip with about 4-mm O.D. It is cut off to the dimensions given in the accompanying figure, fire polished, and fitted snugly to a 3- or 4-in. test tube with a single-hole cork or stopper.

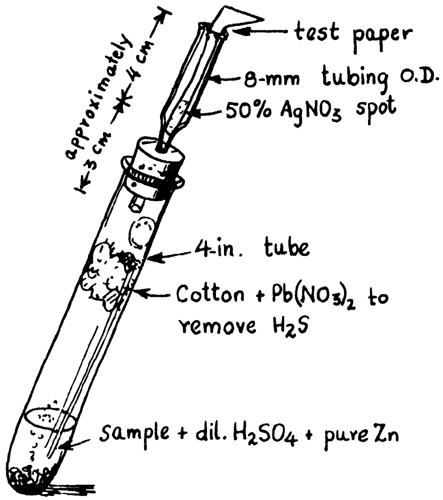


FIG. 14-4. The Gutzeit-Fleitmann apparatus.

6. ***Platinum Wire.*** Seal a 2-in. piece of 24- or 26-gauge platinum wire into a piece of glass tubing or rod by heating the glass until soft and pushing the wire into it. Anneal the metal-to-glass seal with a semi-luminous

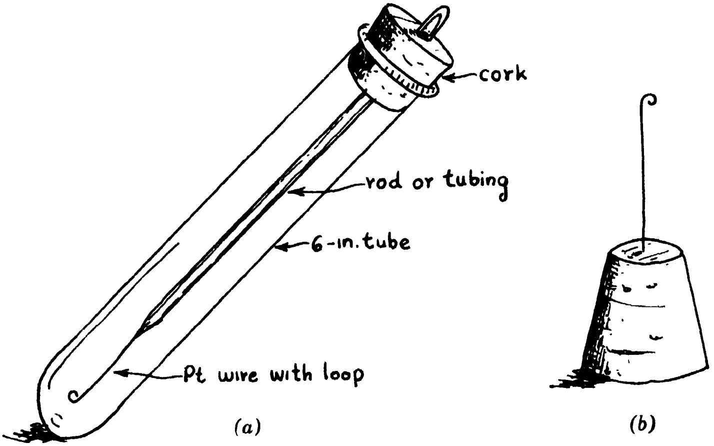


FIG. 14-5. (*a*) Pt wire in a test tube. (*b*) Nichrome wire with cork handle.

flame for at least a minute. Assemble the rest of the apparatus as pictured. Use is made of this in the first parts of special experiments 4 and 5.

Nichrome (Ni—Cr—Fe alloy) wire may be used in most cases as a substitute for platinum. When it becomes contaminated it is simply discarded. Two-inch pieces are bent into a loop at one end and pushed into a small cork at the other.

7. ***Wash Bottle.*** The correct angles for the glass bends are conveniently made by drawing them on an asbestos board, then bending hot 6-mm tubing to fit the pattern, and later cutting to the dimensions. The tip is drawn out as described in section 1. Its I.D. should be about 1 mm. A 125-, 200-, or 250-ml Erlenmeyer or Florence flask may be used for a wash bottle, and heavy string may be wound around the neck for insulation in case hot water is the wash liquid. A combination of cork sheet and tape works in the same capacity.

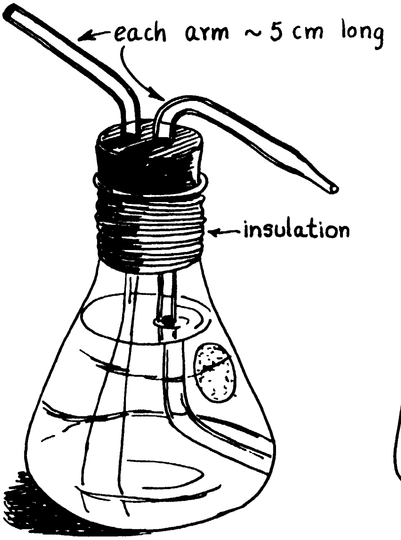


FIG. 14–6. Wash bottle made from a 125-ml Erlenmeyer.

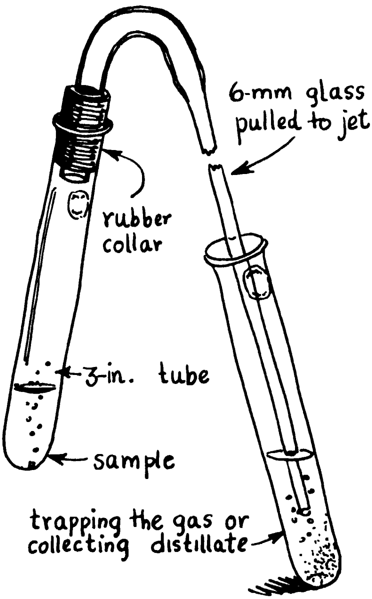


FIG. 14–7. Gas delivery or distillation setup.

8. ***Gas Delivery and Small Distillations Apparatus.*** In the investigation of gas-releasing reactions or in carrying out distillations, the device in Fig. 14–7 is useful. The reaction mixture is placed in the test

tube and the delivery tube is placed inside another tube. This second tube may contain an absorbing solution, as $Ca(OH)_2$, to trap CO_2 or SO_2, or may stand in a beaker of cold water for condensation of vapors, as in the distillation of HSCN.

9. Spoon for Solids. Seal one end of a piece of 4-mm tubing shut (1) by heating, and while hot, blow a small bulb on it (2). Direct a small, pointed flame to one side of the bulb and when it becomes hot, suck in slowly at the open end of the tube to pull in the glass and form a spoon (3). Cut the tubing off at a convenient length, say about 10 cm, then seal shut that end in the flame (4).

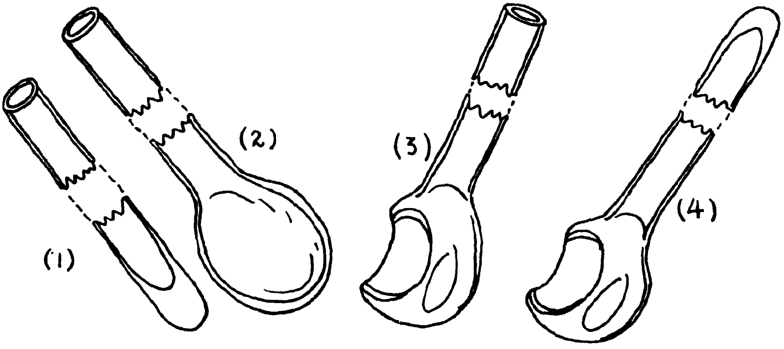


FIG. 14-8. Steps in blowing a glass spoon.

Techniques

Methods of conducting special tests like those involving the blow pipe, filter paper spots, borax beads, fusions, etc., are described in the appropriate laboratory directions. Some general techniques of using the locker equipment are summarized below.

10. Heating Solutions. Solutions boiled in small test tubes tend to superheat and suddenly bump out. This may be avoided by slow, careful heating near the top of the liquid if a direct flame is used, though there is always still a danger that solutions may "bump" or be inadvertently heated to dryness and the residues baked. One can circumvent this by the use of air or water baths as illustrated in Fig. 14-9. Such baths are purchased or made from beakers of desired sizes with a lead, aluminum or copper sheet bent over the top and having in it holes of sizes to fit test tubes or micro beakers. Alternatively, a twisted wire can be made to do the holding. Rings cut from rubber tubing are put on the tubes as collars to fix their positions in the perforated plate, or the test tube holder is left on a tube for the same purpose. Rubber bands should be replaced regularly as they dry out and become brittle.

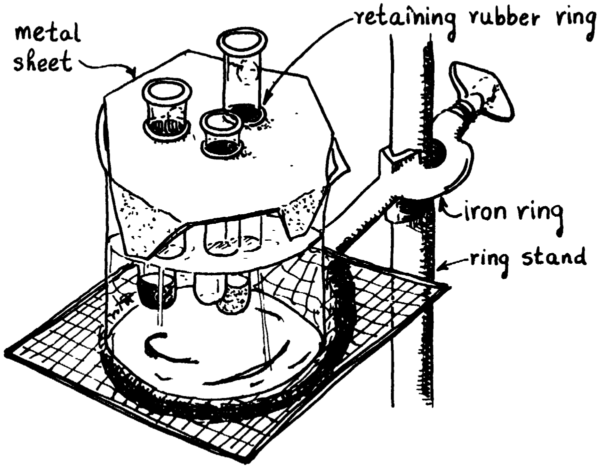


FIG. 14–9. Water bath made from a perforated metal sheet bent over a beaker. Water is emptied and the vessel is used dry as an air bath.

Care must be taken with evaporations if the setup is used as an air bath, because bumping due to super heating can occur. This is avoided by using a low flame and allowing some minutes for the operation. As the whole apparatus retains heat after the fire is shut off, evaporation continues and the last few drops of moisture in a tube should be driven off in this way. Too much heat can change the chemical composition of some residues. Evaporations giving noxious fumes are to be done under the hood.

11. Handling Solids. It is best to handle solids in glass only in order to guard against reaction with or contamination from paper or metal spatulas. A spatula should not be used to transfer solid chemicals from a stock bottle to another container; rather one taps out the material on a watch glass and measures with the balance, spatula, or spoon what is needed from that, in order to keep the original chemical supply of unquestioned purity. A little practice in quantity estimation helps.

Small amounts of solids can be pulverized using a short, blunt 8-mm stirring rod in one of the depressions of a spot plate. Using a very fine carborundum dust on one depression with the rod will give grinding surfaces like those of a mortar and pestle, and solids will not slip out when put under pressure. These rough surfaces must be well cleaned before use.

The student should note the remarks on the labels of side-shelf solids in reference to their reaction with CO_2 and H_2O from the air and should keep these chemicals particularly tightly closed when not being transferred.

The glass spoon described in section 9 may be calibrated by filling it level with a solid like NaCl and weighing the salt. Except with technical grade chemicals, the spoon should not be used to remove solids from bottles because of the danger of contamination of the main supply, even though this smooth spoon can be readily cleaned.

12. Separations. Mixtures of liquids and solids are separated by means of a *centrifuge* unless the particulate phase settles rapidly and/or only an approximate separation is needed, whereupon simple *decantation* is used. The *supernatant liquid* is called the *centrate* or *decantate*, respectively, in these operations, and the solid is called the *residue*. The liquid is drawn off as pictured in Fig. 14–10, with the operator being careful not to remove it too rapidly or some residue may come with it. If more complete separation is demanded, the solid is mixed with wash liquid,

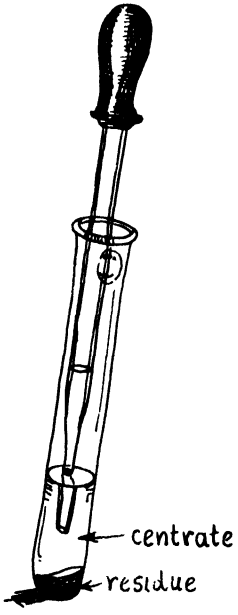


FIG. 14–10. Taking off the centrate with a pipet after centrifuging.

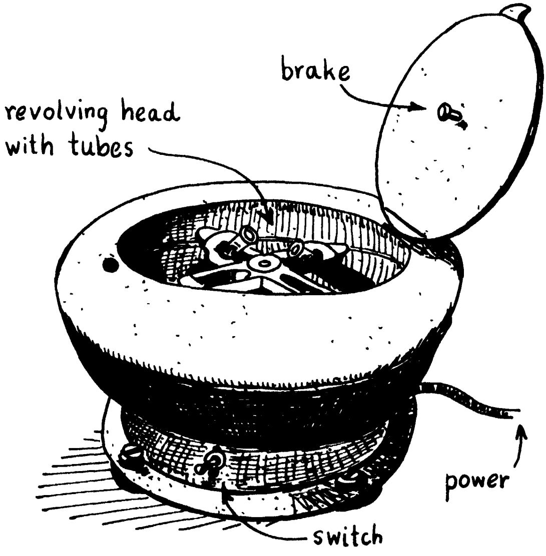


FIG. 14–11. A centrifuge.

perhaps heated, then recentrifuged, and the wash liquid removed as before. Laboratory directions will be explicit on this.

Pipets and droppers are never to be used to withdraw liquids from reagent shelf bottles.

A *motor-driven centrifuge* is recommended, having head openings and cylinder depths to fit both 3- and 4-in. test tubes. *The solution to be centrifuged is balanced on the opposite side of the machine with another tube containing the same amount of solution or water so that the bearings will not be worn unduly. Tubes are not to be over two-thirds full. Any solution spilled on the centrifuge should be cleaned up immediately and if such an accident occurs with corrosive fluids the instructor should be notified so he may keep damage to the machine at a minimum.*

A good centrifuge operates at 1500–4000 revolutions per minute (rpm) and the usual laboratory type has a radius of 8–10 cm. Maximum speed is attained in 15–30 sec and most precipitates are settled by the centrifugal force in 30–60 sec, after which time the switch is turned off and the revolving head slowed with gentle brake or hand pressure. *The centrifuge is a relatively expensive instrument and is not to be mistreated.*

The centrifugal force, f, acting on a settling particle of mass, m, is

$$f = 4\pi^2 mRV \qquad (14\text{–}1)$$

where R is the centimeter radius measured from the center of the centrifuge to the end of the test tube, and V is the rpm. (Most physics books derive this formula.) For purposes of contrast with gravitational induced settling it can be shown that the centrifuge's force compared to the gravitational force, g, is related by

$$f = g(1.12 \times 10^{-5})RV^2 \qquad (14\text{–}2)$$

For a centrifuge with a 10-cm radius whirling at 2000 rpm its force is 448 times the gravitational force, or it settles particles in 1/448 the time. The term, m, in equation 14–1 is recognized to be governed by the density of the solid and the size of the particles. Not considered here is the viscosity of the liquid medium and its density as these are not important to us.

13. Washing Equipment. Since only small quantities of materials are handled, general cleanliness must be observed with the laboratory implements. Dirty equipment should be cleaned between analytical operations. For most purposes, a test tube brush and mixture of scouring powder and detergent, followed by rinses with tap and distilled water give good results. In extreme cases where this fails, a little aqua regia (concentrated HCl and HNO_3) heated under the hood may be tried. A clean feather and soap solution can be used to clean pipets and small-diameter tubes, though it is frequently more satisfactory to discard stubbornly soiled glass tubing and to prepare new bends and jets.

14. Mixing Solutions. Solutions can be mixed using a stirring rod in a test tube of solution or by holding the test tube lip between the index finger and thumb of one hand and tapping the lower part of the tube with the index finger of the other hand.

Caution should be used in mixing solutions which are concentrated, contain strong oxidants, or are hot. One should add acids and bases to water, rather than the reverse, to avoid splattering. Add small amounts with stirring to see what will happen before mixing larger quantities. Point the container away from everyone.

Preliminary Experiments

Chapters 15–22, inclusive, deal with the analysis of 32 cations and 18 anions. Of the cations, 24 have been analyzed in beginning qualitative courses for years and schemes of separation and identification are well known and are given here as directions for separating and identifying mixtures of their compounds. Before the unknown sample is run with these *procedures*, however, it is instructive to perform several *preliminary tests* on the ions to be analyzed in order to characterize their chemical behavior as an aid in recognizing them in the samples. One should also get from the preliminaries the reaction equations, the evidences to look for which constitute positive tests, correlations among similarly acting ions, and something of the sensitivities and interferences of the supplementary tests. Some of the tests are *general* for a group of ions while some are *specific* for a single ion. When the latter follow positive reaction with the general reagent, they are called *confirmatory tests.*

The *test solutions* on which preliminary investigations are made contain 10 mg of the ion under analysis per milliliter of solution, so one drop contains about 0.5 mg of that ion. By running tests on various dilutions one is able to compare quantities of precipitates or depths of colors obtained with the sample and so *estimate quantities* in the sample as small, medium, or large. He is also able to determine in this way the *sensitivity* of a given method or reagent and to compare it with other tests. Directions for a number of these opportunities are given later. Prior to running an unknown, one may, if desired, go through a known mixture (made from the test solutions) according to the procedure. If one performs the preliminary studies carefully, takes notes on them and understands their relation to the equations and procedures which follow, he has little trouble with the unknown sample. It is common practice to have an unknown for each group of chemically similar ions and then a general unknown that may contain any combination of them.

The discussion of eight "less familiar" metals in Chapter 20 does not include a procedure for separations, although preliminary tests are given. These tests are sufficient to identify the elements in their usual alloys and matrixes.

Chapter 22 on anion analysis does not contain any general separation procedures beyond the use of three screening reagents, since distinctive evidences are available as outlined in the preliminary tests to identify any of the anions in the presence of any others. One then reuses these tests to analyze the unknowns.

In making any analysis, it is safest to compare results with a check of a known sample from the shelf test solutions, and for specific tests it is wise to run a *blank* to see if unknown factors such as contamination or a deteriorated reagent have given false indications. A blank is a test in which everything but the ion in question is included to give a survey of the other factors present.

Chapter 23 is a compilation of special experiments to illustrate principles, special methods, and applications of qualitative testing.

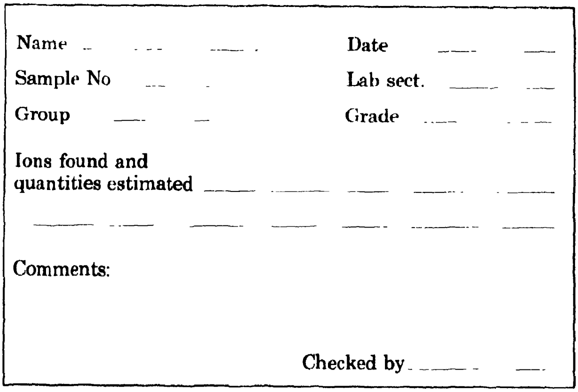
The Laboratory Notebook

Organization of a laboratory notebook is dictated by the instructor's preference. The following is one idea.

A separate notebook is used exclusively for laboratory directions, observations, and results, and is brought to the laboratory each time. An inexpensive spiral bound book containing about 50 sheets of 8½ × 11 in. paper is satisfactory. For each group of ions studied, the student writes in his own words the procedure he will use on the sample. This is done in abbreviated fashion from the text directions and his experience with preliminary tests in such clarity that he can analyze samples from his notes alone. This is not an exercise in penmanship but an evidence that the student really understands the unit of work involved, since he must select for outline all the important ideas. Following the procedure are written observations on the preliminary laboratory work, lecture notes that pertain to the same thing, and answers to laboratory questions that might be chosen from the text or another source. This work being completed, the student is well prepared to tackle the sample. If each person organizes his book in the same way, including numbering of numbered sections and experiments from the text, the notes are easily checked and graded.

Reporting the unknown sample results is again a matter of the instructor's preference. If separate report forms are not used then a space, say

3 × 5 in., is reserved in the notebook. It might look like this in simple form:



Name

Date

Sample No

Lab sect.

Group

Grade

Ions found and quantities estimated

Comments:

Checked by

FIG. 14–12. One form of unknown report.

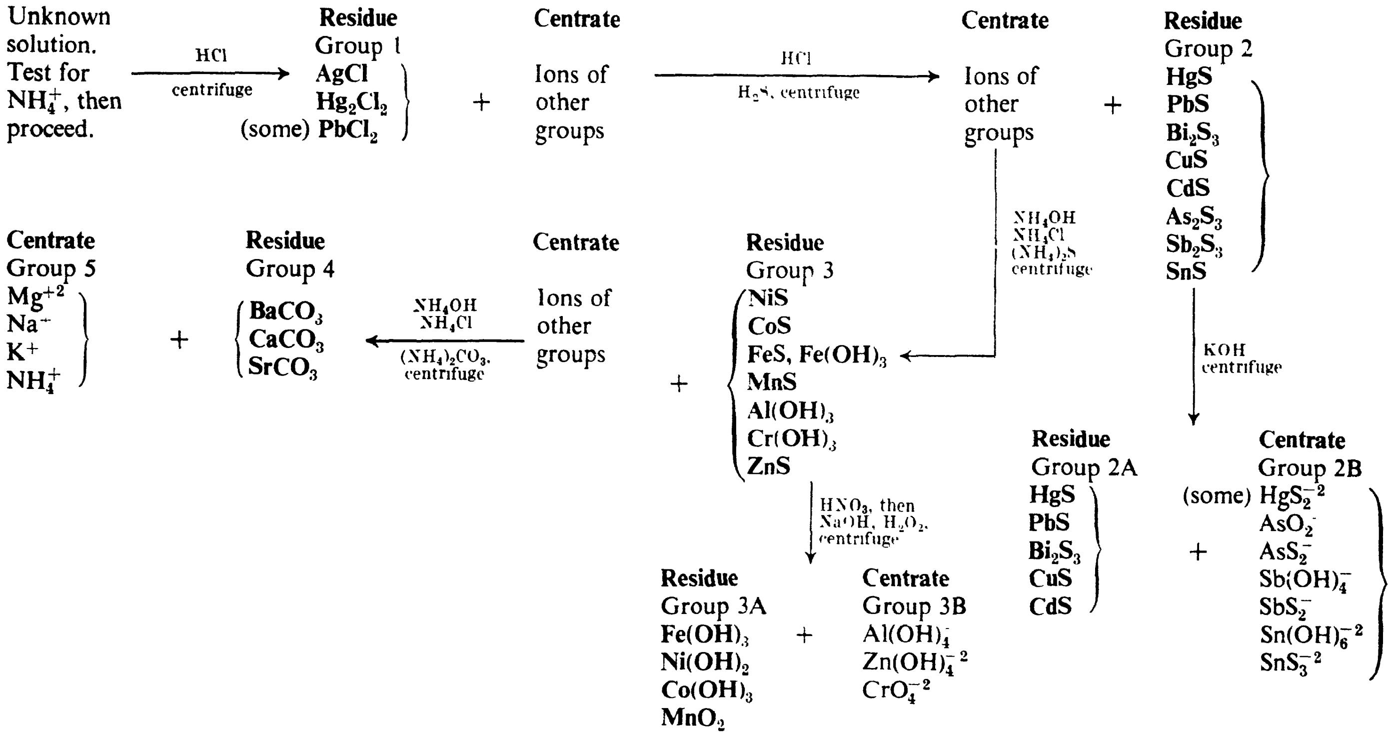
More detailed report forms may call for the results from certain procedural steps, reagents used, colors of important precipitates and solutions, reaction equations, and conclusions.

Survey of Cation Separations

A considerable portion of the laboratory time is usually devoted to analysis of 24 cations (including the two oxidation states of mercury and the ammonium ion), and a brief look at this segment of work is helpful in orientating the student.

If one has a mixture of most any combination of these 24 ions, the *flow sheet* given on p. 229 presents a scheme for separating them into five groups for further investigation, by use of reagents that precipitate only certain ions under given concentration and temperature conditions. Thus, if dilute HCl is added to the general solution mixture, Ag^+, Hg_2^{+2}, and Pb^{+2} precipitate as chlorides and are segregated by centrifugation. These metals are called group 1. The *p*H of the supernatant liquid is adjusted to about 0.6 and H_2S or thioacetamide, CH_3CSNH_2 (a source of H_2S), is put in and group 2 metals precipitate as sulfides. These include Hg^{+2}, Pb^{+2}, Bi^{III}, Cu^{+2}, Cd^{+2}, As^{III}, Sb^{III}, and Sn^{II}. (The mercuric mercury is not obtained in group 1 and lead chloride is not completely precipitated, so these metals may be detected in both groups, although only the mercury is to be reported as a different ion because the two oxidation states have different properties.) The centrate from the precipitation

FLOW SHEET—GROSS SEPARATION OF CATION GROUPS*



* (See flow sheets in Chapters 15, 16, 17, 18 and 19 for the isolation and testing of individual ions.)

again contains ions of subsequent groups and is saved for their separation. The residue of group 2 sulfides is divided chemically into sub-group 2A, sometimes called the "copper group," and subgroup 2B, also called the "tin group," by addition of 6 *M* KOH, which dissolves the amphoteric B group sulfides of As, Sb, and Sn and leaves the other sulfides unaffected. The centrate from the original group 2 precipitation is buffered with an ammonia system, and $(NH_4)_2S$ is added. In this basic solution the seven ions of group 3 precipitate, Fe^{+3}, Al^{+3}, and Cr^{+3} as hydroxides, Mn^{+2}, Zn^{+2}, Co^{+2}, and Ni^{+2} as sulfides.

The group 3 residue is treated with NaOH and H_2O_2 to divide it into two groups: subgroup 3B, the "aluminum group," which includes Al, Zn, and Cr in solution and leaves behind a residue of the others as subgroup 3A, the "iron group." The centrate from the original precipitation of group 3 is treated with $(NH_4)_2CO_3$ in an alkaline buffer solution which throws out the group 4 ions, Ba^{+2}, Ca^{+2}, and Sr^{+2}, as carbonates. The centrate from this contains Mg^{+2}, Na^+, K^+, and NH_4^+, ions which are called group 5 and need no group precipitating agent. (Since NH_4^+ was added as ammonia or its salts in the procedure, it will always be present in group 5 of the general unknown, so the original sample is tested for this ion.) The five groups are subjected to further separations and their components verified. Detailed directions and equations are given in the ensuing chapters for all necessary steps, and summaries in the form of flow sheets are also presented to give the over-all pictures in minimum detail.

15

CATION GROUP 1

The three heavy metals of group 1 are taken together as an analytical unit because of the low solubility of their chlorides, although they are in three different groups of the periodic table as indicated:

VIII	IB	IIB	IIIA	IVA	VA
			B	C	N
			Al	Si	P
Ni	Cu	Zn	Ga	Ge	As
Pd	**47** **Ag** **107.880**	Cd	In	Sn	Sb
Pt	Au	**80** **Hg** **200.61**	Tl	**82** **Pb** **207.21**	Bi

FIG. 15-1. The periodic table in the vicinity of the group 1 metals.

Silver

This element has the highest heat, electric conductance, and light reflectivity of any metal and is second only to gold in ductility. It is found free in nature as well as in sulfide (silver glance) and chloride (horn silver) minerals. The metal is dissolved from ores by sodium cyanide solutions in which soluble silver cyanides form. They are later decomposed with zinc:

$$AgCl + 2CN^- = Ag(CN)_2^- + Cl^-$$

The potential is

$$Ag + 2CN^- = Ag(CN)_2^- + e^- \qquad E^\circ = 0.29$$

The metal is used in mirrors, dinnerware, plating, jewelry, and coinage. Silver halides are photosensitive and used in photographic emulsions. Silver is fairly inert but will dissolve in nitric acid, alkali cyanides, and molten strong alkalis in the presence of air. Its sp. gr. is 10.5, its b.p. is 1940 C, and m.p. is 960.5 C.

The *oxidation states* of the metal are (I), (II), and (III), as are those of the other *coinage metals*, Cu and Au, but only (I) is important. The higher states can be produced by anodic, peroxydisulfate, or ozone oxidations of Ag^+, three methods which are common in research on higher oxidation states of many elements. In nitric acid for example

$$Ag^+ + O_3 = AgO^+ + O_2 \quad \text{(slow)}$$

$$Ag^+ + AgO^+ + 2H^+ = 2Ag^{II} + H_2O \quad \text{(fast)}$$

These unfamiliar oxidation states have large negative potentials as expected:

$$Ag^+ + H_2O = AgO^+ + 2H^+ + 2e^- \qquad E^\circ = -2.0$$

$$Ag^{+2} + H_2O = AgO^+ + 2H^+ + e^- \qquad E^\circ = -2.1$$

which indeed are so large that they decompose water with the evolution of oxygen. Ag^{II} coordinates four groups.

The Ag^+ ion is colorless and easily reduced. The half reaction is

$$Ag = Ag^+ + e^- \qquad E^\circ = -0.80$$

It forms many compounds of low solubility and many stable complex ions having 2-coordination. Table 15–1 lists some of the very slightly soluble silver compounds in order of decreasing equilibrium $[Ag^+]$. Among the halides, AgF is peculiar in being quite soluble; its saturated solution is about 14 *M* at room temperature. *Silver nitrate* is the most common silver compound and its solubility is also high, 3000 g dissolving in a liter of H_2O at 30 C. It is made by the action of nitric acid on the metal. Silver nitrate does not dissociate strongly in water and is appreciably soluble in many organic liquids. With strong bases, Ag^+ gives Ag(OH), which spontaneously changes to black, insoluble Ag_2O, an oxide with alkaline reactions strong enough to indicate that silver salts are not going to be hydrolyzed greatly. Among other silver compounds worthy of mention, the *nitrite*, *sulfate*, and *acetate* are of moderately low solubility, and some of the other silver salts are of interest because their colors give the analyst a clue to their identity: Ag_3PO_4 is yellow, Ag_2CrO_4 dark red, and $Ag_4[Fe(CN)_6] \cdot H_2O$ yellow.

Soluble complexes other than the *cyanide* already mentioned are those with *halides*, *ammonia*, and *thiosulfate*, as $AgCl_2^-$, $Ag(NH_3)_2^+$, and $Ag(S_2O_3)_2^{-3}$. The first accounts for the fact that AgCl is considerably more soluble in moderately strong HCl solutions than in H_2O, the common ion effect notwithstanding; the second is of analytical importance because of its formation when AgCl from the group 1 precipitation is solubilized in NH_4OH; and the third has practical value because it is the soluble product from treatment of exposed film (containing unreacted silver salts) with sodium thiosulfate (hypo).

In the qualitative analytical procedure, silver is precipitated as the chloride, dissolved as the ammine complex, and reprecipitated by nitric acid, which breaks up the complex and permits recombination of silver and chloride ions:

$$AgCl + 2NH_3 = Ag(NH_3)_2^+ + Cl^-$$

$$Ag(NH_3)_2^+ + Cl^- + 2H^+ + 2NO_3^- = AgCl + 2NH_4^+ + 2NO_3^-$$

The following table summarizes silver reactions with regard to slightly soluble compounds and slightly dissociated Werner ions. *The order in all*

TABLE 15–1. EQUILIBRIUM CONSTANTS FOR SOME SILVER REACTIONS

Reactions (in order of decreasing $[Ag^+]$)	K	Formula Weight
$AgAc = Ag^+ + Ac^-$	2.3×10^{-3}	166.92
$AgNO_2 = Ag^+ + NO_2^-$	1.2×10^{-4}	153.89
$Ag_2CO_3 = 2Ag^+ + CO_3^{-2}$	8.2×10^{-12}	275.77
$AgIO_3 = Ag^+ + IO_3^-$	3×10^{-8}	282.80
$Ag_2CrO_4 = 2Ag^+ + CrO_4^{-2}$	1.9×10^{-12}	331.77
$AgCl = Ag^+ + Cl^-$	2.8×10^{-10}	143.34
$AgSCN = Ag^+ + SCN^-$	1×10^{-12}	165.96
$AgBr = Ag^+ + Br^-$	5×10^{13}	187.80
$AgCN = Ag^+ + CN^-$	1.6×10^{-14}	133.90
$Ag(NH_3)_2^+ = Ag^+ + 2NH_3$	5.9×10^{-8}	141.94
$AgI = Ag^+ + I^-$	8.5×10^{-17}	234.80
$Ag(S_2O_3)_2^{-3} = Ag^+ + 2S_2O_3^{-2}$	6.0×10^{-14}	332.14
$Ag(CN)_2^- = Ag^+ + 2CN^-$	1.8×10^{-19}	159.90
$Ag_2S = 2Ag^+ + S^{-2}$	1×10^{-50}	247.82

following compilations of this type is that of decreasing equilibrium molar concentration of the ion under discussion. Thus Ag_2S, having the least $[Ag^+]$ in equilibrium with it, will form by the addition of S^{-2} to any other silver compound or ion, etc. *For the purpose of these tables, complex ions and complexing agents will be taken as* 1 *M and the metal ion calculated accordingly.* Thus, if a solution of $Ag(NH_3)_2^+$ is 1 *M*, and the $[NH_3]$ in the solution is also 1 *M* $[Ag^+]$ is 5.9×10^{-8} *M*.

Silver is analyzed *quantitatively* by both gravimetric and volumetric means. It is either precipitated as the chloride, dried at 110 C, and weighed as AgCl, or the Ag^+ is titrated with standard thiocyanate (Volhard method). Ferric ion is used as an indicator in the latter—red $Fe(SCN)^{+2}$ forms when the silver has just been quantitatively precipitated as AgSCN.

Lead

Lead is a soft, malleable, not very ductile metal. The ore, galena, PbS, is roasted to provide PbO which is carbon reduced. Lead is used in radiation shielding and on electric cables and in important soft, low-melting mixtures with Sn, Sb, Bi, and Cu to form such alloys as pewter, battery plate, shot, solder, white metal, rose metal, and type metal. Important industrial lead compounds are the *sulfate*, *chromate*, *basic carbonate*, and *oxides* which are used in paints, and the *silicate* which is used occasionally in glass and ceramic manufacture. The metal's sp. gr. is 11.337, m.p. is 327.4 C, and b.p. 1613 C.

Two *oxidation states* of lead are known, (II) and (IV). Oxides of both are amphoteric, leading to four series of lead compounds: Pb^{+2}, *plumbous*; Pb^{IV}, *plumbic*; *plumbites* possibly as $Pb(OH)_4^{-2}$ or as PbO_2^{-2} and $HPbO_2^-$ in less basic media; and *plumbates* as $HPb(OH)_6^-$. Pb^{IV} compounds can be prepared by anodic oxidation. The most familiar of these is PbO_2, which is pressed on to storage battery plates. The battery discharge reaction is

$$\mathbf{Pb + PbO_2} + 4H^+ + 2SO_4^{-2} = \mathbf{2PbSO_4} + 2H_2O$$

and the half cells from which one can calculate an emf for the whole cell are

$$\mathbf{Pb} + SO_4^{-2} = \mathbf{PbSO_4} + 2e^- \qquad E^\circ = \quad 0.36$$

$$\mathbf{PbSO_4} + 2H_2O = \mathbf{PbO_2} + SO_4^{-2} + 4H^+ + 2e^- \qquad E^\circ = -1.68$$

Pb^{IV} compounds are easily hydrolyzed and reduced in water solution, and as far as analysis here will be concerned, only Pb^{+2} compounds will be considered.

Pb^{+2} is colorless and stable in water solutions below *p*H 7. Between *p*H 7 and 13, $Pb(OH)_2$ (hydrated) is formed, and above 13, plumbites result. The *acetate*, *chlorate*, and *nitrate* are soluble though they ionize but feebly and hydrolyze (unless some acid is present) to precipitate basic salts of variable composition nominally written as Pb(OH)Cl, etc. Most lead salts have low solubility. Lead does not form complexes as readily as does silver, and other than the hydroxides listed above, the *chloro complexes* like $PbCl_4^{-2}$ will be the only ones mentioned here.

TABLE 15–2. EQUILIBRIUM CONSTANTS FOR SOME LEAD REACTIONS

Reactions (in order of decreasing $[Pb^{+2}]$)	*K*	Formula Weight
$PbCl^+ = Pb^{+2} + Cl^-$	7.75×10^{-1}	242.67
$PbCl_2 = Pb^{+2} + 2Cl^-$	1.6×10^{-5}	278.12
$PbBr_2 = Pb^{+2} + 2Br^-$	4.6×10^{6}	367.05
$PbF_2 = Pb^{+2} + 2F^-$	4×10^{-8}	245.21
$PbI_2 = Pb^{+2} + 2I^-$	8.3×10^{-9}	461.05
$PbSO_4 = Pb^{+2} + SO_4^{-2}$	1.3×10^{-8}	303.27
$Pb(OH)_2 = Pb^{+2} + 2OH^-$	4×10^{-15}	241.23
$PbC_2O_4 = Pb^{+2} + C_2O_4^{-2}$	8.3×10^{-12}	295.23
$PbCO_3 = Pb^{+2} + CO_3^{-2}$	1.5×10^{-13}	267.22
$PbCrO_4 = Pb^{+2} + CrO_4^{-2}$	2.0×10^{-16}	323.22
$Pb_3(PO_4)_2 = 3Pb^{+2} + 2PO_4^{-3}$	1×10^{-54}	811.59
$PbS = Pb^{+2} + S^{-2}$	4×10^{-26}	239.27

Lead is gravimetrically determined in *quantitative analysis* by oxidation to PbO_2 at a Pt electrode from HNO_3 solution or by precipitation and weighing as $PbSO_4$. Dithizone is a very sensitive color reagent for lead and used to measure it quantitatively in concentrations even below 1 ppm. (See special experiment 10.)

Mercury

Mercury is the only metallic element which is a liquid at 25 C and one atmosphere (melting points of other low melting metals are Cs = 28.5 C, Ga = 29.75 C). The common ore is cinnabar, HgS, which is roasted to give the oxide, which in turn decomposes with heat yielding oxygen and mercury. The metal is commercially distilled for purification in the presence of air which oxidizes usual impurities of more active metals like Cd to drosses that are left behind when Hg is vaporized. Washing in dilute HNO_3 followed by a vacuum redistillation yields almost 100% pure Hg. Its sp. gr. is 13.546, m.p. is − 38.87 C, and b.p. 356.95 C. The metal has a near linear expansion with temperature which makes it useful in thermometers. It is also used in precision casting to make unusually smooth ceramic molds for the production of close tolerance radar and jet engine components. Hg conducts electricity relatively well in the liquid state and is utilized in switches; it also conducts in the vapor (monatomic) state, the mercury vapor lamp giving a brilliant bluish light. Most metals, Pt, Co, Ni, and Fe excepted, dissolve in mercury. The liquid mixtures are called amalgams (some are true solutions, others suspensions) and use is made of them in gold and silver recovery and in dental fillings. Mercury compounds do not have wide utilization; all the soluble ones are poisonous. *Mercurous chloride*, calomel, is used as a medicine for liver stimulation. *Mercuric fulminate*, $Hg(CNO)_2$, is used in caps to set off dynamite.

The two oxidation states are (I) *mercurous* and (II) *mercuric*. There is probably no Hg^+; instead, mercurous mercury exists in the solid compounds and in solution as Hg_2^{+2}. See problem 13, p. 246. This doubled ion is possible because the electron structure of the Hg atom is complete through the 5*d* shell and has two more electrons in the 6*s*. Loss of one of the 6*s* electrons and coupling of two such ions by sharing their remaining 6*s* electron gives mercurous ion the structure $^+Hg\!:\!Hg^+$. There are various methods of proving this from (*a*) equilibrium constant evaluation experiments as explained in Chapter 9 for the I_3^- ion; (*b*) conductivity comparison with other heavy metal salts of both possible types MX_2 and MX; and (*c*) X-ray studies on the crystal structure of mercurous chloride. The last method shows, for example, that the arrangement is $(\text{—Cl—Hg—Hg—Cl—})_x$, whereas in silver chloride the structure is $(\text{—Cl—Ag—Cl—Ag—})_x$. Most of the reactions of mercurous salts are those of reduction to the metal or oxidation to Hg^{+2}. The potentials are

$$2Hg = Hg^{+2} + 2e^- \qquad E^\circ = -0.79$$

$$Hg_2^{+2} = 2Hg^{+2} + 2e^- \qquad E^\circ = -0.92$$

$$Hg = Hg^{+2} + 2e^- \qquad E^\circ = -0.85$$

These show that reductions from mercuric to mercurous ion and to the free metal are easy, a fact utilized as a test for the element.

The mercurous salts are freely ionized and Hg_2^{+2} forms few complexes. Most mercurous salts have low solubility. Hg_2Cl_2 is the most common mercurous compound and is precipitated in cation group 1; it is more soluble than the *bromide*, *iodide*, or *sulfide*. The common soluble mercurous salts are the *acetate*, *nitrate*, and *sulfate*, but Hg_2^{+2} hydrolyzes slowly and basic salts are prone to precipitate from these solutions. Adding strong base to Hg_2^{+2} results in precipitation of Hg_2O, which on prolonged standing disproportionates to $HgO + Hg$.

Mercuric compounds resemble those of lead and cadmium in that most are only a few per cent dissociated at moderate dilutions, and the amount varies with the anion present. The Hg^{+2} ion hydrolyzes in water since $Hg(OH)_2$ is a weak base giving *basic* (*hydroxy*) *salts*, and ammonolyzes with ammonia in similar fashion to give *basic* (*amido*) *salts*. Hg^{+2} forms a soluble *tetraammine complex* but it is stable only in concentrated NH_4OH. A salt both ammonolyzed and hydrolyzed is HO—Hg—NH—Hg—I, the product from Nessler's test (see Chapter 16, Hg^{+2} tests). *Mercuric sulfide* is the most insoluble mercury compound, but it will dissolve appreciably in alkaline sulfides or polysulfides to give HgS_2^{-2}, and dissolves completely in aqua regia, giving $HgCl_4^{-2}$. Hg^{II} is found in a number of soluble complexes as listed below; the coordination number is 4. Normal salts which are soluble include $HgCl_2$, therefore Hg^{+2} does not precipitate as a group 1 chloride.

In the qualitative scheme of testing, both mercury valences, as well as the free metal, are involved, since when mercurous chloride is precipitated and reacted with ammonia, *mercuric amido chloride* and mercury are products:

$$Hg_2Cl_{2_W} + 2NH_3 = Hg(NH_2)Cl_W + Hg_B + NH_4^+ + Cl^-$$

These valence states also appear in the reaction between (excess) stannous ion and mercuric ion later in the analytical procedure:

$$2Hg^{+2} + Sn^{II} + 2Cl^- = Hg_2Cl_2 + Sn^{IV}$$

$$Hg_2Cl_2 + Sn^{II} = 2Hg + Sn^{IV} + 2Cl^-$$

TABLE 15-3. EQUILIBRIUM CONSTANTS FOR SOME MERCURY (I) REACTIONS

Reactions (in order of decreasing [Hg_2^{+2}])	*K*	Formula Weight
$Hg_2CrO_4 = Hg_2^{+2} + CrO_4^{-2}$	2×10^{-9}	517.23
$Hg_2C_4H_4O_6 = Hg_2^{+2} + C_4H_4O_6^{-2}$	1×10^{-10}	549.26
$Hg_2C_2O_4 = Hg_2^{+2} + C_2O_4^{-2}$	1×10^{-13}	489.24
$Hg_2Cl_2 = Hg_2^{+2} + 2Cl^-$	1.1×10^{-18}	472.14
$Hg_2(SCN)_2 = Hg_2^{+2} + 2SCN^-$	3×10^{-20}	517.38
$Hg_2Br_2 = Hg_2^{+2} + 2Br^-$	1.3×10^{-22}	561.06
$Hg_2CO_3 = Hg_2^{+2} + CO_3^{-2}$	9.0×10^{-17}	461.23
$Hg_2I_2 = Hg_2^{+2} + 2I^-$	4.5×10^{-29}	655.06
$Hg_2(CN)_2 = Hg_2^{+2} + 2CN^-$	5×10^{-40}	453.26
$Hg_2S = Hg_2^{+2} + S^{-2}$	1×10^{-45}	433.28

Note again the conventions given above Table 15-1 regarding how metallic concentrations from complex ions will be calculated.

TABLE 15–4. EQUILIBRIUM CONSTANTS FOR SOME MERCURY(II) REACTIONS

Reactions (in order of decreasing [Hg^{+2}])	K	Molecular Weight
$Hg(IO_3)_2 = Hg^{+2} + 2IO_3^-$	3×10^{-13}	550.45
$HgCl_4^{-2} = Hg^{+2} + 4Cl^-$	8.3×10^{-16}	342.45
$Hg(NH_3)_4^{+2} = Hg^{+2} + 4NH_3$	5.2×10^{-20}	268.73
$Hg(SCN)_4^{-2} = Hg^{+2} + 4SCN^-$	5×10^{-20}	432.93
$HgBr_4^{-2} = Hg^{+2} + 4Br^-$	2.3×10^{-22}	520.29
$HgS = Hg^{+2} + S^{-2}$	1×10^{-50}	232.67
$HgI_4^{-2} = Hg^{+2} + 4I^-$	5.3×10^{-31}	808.25
$Hg(CN)_4^{-2} = Hg^{+2} + 4CN^-$	4×10^{-42}	304.65

In volumetric *quantitative analysis*, one titrates with SCN^- using Fe^{+3} as an indicator: $2SCN^- + Hg^{+2} = Hg(SCN)_2$. In the gravimetric procedure, one uses a weighed gold foil with which mercury vapor amalgamates in a specially designed heating apparatus.

Group 1 Analysis—General Discussion

To a neutral or slightly acid solution, 6 M HCl is added dropwise until precipitation is complete, then a drop in excess. The three group 1 ions precipitate as white chlorides, AgCl, $PbCl_2$, and Hg_2Cl_2. The centrate from their separation is drawn off and saved for groups 2–5 analysis if those ions might be present. Water is added to the residue, the mixture is heated, and recentrifuged. $PbCl_2$ is more than three times as soluble at 100 C as at 20 C and it is solubilized and separated by this means, leaving AgCl and Hg_2Cl_2 as a residue. The centrate may be divided into two portions: H_2SO_4 added to one, K_2CrO_4 to the other. If lead is present, white $PbSO_4$ and yellow $PbCrO_4$ will furnish the evidence. The residue of silver and mercurous chlorides is mixed with NH_4OH, resulting in formation of soluble, colorless $Ag(NH_3)_2^+$ and a grey–black insoluble mixture of mercury disproportionation products: white $HgNH_2Cl$ and black Hg. The mixture is centrifuged, and the silver-containing centrate isolated and acidified with HNO_3. This decomposes the complex and Ag^+ and Cl^- again combine as shown by a white precipitate which darkens to metallic silver in the sunlight. The black mercury mixture is proof enough that that element was a constituent of the sample but it may be confirmed by solution in aqua regia and reduction to white Hg_2Cl_2 plus black Hg by stannous tin.*

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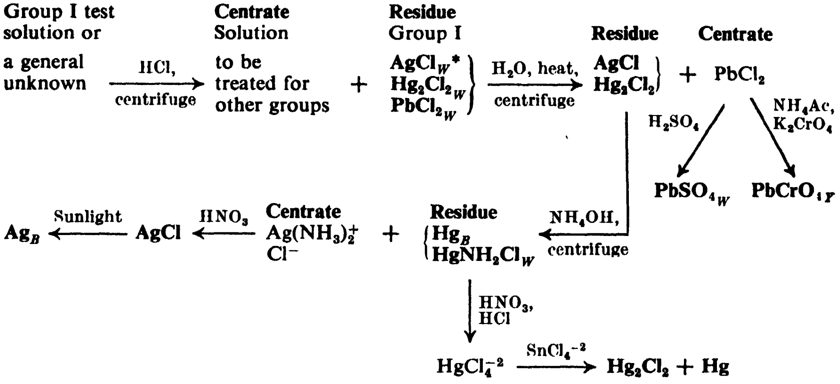
* A summary of this appears on page 239 in the form of a "*flow sheet*" and on the same page in an alternate "*block outline*." Subsequent groups will be treated with description and flow sheet only.

FLOW SHEET—GROUP 1



* Subscript letters refer to the color of the substance. The abbreviations are listed in Appendix A27. Colors will be given only once per page or per group of related equations.

BLOCK OUTLINE†—GROUP 1

Add 6 *M* HCl dropwise to the sample with stirring, until precipitation is complete, then add a drop more. Centrifuge, wash the residue with a little 1 *M* HCl and combine washings with original centrate, and save for groups 2–5. Proceed below with the residue of group 1 chlorides.

<table>
<tr><td colspan="4">Residue: AgCl, $PbCl_2$, Hg_2Cl_2. Add H_2O and boil. Centrifuge.</td></tr>
<tr><td colspan="2">Residue: AgCl, Hg_2Cl_2. Add 6 <i>M</i> NH_4OH and centrifuge</td><td colspan="2">Centrate: $PbCl_2$. Divide into two portions, A and B</td></tr>
<tr><td>Residue: $HgNH_2Cl$, Hg. This is sufficient to confirm mercury.</td><td>Centrate: $Ag(NH_3)_2Cl$. Add 6 <i>M</i> HNO_3 until acidic. A white precipitate of AgCl, turning dark in the sunlight, confirms silver.</td><td>A. Add a few drops of NH_4Ac and K_2CrO_4; a yellow precipitate of $PbCrO_4$ confirms lead.</td><td>B. Add a little 6 <i>M</i> H_2SO_4. A white precipitate of $PbSO_4$ confirms lead.</td></tr>
</table>

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† This method of giving a condensed view of the analysis is presented as an alternate to the flow-sheet method. The outline form may be used in the student laboratory notebook by adding the quantities of reagents described in the procedures for the samples.

PRELIMINARY TESTS WITH GROUP 1 IONS

Test solutions contain 10 mg of the metal per milliliter unless stated otherwise. All laboratory solutions are listed in the appendix. Most of these tests are best conducted in 3- or 4-in. test tubes. Results and answers to questions are to be recorded in the laboratory notebook, using the numbering system below. Reaction equations for the systematic analysis follow this section.

Test 15–1. Precipitation of AgCl; Effect of Concentration. (*a*) Decide how to make 2 ml of each of the following Ag^+ solutions and prepare them in separate test tubes: 10 mg/ml, 5 mg/ml, 1 mg/ml, and 0.2 mg/ml. To each add 1 drop of 6 *M* HCl, mix briefly, and note the result both as to quantity of ppt., curdy character of the residue, and rate of settling. Centrifuge by balancing the tubes opposite each other in the centrifuge and again note the vol. of the solid phase.

By preparing known dilns. in this way, one is able to estimate by residue size, or sometimes color intensity of the liquid, the concn. represented by the ion under test in an unknown soln. If on the other hand one wishes to determine the sensitivity of a method, he makes dilns. to determine the one where the positive test result is just capable of detection. Such techniques will be valuable all semester.

Save the first standard for Test 15–2.

Test 15–2. Solution and Reprecipitation of AgCl; Confirmatory Reactions. *Throughout the lab work with unknown samples, the student will find the need to check first indications or inconclusive experiments with supplementary investigations known as confirmatory reactions or tests.* The following examples of this idea illustrate some methods of proving that the curdy ppt. from test 15–1 is AgCl.

(*a*) To the test 15–1 residue, add 10 drops of dil. NH_4OH and mix well. Explain, using equation 4 in the list of equations at the end of the chapter.

(*b*) To the soln. from (*a*), add a drop of phenolphthalein, then add dil. HNO_3 until the indicator changes, and then 2 drops in excess. See equation 5.

(*c*) Allow the residue from (*b*) to stand in the sunlight. The photochemical reduction of Ag^+ to black Ag is another confirmatory test.

Test 15–3. $PbCl_2$; Character of Precipitates. *The student should observe not only the color and quant. of ppts. but also their physical appearance.* The slower a ppt. forms, the larger are its particles generally, and some well defined crystalline ppts. may be identified by appearance alone under a lens. Whereas AgCl and Hg_2Cl_2 are curdy, $PbCl_2$ forms nice crystals.

Precipitate some $PbCl_2$, centrifuge, and decant the liq. Add 1–2 ml of H_2O, heat to boiling, and allow to cool. If pptn. does not reoccur, boil off some of the H_2O and let the tube cool again. Note the difference between the appearance of AgCl from test 15–1 and this prep., both of which are usually incompletely described simply as white ppts. If a lens or microscope is available, examine and describe the crystals more completely.

Test 15-4. Some Hg_2^{+2} Reactions; Blank Tests. *A blank test is one which is run as a check on solvents, reagents and conditions and includes everything but the substance being tested. This allows one to determine that no unknown factors such as contaminated reagents are giving false analytical results.* The student will use this technique from time to time.

/ Add a few drops of dil. HCl to a few drops of Hg_2^{+2} test soln. Now add a few drops of dil. NH_4OH and several in excess to make the mixt. basic. ★ centrifuge,* discard the centrate, and warm and stir the residue with a mixt. of 12 drops of concd. HCl and 4 drops of concd. HNO_3. When the ppt. has dissolved, transfer to a beaker and evap. in the hood, just to dryness, using a moving flame to avoid splattering. Cool. Add 10 drops of H_2O, 6 drops of $SnCl_4^{\ 2}$ ($SnCl_2$ in HCl), and note the result. See the mercury equations toward the end of the chapter.

If one now wants to check to find if the reagents alone were capable of giving any of the changes noted, and hence would give a false test for Hg_2^{+2} with no mercury present, he will omit the Hg_2^{+2}, mix the reagents in the same order as before, and discover that without mercurous ion, no ppts. are obtained, thus clearing the reagents and procedure of suspicion.

Test 15-5. Group 1 Chromates; Checking Against Knowns. *A good check on a mixture or single substance is to obtain the same from the shelf of ion test solns. and run whatever investigation is necessary to show that the known and unknown are the same or different.*

Put 5 drops of Ag^{+} soln. in one tube, 5 of Pb^{+2} in another, and 5 of Hg_2^{+2} in another. Label the tubes. Ask another student to put 5 drops of one of the group 1 ions in a fourth tube as an "unknown". Add 3 drops of K_2CrO_4 to the unknown and note the color. Now add 3 drops of K_2CrO_4 to each known. This simple comparison test method will be used many times.

Test 15-6. Other Group 1 Precipitates; Devising Original Tests. *It is possible that the enterprising student who is familiar with the chemistry in the flow sheets, and looks over such tables as the one in the back cover, can devise short cuts in the procedure and originate tests not described here. Such methods are not to be relied upon exclusively, of course, since there is no substitute for a careful following of the formal procedure. The student should consult the instructor before using powerful oxidizers like $KClO_3$, conc. HNO_3, Na_2O_2, etc. in original investigations.*

As described in test 15-5, the following may also be of aid in differentiating group 1 ions: $NaHPO_4$, KI, NaF, and NaOH. As time permits, try 1 drop of reagent with 5 drops of test ion solution, then add 6 more drops of reagent with good mixing, and record the results with equations.

Analysis of a Known Mixture

Upon the instructor's directions students may be given, or may themselves prepare, a known mixture of group 1 ions for analysis prior to

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* ★ This symbol refers to part (*G*), p. 244, of the procedure with the unknown sample as a starting point for the Hg confirmatory test.

running the unknown sample; or they may be directed to proceed directly to the unknown after completion of any or all of the preliminary experiments. At this point, the notebook write up should be complete and the student should have read through the following procedure and have the outline of it in mind. Any questions the student has on the group thus far should be answered, since the same problems may arise with the sample.

ANALYTICAL REACTIONS OF GROUP 1 CATIONS

A. Chloride Precipitations

(1) $Ag^+ + Cl^- = \mathbf{AgCl}_W$

(2) $Hg_2^{+2} + 2Cl^- = \mathbf{Hg_2Cl_2}_W$

(3) $Pb^{+2} + 2Cl^- = \mathbf{PbCl_2}_W$

B. Silver

(4) $\mathbf{AgCl} + 2NH_4OH = Ag(NH_3)_2^+ + Cl^- + 2H_2O$

(5) $Ag(NH_3)_2^+ + Cl^- + 2H^+ = 2NH_4^+ + \mathbf{AgCl}$

(6) $2Ag^+ + CrO_4^{-2} = \mathbf{Ag_2CrO_4}_R$

C. Mercurous Mercury

(7) $\mathbf{Hg_2Cl_2} + 2NH_4OH = \mathbf{Hg(NH_2)Cl}_W + \mathbf{Hg}_B + NH_4^+ + Cl^- + 2H_2O$

(8) $\mathbf{Hg(NH_2)Cl} + 4H^+ + 6Cl^- + 2NO_3^-$

$= 2HgCl_4^{-2} + \mathit{N}_2 + 2\mathit{NO} + 4H_2O$

$\mathbf{3Hg} + 8H^+ + 12Cl^- + 2NO_3^-$

$= 3HgCl_4^{-2} + 2\mathit{NO} + 4H_2O$

$4H^+ + 3Cl^- + NO_3^- = \mathit{NOCl} + \mathit{Cl}_2 + H_2O$ (aqua regia)

$2\mathit{NOCl} = 2\mathit{NO} + \mathit{Cl}_2$

$HgCl_4^{-2} = Hg^{+2} + 4Cl^-$

(9) $2Hg^{+2} + SnCl_4^{-2} + 4Cl^- = \mathbf{Hg_2Cl_2}_W + SnCl_6^{-2}$

$\mathbf{Hg_2Cl_2} + SnCl_4^{-2} = \mathbf{2Hg} + SnCl_6^{-2}$

(10) $Hg_2^{+2} + CrO_4^{-2} = \mathbf{Hg_2CrO_4}_{Or}$

D. Lead

(11) $\mathbf{PbCl_2} + H_2O \overset{\Delta}{=} Pb^{+2} + 2Cl^- + H_2O$ (some ionization)

(12) $Pb^{+2} + SO_4^{-2} = \mathbf{PbSO_4}_W$

$\mathbf{PbSO_4} + 2Ac^- = PbAc_2 + SO_4^{-2}$

(13) $Pb^{+2} + CrO_4^{-2} = \mathbf{PbCrO_4}_Y$

PROCEDURE FOR GROUP 1 ANALYSIS

(*A*) Put 1 ml of sample at about *p*H 7 in a 4-in. tube and add 2 drops of 6 *M* HCl. Shake or stir and allow it to stand a half minute to complete the precipitation and make sure that $PbCl_2$ supersaturation has not occurred. No precipitate at this point indicates that Ag^+ and Hg_2^{+2} were not in the sample and that only a small amount of Pb^{+2} is possibly present. (If this is the observation on a sample that may contain only group 1 ions, a separate neutral milliliter portion is tested for lead by adding a drop of NH_4Ac followed by 2 drops of K_2CrO_4. A yellow *turbidity* or fine, slowly settling precipitate is $PbCrO_4$. Lead is confirmed in the $PbCrO_4$ by centrifuging, isolating the residue, and warming it with a few drops of dilute HCl in which lead chromate is soluble. If the original sample was a general one that might contain cations of other groups, the milliliter acidified with HCl and yielding no group 1 precipitate is carried to the group 2 procedure in the next chapter. Any lead not isolated as the chloride will be precipitated as the sulfide there.)

(*B*) If a white precipitate was the result of HCl addition in (*A*), the tube is counterbalanced with another in the centrifuge and centrifuged for 20–60 sec. The centrate is withdrawn and saved in a corked tube for further group analysis if such is indicated, or is neutralized with NH_4OH, buffered with NH_4Ac, and tested for traces of lead with chromate, as described in (*A*) if the sample is known to contain only group 1 metals.

(*C*) The white precipitate from (*B*) may be any combination of AgCl, $PbCl_2$, and/or Hg_2Cl_2. Wash the solid with 4 drops of 1 *M* HCl, centrifuge, and discard the *centrate*. Add 1.5 ml of H_2O to the residue, place the tube in a water bath, and keep it hot for 3–4 minutes, stirring once in a while with a rod resting in the tube. If all the residue dissolves, only Pb^{+2} was in the sample. If some residue remains, centrifuge while hot and put the centrate in a separate tube. Wash the residue with 1 ml of hot water as before, centrifuge, and combine the wash water with the other centrate. Save this solution for (*D*) and the residue for (*E*).

(*D*) To the centrate from (*C*) which contains $PbCl_2$, add 2 drops of NH_4Ac and 4 drops of K_2CrO_4. A yellow precipitate is $PbCrO_4$ and confirms lead.

(*E*) The residue from (*C*) is mixed with 6 drops of dilute NH_4OH, stirred, and 4 drops of H_2O are added. If all the solid dissolves and no dark particles are to be seen, the solid was only AgCl. If the solid turns from grey to black, some Hg_2Cl_2 was present in it and AgCl may have been present also and will have to be tested for in the solution. If only AgCl is suspected, proceed to (*F*). If a black precipitate is in evidence, centrifuge, collect the centrate and combine it with 10 drops of the 1 *M*

NH_4OH wash liquid used on the mercury residue, and use it as directed in (*F*). Save the black residue for (*G*).

(*F*) The combined centrate and washings from (*E*) may contain Ag as $[Ag(NH_3)_2]Cl$. Add a drop of phenolphthalein, then 6 *M* HNO_3 dropwise until the indicator becomes colorless, then 2 drops more. A white precipitate of AgCl separates if silver was present, and it gradually turns dark violet in the sunlight, confirming silver.

(*G*) The dark residue from (E) is a mixture of $Hg(NH_2)Cl$ and Hg and is a good enough indication by itself to say that the unknown contained mercurous mercury.

If confirmation is desired, it is done according to test 15–4, starting at the sign ★.

If the black residue is large and one is working with samples which can contain a comparatively small quantity of silver, the mercury residue should be tested for silver if none was found above in (*F*).* This is done by dissolving the combined residue in aqua regia, as in test 15–4, which solubilizes the metals as chloro complexes, H_2AgCl_3, H_3AgCl_4, H_2HgCl_4, etc. If this solution is diluted, AgCl precipitates. It can then be removed by centrifugation, washed, dissolved with NH_4OH, and tested as in (*F*). The diluted aqua regia-mercuric solution may be analyzed as in test 15–9.

PROBLEMS

1. Which group 1 metal(s) give(s):

(*a*) A chloride soluble in hot H_2O?
(*b*) A fluoride soluble in H_2O?
(*c*) A yellow phosphate?
(*d*) A dark red chromate?
(*e*) A chloride that does not turn dark or dissolve in NH_4OH?

2. What single reagent, observation, or test could one use to differentiate between the members of each pair:

(*a*) Hg_2Cl_2 and $HgCl_2$?
(*b*) AgCl and Hg_2Cl_2?
(*c*) Hg_2Cl_2 and $Hg(NH_2)Cl$?
(*d*) $PbCl_2$ and PbI_2?
(*e*) $HgCl_4^{-2}$ and Hg_2Cl_2?
(*f*) $Pb(OH)_2$ and Ag(OH)?
(*g*) $AgNO_3$ and AgCl?
(*h*) HCl and HNO_3?
(*i*) K_2CrO_4 and $K_2Cr_2O_7$?
(*j*) $MgSO_4$ and $MgCl_2$?

3. Jackson P. Slipshod, a man noted for the rapid formulation of schemes of

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* This is because metallic mercury in step (*E*) can reduce some silver:

$$2Hg + 2Ag(NH_3)_2^+ + 2Cl^- = 2Ag + 4NH_3 + Hg_2Cl_2,$$

and traces of Ag^+ would go undetected.

analyses that are not always rigorous, gives the following three-step method for handling a group 1 unknown:

(*a*) "Add an iron nail to a portion of the unknown; a silvery deposit indicates Ag by virtue of its position in the activity series with respect to Fe.

(*b*) "Add PO_4^{-3} to another portion; a white precipitate is lead phosphate since the solubility of that compound is known to be small.

(*c*) "To a third portion add I^- to throw out yellow PbI_2, a better test than using Cl^-, since the iodide is much less soluble."

"With these tests one needs no procedure."

Are there any pitfalls in the Slipshod technique?

4. Show by calculation that in test 16-1, 1 drop of 6 *M* HCl gives enough Cl^- to precipitate all the Ag^+ contained in 2 ml of silver solution containing 10 mg Ag^+/ml.

5. Balance, showing methods:

(*a*) $AgCl + Hg = HgCl_2 + Ag$

(*b*) $AgCl + Zn = Ag + Zn^{+2} + Cl^-$

(*c*) $Hg_2Cl_2 + Sn^{+2} + Cl^- = ?$

(*d*) $Hg_2^{+2} + NO_3 + H_2O = Hg_2(OH)NO_3 + H_3O^+$

(*e*) $Pb^{+2} + OH^- = HPbO_2^- + H_2O$

(*f*) Rewrite equations 4 and 7 from the list of Analytical Reactions of group 1 cations using NH_3 in place of NH_4OH. (See p. 242.)

6. (*a*) An industrial concern calls you in to give them a test to tell when all the brine (NaCl solution) has been rinsed out of a water demineralizer. What is your test?

(*b*) There is a question about a certain synthetic detergent as to whether or not it contains substantial quantities of Na_2SO_4 as a cheap process by-product (which does not improve or hinder detergency but does add bulk). Assuming the remainder of the material is the soluble sodium salt of an organic derivative which will not interfere with ordinary analysis, how will you make the determination? How could it be done quantitatively?

(*c*) A mining company has a crushed ore that assays 20 lbs of horn silver to the ton. The gangue is sand. This ore is good enough to develop if a cheap recovery of silver is available. You are asked to propose a method of producing silver metal from the ore.

7. Define: (*a*) centrate (*b*) confirmatory test (*c*) supernatant liquid (*d*) disproportionation, and (*e*) sensitivity of an analytical test.

8. A colorless solution gives a white precipitate with HCl. Part of the solid is soluble upon shaking with a large volume of water and the remainder is soluble in strong NH_4OH. What can one deduce?

9. One has a solid mixture known to be equal parts of silver metal powder, AgCl and $PbCl_2$. Organize a flow sheet to effect its separation.

10. Experiments have shown that the solubility of AgCl at 21 C in pure H_2O is 6.2 mg/liter; in 1% HCl is 0.2 mg/liter and in 10% HCl is 74 mg/liter. Draw a rough graph of AgCl solubility vs. % HCl to illustrate the data, and explain the experimental observations in a well organized paragraph.

11. In the reaction between NH_4OH and Hg_2Cl_2, it is found that half the

mercury is converted to Hg^{II} and half to Hg. Could the reaction have given 40% of one and 60% of the other, for example, instead?

12. From reference to a table of solubilities and the preliminary experiments, devise an analytical procedure of your own for the separation of the group 1 ions and their confirmation, assuming only that they are present in solution. Explain with the aid of a flow sheet or outline.

13. In an experiment to determine whether mercurous ion is Hg^+ or Hg_2^{+2}, mercuric nitrate was dissolved in water to make three solutions of various $[Hg^{+2}]$. To each was added a substantial excess of mercury metal and after long shaking and equilibrium was established, the concentrations of remaining mercuric ion and of mercurous ion formed by the oxidation-reduction were determined. From these, equilibrium constants were calculated. The two possible reactions and equilibrium statements are:

(a) $$Hg^{+2} + Hg = Hg_2^{+2}$$
$$K_1 = [Hg_2^{+2}]/[Hg^{+2}]$$

and

(b) $$Hg^{+2} + Hg = 2Hg^+$$
$$K_2 = [Hg^+]^2/[Hg^{+2}]$$

Concentrations of ions in the three experiments were found to be as follows:

Experiment	$[Hg^{+2}]$	[Mercurous]
1	1.2×10^{-3}	1.4×10^{-1}
2	5.0×10^{-3}	5.6×10^{-1}
3	8.7×10^{-3}	10.4×10^{-1}

Explain what has been proved, and demonstrate with calculations. How do you suggest the ionic concentrations be quantitatively determined in this experiment?

Is the value of K found by this experiment consistent with one found from cell data? Demonstrate.

14. When either SO_4^{-2} or CrO_4^{-2} is added to saturated $PbCl_2$ solution, a precipitate forms. If CrO_4^{-2} is added to saturated $PbSO_4$ solution a precipitate forms. If solid $PbSO_4$ is heated with NH_4Ac solution it dissolves, but if $PbCrO_4$ instead of $PbSO_4$ is used, no change is visible. Are these experimental observations compatible with one another? How do they establish the relative solubilities of the three lead compounds?

REFERENCE

1. J. C. Bailer, *J. Chem. Educ.*, 21, 523 (1944). (Silver oxidation states)

16

CATION GROUP 2

The general chemistry of lead and mercury was discussed in the last chapter. For reasons noted there these elements are in both analytical groups. The periodic relationships among the metals of group 2 are indicated below.

VIII	IB	IIB	IIIA	IVA	VA	VIA
			B	C	N	O
			Al	Si	P	S
Ni	**29** **Cu** **63.54**	Zn	Ga	Ge	**33** **As** **74.91**	Se
Pd	Ag	**48** **Cd** **112.41**	In	**50** **Sn** **118.70**	**51** **Sb** **121.76**	Te
Pt	Au	**80** **Hg** **200.61**	Tl	**82** **Pb** **207.21**	**83** **Bi** **209.00**	Po

FIG. 16-1. The periodic table in the vicinity of the group 2 metals.

Bismuth

Bismuth is a hard, brittle metal, sp. gr. 9.80, usually found in the native state. Melting at 271 C it forms the basis for low-melting alloys for automatic sprinklers, metal baths for heat treating other metals, etc. The *oxidation states* are (− III) as BiH_3, (III) as $BiCl_3$, (IV) as BiF_4, and (V) as $NaBiO_3$.

A few compounds are used in medicines but the soluble compounds are poisonous and uses for Bi are few. Most Bi salts are insoluble in water and the soluble ones hydrolyze readily into *complex hydrated oxides*. For the sake of simplification the *bismuthyl ion*, BiO^+ is used to illustrate hydrolysis but X-ray diffraction work on the solid, usually represented as BiOCl, has not shown evidence of this ion.

$$H_2O + BiCl_3 = \mathbf{BiOCl} + 2H^+ + 2Cl^-$$

This hydrolysis is reversible in the presence of additional HCl. The partial

$$\mathbf{Bi} + H_2O = BiO^+ + 2H^+ + 3e^- \qquad E^\circ = -0.32$$

shows that the bismuth ion is about as easily reduced to the metal in acid solution as is Cu^{+2}. The reduction is also easily accomplished in basic solution, so that Bi^{+3}, BiO^+, or $Bi(OH)_3$ all go to black Bi under the reducing influence of an agent such as stannite ion, $Sn(OH)_4^{-2}$. The reaction is used as a reliable qualitative test. Bi_2O_3 in strong alkaline oxidizing solutions yields ill-defined hydroxy compounds. We will consider the important ion present there is bismuthate, BiO_3^-. Bi_2O_3 itself is trimorphic, and its molecular weight is variable due to indefinite composition. Since $Bi(OH)_3$ is not amphoteric and Bi^{III} does not form ammonia complexes, *bismuth hydroxide* is not soluble in bases. Only a few Bi complexes are known, BiI_4^- is one whose yellow color is sometimes utilized in qualitative testing. In acid solution *bismuthic acid* is an oxidizer powerful enough to oxidize manganous ion to permanganate:

$$BiO^+ + 2H_2O = 3H^+ + HBiO_3 + 2e^- \qquad E^\circ = -1.6$$

Bi_2S_3 is quite insoluble in water, NaOH, or alkaline sulfides, but will dissolve in hot dilute HCl. With CrO_4^{-2}, $(BiO)_2CrO_4$ (?), *bismuthyl chromate*, forms from bismuth solutions and is insoluble in NaOH in contrast to $PbCrO_4$, which is also yellow.

TABLE 16-1. EQUILIBRIUM CONSTANTS FOR SOME BISMUTH REACTIONS

Reactions (in order of decreasing $[Bi^{+3}]$)	K	Formula Weight
$\mathbf{BiOCl} = BiO^+ + Cl^-$	7×10^{-9}	260.46
$\mathbf{BiOOH} = BiO^+ + OH^-$	$\sim 1 \times 10^{-12}$	242.01
$\mathbf{Bi_2S_3} = 2Bi^{+3} + 3S^{-2}$	1×10^{-70}	514.18

Quantitatively, Bi is determined by precipitation of the hydroxide and ignition to and weighing as the trioxide. Colorimetry with thiourea, giving yellow complexes such as $Bi[CS(NH_2)_2]^{+3}$, is also used.

Copper

This is a very malleable and ductile metal with excellent heat and electric conduction properties. It is found native as well as in sulfide and oxide ores; typical minerals are chalcopyrite, $CuFeS_2$, azurite, $2CuCO_3 \cdot Cu(OH)_2$, and malachite, $CuCO_3 \cdot Cu(OH)_2$. Ores of this type are roasted to produce *matte copper*, a mixture containing about 50% Cu with Fe, S, and SiO_2. The matte is heated with lime to give an iron–calcium–silicate slag and molten copper which is cast into bars known as *blister copper*. These are made the anodes in an electrolysis of a bath of $CuSO_4$. The cathodes are pure copper rods on which 99.9+% pure copper is deposited. The metal has a sp. gr. of 8.92 and melts at 1063 C. It is used in wires, pipes, switches, cables, heat exchangers, etc. In such service it may become coated with a protective oxide or sulfide film. Alloyed with Zn, Sn, Pb, Ni, etc., Cu makes such important alloys as brass, bronze, monel, coinage metal, German silver, and others. Copper compounds are used in certain paints, fungicides, and algaecides.

Dilute or concentrated HNO_3 or HNO_2 dissolves Cu metal, giving nitrogen oxides and cupric salts, but, in the absence of oxygen, other dilute acids have little effect on the metal. Copper, like silver and gold (which comprise group IB in the periodic table), has *oxidation states* (I), (II), and (III), but only the first two are important and readily interconvertible, and only Cu^{+2} will be considered in the analysis scheme later described in this chapter.

$$Cu^+ = Cu^{+2} + e^- \qquad E^\circ = -0.15$$

Cu(III) can be prepared from Cu(II) in alkaline solution by ozone oxidation, but it is unstable. The electron structure of the copper atom is $1s^2$, $2s^22p^6$, $3s^23p^63d^{10}$, $4s^1$. The $4s$ electron is readily removed and apparently the $3d$ group, despite being filled, is not too stable, and as many as two electrons can be removed from it, giving the higher valence states.

A few compounds of Cu^{+2} (*cupric* copper) are water insoluble, as shown in Table 16–3, but most are more soluble than corresponding members of the *cuprous* (Cu^+) series. Anhydrous cupric salts are white but in water solution are blue due to hydration of the copper ion as $Cu(OH_2)_4^{+2}$. Cu^{+2} is capable of hybridizing orbitals of the dsp^2 type, which leads to a square planar configuration of the four coordinated groups. Cuprous salts are generally lightly colored and like Ag^+, Cu^+ coordinates two groups linearly.

Cupric ion gives a bright blue-green flame test and a blue borax or microcosmic salt bead. (See special experiments 4 and 5.) Cu^{+2} is easily reduced all the way to Cu, as little as 10 ppm copper giving a visible reaction.

$$Cu = Cu^{+2} + 2e^- \qquad E^\circ = -0.34$$

TABLE 16–2. EQUILIBRIUM CONSTANTS FOR SOME COPPER(I) REACTIONS

Reactions (in order of decreasing $[Cu^+]$)	K	Formula Weight
$CuCl = Cu^+ + Cl^-$	3.2×10^{-7}	99.53
$CuBr = Cu^+ + Br^-$	6×10^{-9}	143.98
$CuI = Cu^+ + I^-$	1.1×10^{-12}	190.49
$CuSCN = Cu^+ + SCN^-$	4×10^{-14}	121.65
$Cu(CN)_2^- = Cu^+ + 2CN^-$	1×10^{-16}	115.56
$Cu_2S = 2Cu^+ + S^{-2}$	1.2×10^{-49}	159.20
$Cu(CN)_3^- = Cu^+ + 3CN^-$	5×10^{-28}	141.60

TABLE 16–3. EQUILIBRIUM CONSTANTS FOR SOME COPPER(II) REACTIONS

Reactions (in order of decreasing $[Cu^{+2}]$)	K	Formula Weight
$CuCO_3 = Cu^{+2} + CO_3^{-2}$	2.5×10^{-10}	123.55
$Cu(C_2O_4) = Cu^{+2} + C_2O_4^{-2}$	8.3×10^{-12}	151.56
$Cu(OH)_2 = Cu^{+2} + 2OH^-$	1.6×10^{-19}	97.59
$Cu(NH_3)_4^{+2} = Cu^{+2} + 4NH_3$	4.7×10^{-15}	131.66
$CuS = Cu^{+2} + S^{-2}$	4×10^{-36}	95.63

The final solution in the group 2A scheme may contain Cu^{+2} and Cd^{+2},* and separation of these ions can be accomplished by (*a*) converting them to cyano complexes and then treating with H_2S, whereupon only CdS is capable of precipitating, (*b*) converting Cu^{+2} to the *soluble tartrato complex* and simultaneously precipitating $Cd(OH)_2$ in basic solution, or (*c*) selectively reducing Cu^{+2} to Cu without affecting Cd^{+2} by use of Fe powder or sodium dithionite. These are illustrated in tests 16–5, 16–7. In each of these methods advantage is taken of the reducibility and/or complexibility of Cu^{+2}. The reactions are:

(*a*) $$2Cu(NH_3)_4^{+2} + 8CN^- = 2Cu(CN)_3^{-2} + (CN)_2 + 8NH_3{}^*$$

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* See equation 23, this chapter, for an alternate reaction. Both are possible depending upon conditions.

(*b*) $$Cu^{+2} + 2C_4H_4O_6^{-2} = Cu(C_4H_4O_6)_2^{-2}$$

(*c*) $$Cu(NH_3)_4^{+2} + S_2O_4^{-2} + 2H_2O = Cu + 2SO_3^{-2} + 4NH_4^+$$

(Alkaline solutions of Pb^{II}, Bi^{III}, and Sb^{III} are also reduced to the free metals by dithionite.)

Qualitatively, copper is most often recognized by the deep blue color of its *tetrammine complex*, and *quantitatively* it is determined by electroplating on a weighed platinum electrode or by its action in excess I^- where it liberates a stoichiometric amount of I_3^-. The latter is titrated with standard sodium thiosulfate:

$$2Cu^{+2} + 5I^- = 2CuI + I_3^-$$

$$I_3^- + 2S_2O_3^{-2} = 3I^- + S_4O_6^{-2}$$

The sensitive organic reagent sodium diethyldithiocarbamate (see example 7, Chapter 12) is used in quantitative colorimetry for very dilute copper solutions.

Cadmium

This is a silvery, quite ductile, and malleable metal. The chief ore is the yellow sulfide, greenockite, CdS, but cadmium is also found in most zinc ores, a metal which Cd resembles. The ore is roasted at low temperature to convert it to sulfate which is acid leached then treated with Zn dust to displace Cd and other more noble metals. Cd is volatile and may be purified by sublimation to 99.9+ % purity. The metal is used extensively as a plating for the protection of irons and steels, where it functions about as effectively as zinc galvanizing. It is also used in some low-melting alloys and as CdS in the more expensive yellow paints. Cadmium has been reported to have *oxidation numbers* of (I) and (II), but evidence supporting the lower one is weak and only the latter is considered here. The metal's sp. gr. is 8.65 and the m.p. 320.9 C.

The metal dissolves very slowly in acids giving Cd^{+2} and H_2. The same substances that complex Cu^{+2} usually form the same 4-coordination complex types with Cd^{+2}, except that the latter are tetrahedral whereas the copper complexes are planar. CdS is the most insoluble of the Cd compounds in water and dilute bases, although it will dissolve in dilute mineral acids. *Cadmium cyanide*, *phosphate*, *carbonate*, and *oxalate* are water insoluble but will dissolve in dilute acids or NH_3. Cd is qualitatively identified in group 2, as the only yellow sulfide that is insoluble in alkali or alkaline sulfides.

Quantitatively, Cd is determined, after separation from other metals, by precipitation as the carbonate and ignition and weighing as the oxide,

TABLE 16–4. EQUILIBRIUM CONSTANTS FOR SOME CADMIUM REACTIONS

Reactions (in order of decreasing $[Cd^{+2}]$)	K	Formula Weight
$CdCl_3^- = Cd^{+2} + 3Cl^-$	4×10^{-3}	218.79
$CdC_2O_4 = Cd^{+2} + C_2O_4^{-2}$	1.5×10^{-8}	200.43
$Cd(OH)_2 = Cd^{+2} + 2OH^-$	2.0×10^{-14}	146.43
$CdCO_3 = Cd^{+2} + CO_3^{-2}$	5.2×10^{-12}	172.42
$Cd(NH_3)_4^{+2} = Cd^{+2} + 4NH_3$	1×10^{-7}	180.53
$CdS = Cd^{+2} + S^{-2}$	6×10^{-27}	144.47
$Cd(CN)_4^{-2} = Cd^{+2} + 4CN^-$	1.4×10^{-19}	216.45

or by evaporation of its purified sulfuric acid solution and weighing as $CdSO_4$. A number of organic reagents are available for Cd analysis; see references at the end of Chapter 12.

Arsenic

Arsenic exists in three (and perhaps four) allotropic forms, but only the grey, semimetallic allotrope is stable. Some of its compounds such as As_4O_6 also exhibit polymorphism. The grey arsenic is quite brittle and a poor electric conductor. Its sp. gr. is 5.73 and it sublimes at 615 C. The common ores are oxides, sulfides, and arsenides like elaudetite, As_4O_6, orpiment, As_2S_3, realgar, As_4S_4, and iron arsenide, $FeAs_2$. Roasting, carbon reduction, and sublimation win the metal from these minerals. The element has very limited use in some lead and copper alloys; the compounds are all poisonous and are used to kill weeds, insects, and rodents; to preserve wood, make war gases, etc. Arsenic has *oxidation states* of (— III) as AsH_3, (III) as $AsCl_3$, (IV) as $(As_4O_8)_x$, and (V) as $(As_2O_5)_x$. The last two substances are polymeric and the molecular weights are not known. The (IV) oxide may contain both (III) and (V) arsenic, since on reaction with base it gives arsenites and arsenates. Due to covalent bonding in As_4S_4, the oxidation state of As is not (II) as one might guess. The metal itself will dissolve in hot concentrated acids to give *arsenic acid*, H_3AsO_4, rather than the expected salts. Hydrogen is not liberated. Three important partials are:

$$As + 2H_2O = HAsO_{2(aq)} + 3H^+ + 3e^- \qquad E^\circ = -0.25$$

$$HAsO_2 + 2H_2O = H_3AsO_4 + 2H^+ + 2e^- \qquad E^\circ = -0.56$$

$$AsH_3 = As + 3H^+ + 3e^- \qquad E^\circ = 0.60$$

Heated with oxygen, sulfur, or halogens the metal gives the corresponding trivalent compounds. In water solutions As_2S_3 tends to be colloidal but is coagulated by salts. It is soluble in hydroxides and alkaline sulfides, its amphoteric character putting arsenic with antimony and tin in cation group 2B. Like other members of group VA of the periodic table, it forms a hydride, AsH_3, *arsine*, when an arsenide is reacted with dilute acids or an arsenic(III) compound is reduced in acid solution with an active metal such as zinc. Arsine is a poisonous gas but is valuable as a means of qualitative testing, giving a dark residue of arsenic when burned (Marsh test), or a yellow color with a spot of 50% $AgNO_3$ (Gutzeit test).

Four main series of arsenic-containing compounds are common: *arsenous*, As^{III}, *arsenic*, As^{V}, *arsenites*, AsO_3^{-3}, and *arsenates*, AsO_4^{-3}. The latter two are distinguished by addition of Ag^{+}, giving a yellow *silver arsenite* and brown *silver arsenate*. The As^{III} compounds are more numerous than those of As^{V}; AsF_5 for example is the only known pentahalide of arsenic.

Very few *equilibrium constants* involving As are known.

Arsenous sulfide is soluble in hydroxides or basic sulfides yielding arsenites and *thioarsenites*:

$$As_2S_3 + 4OH^- = AsO_2^- + AsS_3{}^{3} + 2H_2O$$

and is reprecipitated if the solution is acidified and H_2S added:

$$AsO_2^- + 2H^+ + 3H_2S = As_2S_3 + 4H_2O$$

Precipitation of *arsenic(V) sulfide* from arsenate solutions is usually incomplete because not enough time is given for the slow reaction:

$$5H_2S + 2H_3AsO_4 = As_2S_5 + 8H_2O$$

A common procedure is to add NH_4I to the mixture so that iodide will reduce As^{V} to As^{III} and quantitative precipitation of As_2S_3 follows.

Quantitatively, arsenic may be determined by distillation as $AsCl_3$ from strong HCl solution. This is followed by titration (oxidation) in basic solution with standardized iodine, the end point indicated with starch. The main reaction is

$$2HCO_3^- + H_3AsO_3 + I_3^- = H_3AsO_4 + H_2O + 2CO_2 + 3I^-$$

For small amounts, the Gutzeit test (p. 263) is adaptable to quantity estimation.

Antimony

This is a silvery, brittle metal; its sp. gr. is 6.68 and m.p. is 630.5 C. The chief ore is stibnite, Sb_2S_3, which usually occurs black rather than the familiar orange sulfide from group 2B. Roasted, the sulfide converts to the trioxide Sb_4O_6 which is separated by sublimation and reduced by heating with carbon. The metal finds use in a few low-melting soft alloys for bearings, type metal, and storage battery plates. A limited number of compounds such as "tartar emetic," $KSbOC_4H_4O_6$ (*potassium antimonyl tartrate*), are used in medicine but most are poisonous as is typical of all heavy metals.

The *oxidation states* of antimony are (— III), (III), (IV), and (V), representative compounds being SbH_3, Sb_4O_6, $(SbS_2)_x$, and $KSb(OH)_6$. There are no well defined Sb^{IV} compounds and some of the others are also polymeric and of uncertain molecular weights. Acids usually convert the metal to Sb_4O_6, strong HCl giving *antimony trichloride* from that. $SbCl_3$ and similar compounds hydrolyze strongly to give *insoluble oxy* (or *suboxide*) *derivatives*, as SbOCl, whose formulas are not definite and are written only as approximations in equations. The antimonyl ion, SbO^+, has not been shown present in these materials which are polymers of covalently bonded Sb and O atoms. The *trioxide* Sb_4O_6 is amphoteric and will dissolve in bases to give slightly soluble (meta) antimonites as $NaSbO_2 \cdot 2H_2O$ which are powerful reducing agents. Hot concentrated HNO_3 on Sb_4O_6 yields some (ortho) *antimonic acid* which, unlike the corresponding *arsenic acid*, has the formula $HSb(OH)_6$ in which the metal coordination is 6. The *sulfides* of antimony(III) and (V) are soluble in alkaline sulfide solutions, respectively forming *thioantimonites*, SbS_2^-, and *thioantimonates*, SbS_4^{-3}. This behavior puts Sb with As and Sn in group 2B.

Potentials related to the discussion are:

$$SbH_3 = Sb + 3H^+ + 3e^- \qquad E^\circ = 0.51$$

showing the ease of oxidation of the (— III) state, and its acidic character;

$$Sb + H_2O = SbO^+ + 2H^+ + 3e^- \qquad E^\circ = -0.21$$

and

$$SbO^+ + 5H_2O = HSb(OH)_6 + 3H^+ + 2e^- \qquad E^\circ \cong -0.7$$

showing the tendency of Sb^{III} and Sb^V to be reduced in acid solution, whereas in alkaline solution, oxidation is easy:

$$2S^{-2} + SbS_2^- = SbS_4^{-3} + 2e^- \qquad E^\circ_B = 0.6$$

Compare these with the arsenic equations in the preceding section.

Equilibrium constants are not accurately known for most Sb reactions.

The brilliant orange color of Sb_2S_3 and the evolution of *stibine gas*, SbH_3 (which is tested like AsH_3), are two good qualitative indications of antimony.

Differentiation between AsH_3 and SbH_3 can be made in several ways. With the Gutzeit test, both give a yellow or yellow and black color on the $AgNO_3$ spot, but, by using NaOH instead of H_2SO_4 in the generator (the Fleitmann modification), only AsH_3 is released. If the Marsh test is used, hypochlorite or hypobromite will dissolve the deposit of metallic arsenic but not antimony, because of the former's greater ease of oxidation:

$$2As + 5OCl^- + 6OH^- = 2AsO_4^{-3} + 5Cl^- + 3H_2O$$

Quantitatively, Sb is analyzed by an iodometric method; it is complexed with tartrate which not only keeps Sb^{III} in solution, but also lowers the oxidation potential so that triiodide quantitatively oxidizes it to Sb^V:

$$SbOC_4H_4O_6^- + I_3^- + H_2O = SbO_2C_4H_4O_6^- + 3I^- + 2H^+$$

Starch is the indicator in iodine titrations.

Tin

This metal has three allotropic forms, the α or white form being the common, stable one at room temperature. Its sp. gr. is 7.31 and its m.p. is 231.8 C. At low temperatures this is reversibly convertible to gray or β-tin. The gray form is brittle and easily powdered, whereas the white form is ductile and malleable unless heated to temperatures above 232 C where transformation to γ-tin, another brittle allotrope, occurs. The chief ore is cassiterite, SnO_2, which is reduced by carbon; the metal is electrolytically refined. Tin is used in electrolytically-prepared tin plate for "tin" cans and in some important soft alloys like bronze, babbit, solder, pewter, type metal, and pot metal.

Tin has three *oxidation states*, (II), (III), and (IV), and being amphoteric forms four main compound types: *stannous*, Sn^{II}; *stannic*, Sn^{IV}; *stannites*, SnO_2^- (or $Sn(OH)_3^-$); and *stannates*, SnO_3^{-2} (or $Sn(OH)_6^{-2}$). Little is known about tin(III). The metal dissolves in HCl giving H_2 and the *tetrachloro complex* $SnCl_4^{-2}$, but with HNO_3, *metastannic acid*, H_2SnO_3 (or hydrated stannous oxide, $SnO_2(H_2O)_x$) is the result. Salts of both tin valences are considerably covalent, ionize feebly, hydrolyze readily, and must be kept in acid solution or precipitation of hydrated oxides occurs. The sulfides are soluble in acid, base, or alkaline sulfides and polysulfides, the last reagents giving *thiostannate*, SnS_3^{-2}, from either brown SnS and yellow SnS_2.

Three tin half reactions are

$$\begin{aligned} Sn &= Sn^{+2} + 2e^- & E^\circ &= 0.14 \\ Sn^{+2} &= Sn^{IV} + 2e^- & E^\circ &= -0.15 \\ SnS + 2S^{-2} &= SnS_3^{-2} + 2e^- & E_B^\circ &= > 0.6 \end{aligned}$$

Equilibrium constants are not known accurately for most tin reactions. The K_{SP} of $Sn(OH)_2 = 3 \times 10^{-27}$, of $Sn(OH)_4 \cong 10^{-57}$ and of SnS $= 1 \times 10^{-26}$.

In the analytical process for group 2B, Sn^{IV} and Sb^{III} come out in solution together and are tested in each other's presence. This is done by (*a*) complexing tin with oxalate and precipitating antimony with H_2S and/or (*b*) reducing antimony to black Sb and tin to Sn^{II} with iron and acid, then reacting the latter with mercuric chloride to effect reduction to white Hg_2Cl_2 and black Hg. The tin reactions in these steps are

(*a*)
$$Sn^{IV} + 3C_2O_4^{-2} = Sn(C_2O_4)_3^{-2}$$
$$Sn(C_2O_4)_3^{-2} + H_2S = \text{No reaction}$$

(*b*)
$$Sn^{IV} + Fe = Fe^{+2} + Sn^{II}$$
$$2Sn^{II} + 4HgCl_2 = \mathbf{Hg_2Cl_2} + \mathbf{2Hg} + SnCl_6^{-2}$$

The stannous solution can also be tested for Sn^{II} by means of a flame test; the color is bright blue.

Quantitative methods usually call for precipitation of H_2SnO_3 from HNO_3 solution, then filtration on ashless paper, and ignition at 800 C to SnO_2. If the original precipitate is impure and the SnO_2 colored, tin can be volatilized from it as SnI_4 by heating with NH_4I, and the tin content calculated by the loss in weight.

Group 2 Analysis—General Description

A solution containing only group 2 ions, or a general unknown solution that has been freed of group 1 ions except some Pb^{+2}, is treated with NH_4OH and HCl to adjust the *p*H at about 0.6. The mixture is then treated directly with H_2S gas or with thioacetamide which hydrolyzes to release H_2S, and precipitation of the group 2 sulfides takes place.* If thioacetamide is used, the mixture is then diluted to give a *p*H of about 1.0 and reheated to complete the precipitation reaction. By this procedure the K_{SP}'s of group 2 sulfides alone are exceeded and group 3, 4, and 5 metals remain in the centrate when the mixture is separated by centrifugation.

The group 2 residue is treated with hot, 6 *M* KOH and centrifuged, dividing it into those elements whose sulfides are not amphoteric and hence not soluble [HgS (some), PbS, Bi_2S_3, CuS, CdS] and those whose sulfides are amphoteric and base-soluble [HgS (some), As_2S_3, Sb_2S_3, SnS]. *The residue is called subgroup 2A or the "copper group," the centrate is subgroup 2B, or the "tin group."*

The group 2A residue is stirred with dilute HNO_3, putting into solution all the sulfides except HgS, which remains after centrifuging as HgS or as the insoluble double salt $2HgS \cdot Hg(NO_3)_2$. This is dissolved in aqua

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* Strong oxidizing agents like HNO_3 must be absent or H_2S is oxidized. In general these substances are not present or are reduced before group 2 is begun.

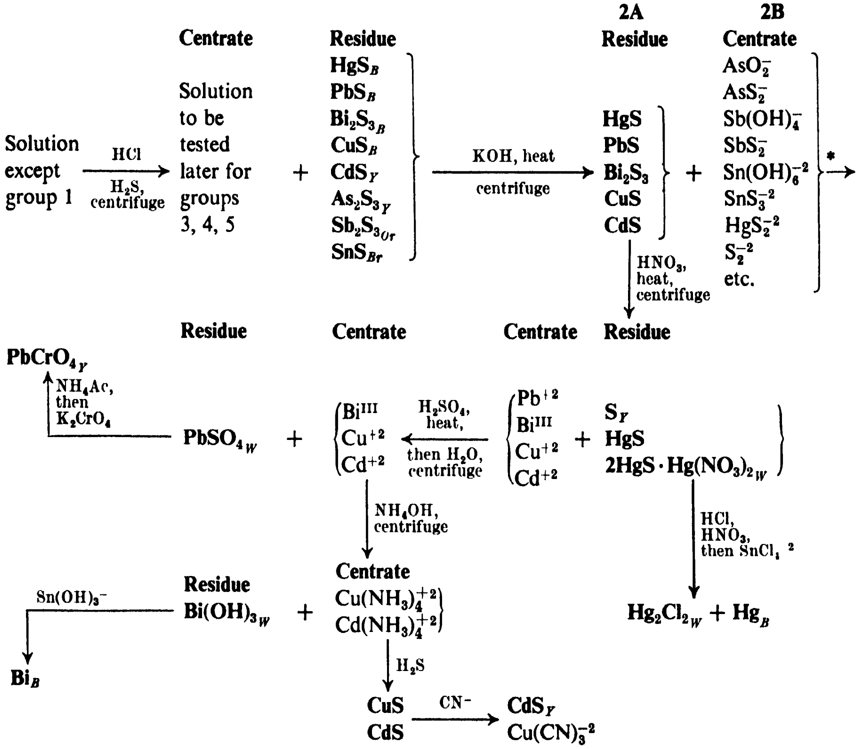
regia and confirmed with Sn^{II} as in group 1. The centrate from HgS removal is mixed with dilute H_2SO_4, evaporated to drive off HNO_3 (which interferes with the formation of $PbSO_4$), then diluted and centrifuged, leaving $PbSO_4$ as a residue if Pb^{+2} is present, and retaining Bi^{III}, Cu^{+2}, and Cd^{+2} in solution. Lead is confirmed by solution of $PbSO_4$ in NH_4Ac and reprecipitation as yellow $PbCrO_4$. Addition to the Bi—Cu—Cd mixture of excess NH_4OH complexes copper and cadmium as soluble tetrammine ions, blue $Cu(NH_3)_4^{+2}$ and colorless $Cd(NH_3)_4^{+2}$, and precipitates any Bi^{III} present as white $Bi(OH)_3$ (or $BiO(OH)_2$). This residue when treated with stannite ion, $Sn(OH)_3^-$, yields a confirmatory, black residue of metallic bismuth. If the centrate from the bismuth separation is dark blue, copper is present but Cd^{II}, being colorless, must be tested further. Thioacetamide or H_2S is added to the mixture of complexes, a black precipitate showing CuS and a yellow precipitate showing CdS if those metals are present. If copper was present, CuS would generally obscure any yellow CdS so NaCN is next added. The black sulfide will dissolve to form the very stable $Cu(CN)_3^{-2}$, leaving the cadmium precipitate unaffected. The yellow color confirms Cd^{+2}. (Two alternate, noncyanide methods are also given in the formal procedure.)

The group 2B centrate described in the second paragraph above, is mixed with dilute HCl and centrifuged. The residue contains some S and HgS and all the As_2S_3, Sb_2S_3, and SnS. Hot dilute HCl dissolves the latter two sulfides and they are separated with the centrifuge. The residue of the other two is reacted with a mixture of dilute NH_4OH and H_2O_2, dissolving As_2S_3, forming AsO_4^{-3}, which later is confirmed by precipitation as white $(NH_4)Mg(AsO_4)$, and leaving black HgS which may be combined with that found in group 2A or tested separately as previously explained. Generally most of the HgS is isolated in group 2A. The HCl centrate of antimony and tin contains such chlorocomplexes as $SbCl_4^-$ and $SnCl_6^{-2}$, and is divided between two tubes. To one is added oxalic acid which complexes tin from further action, and, when H_2S (or thioacetamide plus heat) is added, orange Sb_2S_3 comes down and the color is sufficient to prove the ion. Iron filings are used to reduce tin in the other tube to Sn^{II}, and it may be tested with Hg^{+2}; a white-to-grey precipitate of $Hg_2Cl_2 + Hg$ is evidence of reaction as in group 1. Antimony(III) is reduced to Sb by the iron and does not interfere.

Other tests for group 2 ions such as the Gutzeit, flames, and organic reagents are listed in the preliminary studies of these ions and in the procedure for unknowns in later paragraphs of this chapter. A flow chart of the processes just described is given on pp. 258, 259.

See also part 4 of special experiment 9 for group 2 analysis by paper chromatography.

FLOW SHEET—GROUP 2



H_2S Gas as a Precipitation Agent

Hydrogen sulfide gas is toxic and should always be handled with caution in good ventilation. The first signs of poisoning are nausea and headache and must be immediately relieved with smelling salts and/or copious breathing of fresh air. In larger doses H_2S is lethal.

H_2S may be supplied in the laboratory in a number of ways. A common source is ferrous sulfide, which is reacted with acid in a student generator or some modification of a central Kipp generator:

$$\mathrm{FeS} + 2\mathrm{H}^{+} = \mathrm{Fe}^{+2} + H_2S$$

Another gas-releasing reaction is that between sulfur and paraffin wax initiated by heating, and approximately* represented as

$$\mathrm{C_{30}H_{62}} + 31\mathrm{S} = 30\mathrm{C} + 31H_2S$$

Because H_2S is poisonous, corrosive, and ill-smelling, it is always best to

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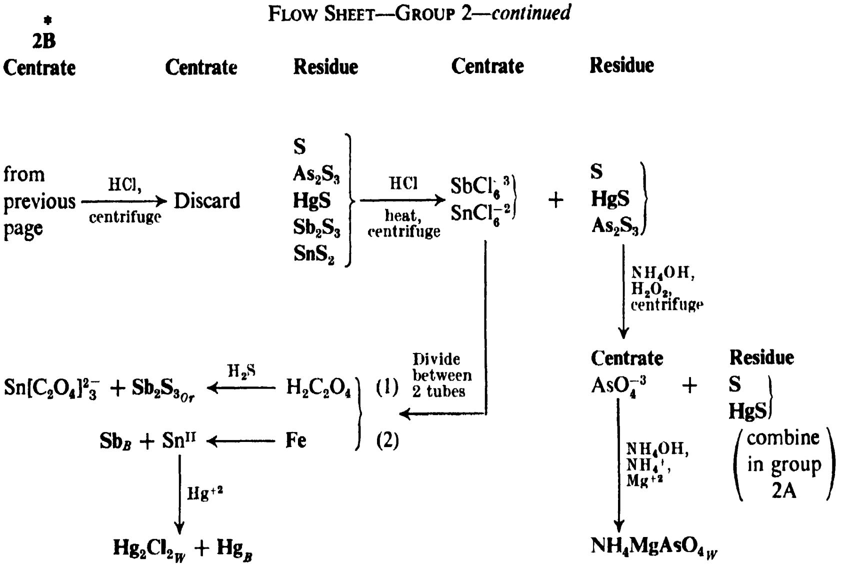
* Paraffin is a mixture of alkane hydrocarbons from about C_{22} to C_{30}. The composition of the residue is more complex than represented.

Flow Sheet—Group 2—*continued*



generate or use only the minimum quantity which will do the job. Air pollution with H_2S should be avoided and reactions and evaporations should be conducted under the hood if possible.

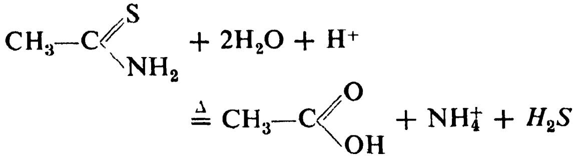
Because of the inconveniences, a number of *non-H_2S systems of qualitative testing* have been invented. For instance, Carnog bases his on the use of alkaline solutions and $(NH_4)_2S$; West, Vick, and LeRosen have devised a system utilizing a benzoic acid-sodium benzoate buffer; and Dobbins and Gilreath suggest a sequence with HCl, $NH_4(H_2PO_4)$, and pyridine-SCN^- (see references, this chapter). As yet, however, the original hydrogen sulfide system of *Fresenius* (1850) is still the one most widely taught. The quantitative separations it affords plus the well investigated yet diverse reactions, theories, tabular data, problem possibilities, and practical applications are features in its favor.

Thioacetamide as a Source of H_2S

For the reasons just mentioned the H_2S system is retained in this edition, but an alternate source of H_2S for the operator's convenience and comfort seems desirable. In 1949 Barber and Grzeskowiak suggested the use of thioacetamide as a source of H_2S for qualitative analysis. The compound was prepared originally in 1877 by Hofmann and Bernthsen and *its synthesis is detailed in special experiment* 12 with references to original literature. Thioacetamide hydrolyzes to slowly release H_2S in hot, dilute strong acids (group 2 precipitating conditions) or in hot, dilute strong bases, but is quite stable at room conditions in aqueous solution at pH 7. This obviates the use of gas generators, gives better H_2S control, denser precipitates, and generally is a neater and handier technique.

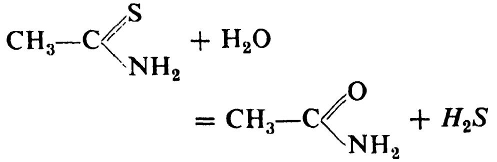
Thioacetamide is a white, crystalline material, somewhat soluble in water and benzene. The chemical is usually used in the form of its 2—8% aqueous solution. At least 5 minutes should be allowed for its reaction with strong acid or base at hot-water bath temperatures. Reactions are:

(pH < 7) rapid



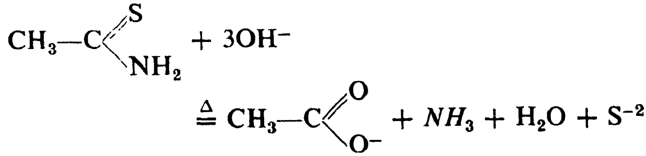
$$CH_3{-}C{\lesssim}^{S}_{NH_2} + 2H_2O + H^+ \overset{\Delta}{=} CH_3{-}C{\lesssim}^{O}_{OH} + NH_4^+ + H_2S$$

(pH = 7) very slow



$$CH_3{-}C{\lesssim}^{S}_{NH_2} + H_2O = CH_3{-}C{\lesssim}^{O}_{NH_2} + H_2S$$

(pH > 7) rapid



$$CH_3{-}C{\lesssim}^{S}_{NH_2} + 3OH^- \overset{\Delta}{=} CH_3{-}C{\lesssim}^{O}_{O^-} + NH_3 + H_2O + S^{-2}$$

As directed by the instructor, either H_2S gas or thioacetamide may be used with this text for the cation group 2 analysis. Directions are given for the organic reagent. In every case where 8% thioacetamide solution is used it is to be understood that saturation with H_2S gas is an equivalent procedure.

PRELIMINARY TESTS WITH GROUP 2 IONS

In all the preliminary tests, use *test solutions* from the side shelf which are made for that purpose and contain 10 mg of the metal ion per milliliter of solution. A few tests are to be made on more concentrated solutions and are specially noted. Most of the reactions may be carried out in 3- or 4-in. test tubes. The thioacetamide solution in each case is an 8% aqueous solution. Questions asked in the text as well as volunteer observations are to be answered in the laboratory notebook.

Test 16–1. Sulfides of the Group. Label nine test tubes as Hg^{+2}, Pb^{+2}, Bi^{III}, Cu^{+2}, Cd^{+2}, As^{III}, Sb^{III}, Sn^{II}, and Sn^{IV}. Put 5 drops of each single soln. in its tube plus 10 drops of water. To each add 8 drops of 8% thioacetamide and to the Hg^{+2}, Pb^{+2}, Cu^{+2}, and Cd^{+2} tubes add a drop of 6 *M* HCl (the other solns. are already acidic). Heat the tubes in a gently boiling water bath for 5 min, then add 10 drops of water to each, and reheat. Note the pptn. order and sulfide colors of the ions of group 2. Centrifuge, or allow the ppts. to settle, and decant, discarding the supernatant liq. in either case. Add 12 drops of H_2O, 1 drop of thioacetamide, and 4 drops of 6 *M* KOH to each tube, and replace them in the hot water bath. During the next 5 min intermittently stir each and note the results. The group 2B sulfides are alkali-soluble, the 2A sulfides are not, and the subgroups are therefore separable. In tabular form, give all results in your notebook including colors and formulas of substances observed. (Reaction equations are given in the section following these preliminary tests.)

Test 16–2. Some Iodide and Phosphate Reactions; Possible Confirmatory Methods (Optional). (*a*) Try a few drops of each group 2 ion with a drop of I^- test soln. Then add several more drops of I^- to each, with mixing. The more distinctive reactions which may aid one in spot testing are: (1) red HgI_2 dissolving to form yellow HgI_4^{-2} (2) orange Bi complexes like BiI_5^{-2}, BiI_6^{-3}, etc., and (3) reduction of Cu^{+2} to Cu^+ and production of brown I_2 and whitish CuI. Write the ionic reactions and note that if the unknown contains certain combinations of cations, this iodide test could be useful in confirmations.

(*b*) Make a soln. of Na_3PO_4 using about 0.2 g of crystals and 2 ml of H_2O. To several drops of each of the group 2A solns., add 8 drops of phosphate soln. and 5 drops of dil. HCl and mix. Note if any phosphates remain undissolved.

Test 16–3. Hydrolysis Reactions of Bi and Sb. Bi^{+3}, Sb^{+3}, Sn^{+4}, Sn^{+2} and As^{+3} hydrolyze (Chapter 10), yielding water-insol. ppts. which can be separated, redissolved in HCl and tested further. The fact that the unknown contains a ppt. or is strongly acidic may indicate one of these ions. See equations 14, 16, 49, this chapter.

Put 20 ml of H_2O in a 50-ml beaker and heat to boiling. Slowly add 3-6 drops of Sb test soln. The ppt. is SbOCl. Write the equation using $SbCl_6^{-3}$ as a reactant. Why does the reaction shift toward the hydrol. products upon diln.? Why is the shelf soln. of $SbCl_3$ approx. 3 *M* in HCl?

Test 16–4. The Reinsch Method. This test is used in criminology as a *screening investigation for heavy metal* poisons. To 5 drops of Hg^{+2} test soln., add 3 drops of dil. HCl and a small piece of copper sheet, copper penny, or a coil of copper wire. Heat in a water bath for several min, then remove the copper, wash, and examine its surface. Note the deposit and the way in which rubbing shines it. This plating is characteristic of heavy metals, though the shiny appearance is typical only of mercury. (Other metals give a flaky or hard grey to black ppt.) List other group 2 metals that would give the test. Try one or two of them and write equations for the reactions. How can this method be modified if only one drop of Hg^{+2} soln. is available for testing? Try your idea and report the result.

Test 16-5. Cd^{+2} in the Presence of Cu^{+2}. Cyanide Method. Put 4 drops of each of the Cd^{+2} and Cu^{+2} test solns. in a tube, add 10 drops of H_2O and 6 drops of dil. NH_4OH, and shake. The deep blue color is proof that Cu^{+2} is present as the tetrammine complex.* ★ Add 12 drops of thioacetamide and heat the mixt. for several min in the water bath. (Both sulfides ppt. since the stability of the NH_3 complexes is not great enough to prevent it.) Remove the tube, centrifuge, and discard the centrate. Add a few crystals of NaCN (or NaCN soln.) and 10 drops of H_2O to the residue and stir. The Cu_2S should gradually dissolve, forming the colorless tricyano copper(I) ion, leaving yellow CdS as evidence that cadmium is present. (See calcn., p. 149, Chapter 9.)

Test 16-6. Cd^{+2} in the Presence of Cu^{+2}. Dithionite Method. To about 1 ml of Cu^{+2}–Cd^{+2} mixt. add 6 drops of dil. NH_4OH and ★ heat in a water bath. When hot, add 60–80 mg of sodium dithionite, $Na_2S_2O_4$ (also called hyposulfite or hydrosulfite) and keep the mixt. hot. Add more dithionite after several min. and reheat for 5 min. If the blue color is not entirely discharged, add more dithionite and reheat. Centrifuge, discard the metallic Cu, and to the centrate, add 2 drops more of NH_4OH, 10 drops of thioacetamide, and reheat. A yellow ppt. is CdS. This test works as a spot reaction for Cd^{+2} in group 2 unknowns if arsenic is absent. (See reference 3, p. 276.)

Test 16-7. Cd^{+2} in the Presence of Cu^{+2}. Tartrate Method. ★Place in a crucible about 1 ml of the Cu^{+2}–Cd^{+2} mixt., acidify with dil. HNO_3, and add 2 drops in excess. In the hood, slowly evap. the soln. and bake it for several min to destroy NH_4^+ salts (which would be present from the $Bi(OH)_3$ pptn. in general unknown sample procedure). When cool, add 1 drop more of HNO_3, 1 ml of H_2O, then 8 drops of 6 *M* NaOH, 1 ml of 0.1 *M* sodium potassium tartrate, $NaK(C_4H_4O_6)$, and mix well. Transfer the mixt. to a test tube and centrifuge. The white ppt. is $Cd(OH)_2$, the blue soln. is a tartrate–copper complex, $Cu(C_4H_4O_6)_2^{-2}$, and this blue color confirms copper. Wash the residue twice with H_2O, discard the washings, suspend the residue in about 1 ml of H_2O, add 1 drop of NaOH and 6–10 drops of thioacetamide, and heat in a water bath. Yellow CdS proves Cd^{+2}. (See reference 6, p. 276.)

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* ★ This sign refers to procedure (*J*). Ignore the signs when only making preliminary tests. If one is working with an unknown sample, however, he may start at these points with his Cd–Cu mixture and use the directions for Cd^{+2} analysis.

Test 16–8. Sodium Diethyldithiocarbamate for Cu^{+2}. Review example 7 of Chapter 12, p. 194. Prepare a series of dilutions contg. 0.02–5 ppm Cu^{+2} in 4-in. tubes. Add 4 drops of 2 *M* NH_4OH and 2 drops of organic reagent (Table A–15), and note the colors. Notice also that because the soln. is so dil., no blue color of ammine complex is observed when NH_4OH is added yet the organic reagent gives a good test series. The color gradation is used in quant. estimation. An unknown sample may be diluted considerably to minimize interferences and still yield this test for Cu.

Test 16–9. The Gutzeit Method for Arsenic and Antimony. Prepare the semimicro Gutzeit apparatus as diagrammed in Fig. 14–4. Wet the lower half of the paper strip with 50% $AgNO_3$. Put about 150 mg of As-free zinc granules in the test tube and add 6 drops of H_2O and 1 drop of dil. H_2SO_4. Put the top on and note that the $AgNO_3$ spot on the paper does not turn color in the presence of H_2 gas. A "blank" determination like this is always advisable to check the purity of the reagents. Remove the top, add 2 drops of As^{III} test soln. or 6 drops of unknown, put in a loose bit of cotton to prevent spotting of the paper by splattering, replace the top, and observe the reaction for the next few min. If too much foaming occurs, cool tube under the tap; if reaction is too slow add another drop or two of acid or warm the tube. The method can be semi-quantitative in the range 0.3–3 ppm of As, if one measures the length of the yellow area on the paper.

(*Optional*) Saturated $HgCl_2$ or 20% $HgBr_2$ in methyl alcohol have been suggested in the literature as substitutes for $AgNO_3$. The interested student might try impregnating filter paper in this way and report on the diff. color, sensitivity and reaction rate.

Interferences to the test include phosphides which liberate PH_3, antimony compounds which give SbH_3, and sulfides which give H_2S. These *poisonous gases* react to give colored products with $AgNO_3$.

If only sulfide is an interference it may be absorbed by impregnating the cotton with $PbAc_2$ solution and trapping H_2S as black PbS. Antimony is an interference; see test 16–10. Mercury compds. also interfere but in a different way: they ppt. mercury, which amalgamates with the zinc, slowing its reaction. Pentavalent arsenic should be reduced with NH_4I or Sn^{II} before running this test. Repeat the test using Sb test soln. instead of As.

Wash the apparatus well after each test. Any left over, solid zinc should go in the waste jar, not the sink.

Test 16–10. The Fleitmann Method for Arsenic. Repeat test 16–9 using As^{III}, 6 drops of 6 *M* NaOH in place of H_2SO_4 and a fresh strip of $AgNO_3$ spotted paper. The tube will need intermittent heating as the alkali reacts slowly with the zinc. Antimony under these conditions does not give SbH_3 and hence is not an interference as AsH_3 alone is released.

Test 16–11. Reduction of Sb^{III}. A drop of Sb^{III} test soln. plus a drop of dil. HCl are placed on a piece of platinum foil or silver coin, and a small piece of tin is placed in contact with one side of the drop. A rapidly forming black deposit is free antimony metal. Mercury, bismuth, and arsenic are also displaced by this procedure. If only arsenic is suspected of being present, it may be dissolved in dil. sodium hypochlorite solution, NaOCl (distinction from Sb). Verify this and write equations.

Test 16–12. Rhodamine-B Test for Antimony. Whereas Bi^{III} and Hg^{+2} are interferences in cation group 2 for this test, it is valid in the presence of Sn^{II}, which makes it worthwhile, since antimony and tin appear together in the last reactions of the group 2B scheme. This is our first test in which a *spot plate* is used. Put several drops of Sb^{III} soln. on a spot plate and acidify with 2 drops of dil. HCl. Add a crystal of KNO_2 and when reaction is over, and antimony is oxidized to Sb^{V}, add 2 drops of the dye soln. A pink color turning violet or giving violet flecks is a positive test for Sb. Compare the color with a blank and with Sn^{II} and the reagent. (See rhodamine-B, example 9, Chapter 12.) The violet compd. can be extracted by shaking with a few drops of benzene, C_6H_6, if this test is run in a test tube. The extraction is an extra confirmation of Sb.

Test 16–13. Ammonium Molybdoarsenate. In the absence of PO_4^{-3}, and in the presence of HNO_3 and ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, arsenic is converted to arsenate, AsO_4^{-3}, and reacts in hot soln. to give a yellow ppt., $H_4(NH_4)_3[As(Mo_2O_7)_6]$. See p. 392, on the analogous phosphate reaction.

Put 3 drops of As^{III} test soln. in a tube, add 3 drops of concd. HNO_3, and warm for 2–3 min. Pour this into a second soln. made by dissolving a crystal of ammonium molybdate and several crystals of NH_4NO_3 in 10–12 drops of dil. HNO_3. Keep the mixt. warm in a bath for several min and note the gradual appearance of the yellow ppt. The concentration limit is about 75 ppm As.

Test 16–14. Flame Test for Sn^{II}. Put 10 drops of Sn^{IV} test soln. in a tube and add about 100 mg of powdered iron and 4–6 drops of dil. HCl. Allow the reaction to proceed 5 min. to effect reduction of tin to the dipositive state. Pour a little of this soln. in the bottom of a crucible lid and let it flow around to wet a max. area. Hold the lid, bottom down, in a hot bunsen flame and notice a bright blue flame playing over the porcelain surface. The test only works with stannous tin and will detect amounts larger than about 2 ppm.

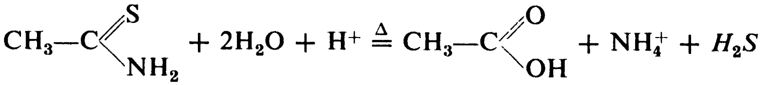
Test 16–15. The Reducing Action of Sn^{II}. As will be shown in cation group 3, Fe^{+3} forms a deep red colored $Fe(SCN)^{+2}$ complex, but Fe^{+2} does not. To 1 drop of Fe^{+3} tests soln. add 1 drop of dil. HCl, 10 drops of H_2O, and 2 drops of KSCN soln. Add this dropwise to 6 drops of Sn^{II} test soln. Write the reaction equations and account for the observed result. Support your conclusion with data from the oxidation potentials table.

Analysis of a Known Mixture

When the student has finished required preliminary studies and recorded the results in his laboratory notebook he may be directed to analyze known mixtures of groups 2A, 2B, or a combination of ions of both subgroups. If not, he is then ready to run the unknown sample. In either case, one portion of sample should be used to run individual tests as given in the prelims or suggested by them, another portion used in following the formal procedure as it appears in the next section, and another portion saved for further tests if results on the first two parts do not appear conclusive.

ANALYTICAL REACTIONS OF GROUP 2A CATIONS

A. Sulfide Precipitations



$$CH_3{-}C\begin{matrix}\nearrow S\\ \searrow NH_2\end{matrix} + 2H_2O + H^+ \overset{\Delta}{=} CH_3{-}C\begin{matrix}\nearrow O\\ \searrow OH\end{matrix} + NH_4^+ + \mathit{H_2S}$$

1. $Hg^{+2} + H_2S = \mathbf{HgS}_B + 2H^+$
   $3Hg^{+2} + 2H_2S + 2Cl^- = \mathbf{HgCl_2 \cdot 2HgS}_W + 4H^+$
2. $Pb^{+2} + H_2S = \mathbf{PbS}_B + 2H^+$
3. $2Bi^{III} + 3H_2S = \mathbf{Bi_2S_3}_B + 6H^+$
4. $Cu^{+2} + H_2S = \mathbf{CuS}_B + 2H^+$
5. $Cd^{+2} + H_2S = \mathbf{CdS}_Y + 2H^+$

B. Mercury

6. $\mathbf{3HgS} + 8H^+ + 12Cl^- + 2NO_3^- = 3HgCl_4^{-2} + 2\mathit{NO} + \mathbf{3S}_Y + 4H_2O$
7. $2HgCl_4^{-2} + SnCl_4^{-2} = \mathbf{Hg_2Cl_2}_W + SnCl_6^{-2} + 4Cl^-$
   $\mathbf{Hg_2Cl_2} + SnCl_4^{-2} = \mathbf{2Hg}_B + SnCl_6^{-2}$

C. Lead

8. $\mathbf{3PbS} + 8H^+ + 2NO_3^- = 3Pb^{+2} + 2\mathit{NO} + \mathbf{3S} + 4H_2O$
9. $Pb^{+2} + SO_4^{-2} = \mathbf{PbSO_4}_W$
10. $\mathbf{PbSO_4} + 2Ac^- = PbAc_2 + SO_4^{-2}$
11. $PbAc_2 + CrO_4^{-2} = \mathbf{PbCrO_4}_Y + 2Ac^-$

D. Bismuth

12. $\mathbf{Bi_2S_3} + 8H^+ + 2NO_3^- = 2Bi^{+3} + 2\mathit{NO} + \mathbf{3S} + 4H_2O$
13. $2Bi^{+3} + 6NO_3^- + 6H^+ + 3SO_4^{-2}$
    $= 2Bi^{+3} + 3SO_4^{-2} + (6H^+ + 6NO_3^-)$ (Boil off)

14. $2Bi^{+3} + 3SO_4^{-2} + 2H_2O = \mathbf{(BiO)_2SO_4}_W + 4H^+ + 2SO_4^{-2}$

15. $2Bi^{+3} + 6NH_4OH = \mathbf{2Bi(OH)_3}_W + 6NH_4^+$

16. $\mathbf{Bi(OH)_3} + 3H^+ = Bi^{+3} + 3H_2O$

    $Bi^{+3} + 3Cl^- + H_2O = \mathbf{BiOCl}_W + 2H^+ + 2Cl^-$

17. $\mathbf{Bi(OH)_3} + 3Sn(OH)_4^{-2} + 3OH^- = \mathbf{2Bi}_B + 3Sn(OH)_6^{-2}$

E. Copper

18. $\mathbf{3CuS} + 8H^+ + 2NO_3^- = 3Cu^{+2}_{Bu} + 2\mathit{NO} + \mathbf{3S} + 4H_2O$

19. $Cu^{+2} + 2NO_3^- + 2H^+ + SO_4^{-2}$

    $= Cu^{+2} + SO_4^{-2} + 2H^+ + 2NO_3^-$ (Boil off)

20. $2Cu^{+2} + SO_4^{-2} + 2NH_4OH = \mathbf{Cu_2(OH)_2SO_4}_{Bu} + 2NH_4^+$

    $\mathbf{Cu_2(OH)_2SO_4} + 8NH_3 = 2Cu(NH_3)^{+2}_{4\,Bu} + SO_4^{-2} + 2OH^-$

21. $Cu(NH_3)_4^{+2} + 4H^+ = Cu^{+2} + 4NH_4^+$

22. $2Cu^{+2} + Fe(CN)_6^{-4} = \mathbf{Cu_2Fe(CN)_6}_{Br}$

23. $2Cu(NH_3)_4^{+2} + 7CN^- + H_2O$

    $= 2Cu(CN)_3^{-2} + CNO^- + 6NH_3 + 2NH_4^+$

24. $Cu(NH_3)_4^{+2} + H_2S = \mathbf{CuS} + 2NH_4^+ + 2NH_3$

25. $Cu(CN)_3^{-2} + H_2S = N.R.$

26. $Cu^{+2} + \mathbf{Fe} = \mathbf{Cu} + Fe^{+2}$

27. $Cu(NH_3)_4^{+2} + 2H_2O + S_2O_4^{-2} = \mathbf{Cu}_{Br} + 2SO_4^{-2} + 4NH_4^+$

F. Cadmium

28. $\mathbf{3CdS} + 8H^+ + 2NO_3^- = 3Cd^{+2} + 2\mathit{NO} + \mathbf{3S} + 4H_2O$

29. $Cd^{+2} + 2NO_3^- + 2H^+ + SO_4^{-2}$

    $= Cd^{+2} + SO_4^{-2} + (2H^+ + 2NO_3^-)$ (Boil off)

30. $Cd^{+2} + 4NH_3 = Cd(NH_3)_4^{+2}$

31. $2Cd^{+2} + SO_4^{-2} + 2NH_4OH = \mathbf{Cd_2(OH)_2SO_4}_W + 2NH_4^+$

    $\mathbf{Cd_2(OH)_2SO_4} + 8NH_3 = 2Cd(NH_3)_4^{+2} + SO_4^{-2} + 2OH^-$

32. $Cd(NH_3)_4^{+2} + 4CN^- = Cd(CN)_4^{-2} + 4NH_3$

33. $Cd(CN)_4^{-2} + H_2S = \mathbf{CdS} + 2HCN + 2CN^-$

34. $Cd^{+2} + 2OH^- + C_4H_4O_6^{-2} = \mathbf{Cd(OH)_2}_W + C_4H_4O_6^{-2}$

ANALYTICAL REACTIONS OF GROUP 2B CATIONS

G. Sulfide Precipitations

35. $2AsO_3^{-3} + 6H^+ + 3H_2S = As_2S_{3_Y} + 6H_2O$

36. $2SbCl_6^{-3} + 3H_2S = Sb_2S_{3_{Or}} + 6H^+ + 12Cl^-$

37. $SnCl_6^{-2} + 2H_2S = SnS_{2_Y} + 4H^+ + 6Cl^-$

$SnCl_4^{-2} + H_2S = SnS_{Br} + 2H^+ + 4Cl^-$

H. Hydroxide Solutions

38. $2As_2S_3 + 4OH^- = AsO_2^- + 3AsS_2^- + 2H_2O$

39. $2Sb_2S_3 + 4OH^- = Sb(OH)_4^- + 3SbS_2^-$

40. $3SnS_2 + 6OH^- = Sn(OH)_6{}^{2} + 2SnS_3^{-2}$

$2SnS + 3OH^- = SnS_2^{-2} + Sn(OH)_3^-$

I. Acid Reprecipitations

41. $AsO_2^- + 3AsS_2^- + 4H^+ = 2As_2S_3 + 2H_2O$

42. $Sb(OH)_4^- + 3SbS_2^- + 4H^+ = 2Sb_2S_3 + 4H_2O$

43. $Sn(OH)_6^{-2} + 2SnS_3^{-2} + 6H^+ = 3SnS_2 + 6H_2O$

$SnS_2^{-2} + Sn(OH)_3^- + S_2^{-2} + 3H^+ = 2SnS_2 + 3H_2O$

J. Arsenic

44. $2As_2S_3 + 12OH^- + 14H_2O_2 = 2AsO_4^{-3} + 20H_2O + 3SO_4^{-2}$

45. $AsO_4^{-3} + NH_4^+ + Mg^{+2} = NH_4MgAsO_{4_W}$

46. Gutzeit test—applies also to antimony.

$As^{III} + 4Zn + 5H^+ = AsH_3 + 4Zn^{+2} + H_2$

$AsH_3 + 6Ag^+ + 3NO_3^- = Ag_3As \cdot 3AgNO_{3_Y} + 3H^+$

$Ag_3As \cdot 3AgNO_3 + 2H_2O = 6Ag_B + HAsO_2^- + 3H^+ + 3NO_3^-$

K. Antimony

47. $2SbCl_6^{-3} + 3Sn \overset{\text{Ag}}{=} 2Sb_B + 3SnCl_4^{-2}$

48. $Sb_2S_3 + 6H^+ + 12Cl^- = 2SbCl_6^{-3} + 3H_2S$

49. $SbCl_6^{-3} + H_2O = SbOCl_W + 2H^+ + 5Cl^-$

50. $2SbOCl + H_2S = Sb_2S_3 + 2H_2O + 2H^+ + 2Cl^-$

L. Tin

51. $SnCl_6^{-2} + Fe = SnCl_4^{-2} + Fe^{+2} + 2Cl^-$

52. $SnCl_4^{-2} + 2Hg^{+2} + 4Cl^- = SnCl_6^{-2} + Hg_2Cl_{2_W}$

$SnCl_4^{-2} + Hg_2Cl_2 = SnCl_6^{-2} + 2Hg_B$

M. Oxidizing Agents with H_2S and H^+

53. $Cr_2O_{7_{Or}}^{-2} + 8H^+ + 3H_2S = 2Cr^{+3}_{Gr} + 7H_2O + 3S$

54. $2Fe^{+3}_Y + H_2S = 2Fe^{+2} + S + 2H^+$

55. $2MnO^-_{4_{Pu}} + 6H^+ + 5H_2S = 2Mn^{+2} + 8H_2O + 5S$

56. $2NO_3 + 2H^+ + 3H_2S = 2\mathit{NO} + 4H_2O + 3S$

N. Organic Reagents with Group 2 Ions

See Chapter 12.

PROCEDURE FOR GROUP 2 ANALYSIS

(*A*) If using a solution known to contain only the metals of group 2, start with 1 ml of sample and add 5 drops of H_2O.

If using a general unknown* adjust the volume of the group 1 centrate to 2 ml by adding H_2O or boiling off as needed.

Both of the above solutions are probably acidic already, but it is necessary to adjust the *p*H to 0.7–0.5 (0.2–0.3 *M* H^+), which is optimum for the precipitation of group 2 sulfides and the simultaneous prevention of precipitation of group 3 sulfides. If the solution is acidic as shown by litmus or other indicator, it is best to make the *p*H about 7 with 6 *M* NH_4OH, then to add dropwise, with good mixing, dilute HCl, checking after each drop the *p*H result with methyl violet paper. This is done by touching a small drop of the mixture on a stirring rod to the indicator paper laid on a spot plate and comparing the color to that developed on the paper with a solution made from 1 ml of H_2O plus 1 drop of 6 *M* HCl.† Do not put the paper itself in either solution. Solution volume at this point should be about 2.5 ml.

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* Certain ions such as NH_4^+ and Ac^- slow the attainment of *p*H adjustment due to their buffering action. They may be removed by evaporation with HNO_3 followed by resolution with dilute HCl. These ions are assumed absent here, although *p*H attainment by use of methyl violet as described is valid in their presence. See list of reagents in appendix for preparation of this indicator paper.

† Other methods for checking the *p*H employ nitrazine paper or indicators like malachite green which are used directly in the solution. Adjustment of *p*H without special indicators may be approximated by making the solution just acid to litmus with NH_3 and HCl as required, followed by addition of 1 drop of 6 *M* HCl for every ml of solution present.

(*B*) Add 1 ml of 8% thioacetamide (or saturate the solution at room temperature with H_2S gas),* and let the tube stand in a boiling water bath for about 7 minutes. Then add 1 ml of H_2O and 12 more drops of thioacetamide and continue to keep the tube hot for 3–5 minutes more. Group 2 sulfides should be completely precipitated by this time and coagulated in a fluffy mass.

(*C*) Centrifuge the mixture, and save the centrate if it may contain ions of groups 3, 4, and 5 for further analysis. The residue is washed by stirring with 1 ml of H_2O to which has been added 1 drop of 0.5 *M* HCl, and, after centrifuging, the wash liquid is combined with the previous centrate for groups 3–5 analysis. (If the sample is known to contain only group 2 metals, both these centrates are discarded.) The centrates, if saved, should be made slightly alkaline with NH_4OH as indicated by a drop of phenolphthalein in the solution, and stored in a corked tube for the group 3 procedure.†

(*D*) The residue from (*C*) is stirred with a mixture of 2 ml of H_2O, 1 drop of thioacetamide, and 12 drops of 6 *M* KOH and heated for 3 minutes in a water bath and stirred 2 or 3 times during this interval. (CAUTION! *Do not allow this caustic solution to splatter by direct heating in an open flame. Wash off any spillage immediately with plenty of water. Neutralize with dilute HAc and more H_2O.*) Centrifuge and save both residue and centrate. Wash the residue twice with 10 drops of H_2O each time, and combine washings with original centrate. The centrate may contain any or all of the following 2B ions: HgS_2^{-2}, AsS_3^{-3}, SnS_2^{-2}, SnS_3^{-2}, SbS_2^{-}, SnO_2^{-2}, $Sb(OH)_4^{-}$, $Sn(OH)_4^{-2}$, $Sn(OH)_6^{-2}$, AsO_2^{-}, etc., as well as OH^-, S^{-2}, HS^-, Ac^-, S_2^{-2}, and NH_4OH. Label this solution 2B and save it for procedure (*K*).

(*E*) The residue from (*D*) may contain any or all the 2A metals as sulfides: HgS, PbS, Bi_2S_3, CuS, CdS. To this washed residue, add 1 ml of H_2O and 1 ml of 6 *M* HNO_3 and heat the mixture with stirring in a water bath for 3 minutes. Centrifuge. If the residue from this step is spongy and tends to float as a lump, it is sulfur and may be removed and

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* If oxidizing agents are present, H_2S will reduce them and itself be oxidized to $H_2O + S$. Four common oxidizing agents are: $Cr_2O_7^{-2}$, MnO_4^-, NO_3^- and Fe^{+3}. These respectively give Cr^{+3}, Mn^{+2}, *NO* and Fe^{+2} at this point, and do not interfere with the analysis except to require additional H_2S to compensate for that oxidized. These metallic ions are all subsequently precipitated in group 3 and analyzed there. It is assumed these are not in the student sample in large quantity.

† The $[S^{-2}]$ does not increase appreciably at room temperature in this solution and oxidation to SO_4^{-2}, which would precipitate group 4 metals prematurely, is not observed. The solution must not be made much more basic than *p*H 8.3 or $Mg(OH)_2$ will precipitate. This is undesirable prior to group 5 testing.

discarded.* If a definite black precipitate is left it is HgS, and a white precipitate is probably $2HgS \cdot Hg(NO_3)_2$. This is combined with HgS also to be found in the 2B centrate and is analyzed to confirm Hg in section (*M*) below. Finely divided sulfur may also appear as a white precipitate here.

(*F*) The centrate from the HNO_3 solution may contain Pb^{+2}, Bi^{III}, Cu^{+2}, and Cd^{+2}. Transfer it to a 20-ml beaker, add 6 drops of concentrated H_2SO_4, and evaporate carefully under the hood *with stirring* and *low*, direct heat until copious white fumes of SO_3 are emitted† and only about 6 drops of liquid plus moist crystals are left. Allow the beaker to cool to room temperature, then *dropwise*, carefully add 1.5 ml of H_2O with stirring to avoid splattering.‡ If a permanent, white, crystalline precipitate remains, it is probably lead sulfate and is tested in the next step.

(*G*) Transfer the entire mixture to a test tube and rinse the beaker contents into that tube with 10 drops of water. Centrifuge and pipet the supernatant liquid to another tube for further testing of 2A metals as directed in section (*H*). Wash the residue with 5–6 drops of H_2O and reject the washings. Add 15 drops of NH_4Ac, warm the mixture on a water bath and stir it. After several minutes the residue should have mostly dissolved. Centrifuge if any remains and test the centrate with a few drops of K_2CrO_4. A yellow precipitate of $PbCrO_4$ confirms Pb (as also obtained in group 1.)

(*H*) The supernatant liquid from the first part of (*G*) may contain Bi^{III}, Cu^{+2}, Cd^{+2}, and H_2SO_4. With stirring, add 15 *M* NH_4OH dropwise until the solution is definitely basic, as evidenced by odor and litmus paper testing; then add 1 drop more. A deep blue color indicates the presence of $Cu(NH_3)_4^{+2}$ and a white, gelatinous precipitate is $Bi(OH)_3$. Centrifuge. Save the residue for (*I*), the centrate for (*J*).

(*I*) In another tube, mix 2 drops of $SnCl_4^{-2}$ with 4 drops of 6 *M* NaOH and shake. An initial precipitate of $Sn(OH)_2$ dissolves to give the stannite ion, $Sn(OH)_4^{-2}$. Pour it over the residue saved from (*H*); a black precipitate of metallic bismuth shows this metal was in the original unknown.

(*J*) The centrate from (*H*) contains copper if the solution is blue and no copper if the solution is not blue. If copper is not present, one may proceed directly to test for Cd by adding 6–8 drops of CH_3CSNH_2,

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* Some S^{-2} is oxidized to SO_4^{-2} here but in a solution of this high ionic strength, $PbSO_4$ does not precipitate.

† HNO_3 must be driven off here, since in its presence $PbSO_4$ is incompletely precipitated.

‡ H_2SO_4 is normally added to water; here the reverse is necessitated.

6–8 drops of H_2O, and heating 5–10 minutes in a water bath. A yellow sulfide, CdS, is sufficient evidence, since this is the only yellow sulfide in group 2 that is insoluble in 6 *M* KOH. If copper is present, it is necessary to remove or complex it in such a way that it does not interfere with tests for cadmium. As directed by the instructor use one of the methods (tests 16–5, 16–6, 16–7) given in the preliminaries, starting at the sign ★ in each case.

This is the end of the 2A procedure.

(*K*) To the alkaline solution and washings from (*D*), add a drop of methyl orange and enough 6 *M* HCl to change the color to orange, $pH \cong 4$, then put in 3 drops of thioacetamide and heat in a water bath 5–8 min with occasional agitation. Centrifuge, discard the centrate, and save the residue for (*L*). If the solution was only milky before centrifuging and contained no well defined residue, only very small amounts of 2B ions can be present.* If this is suspected, the solution is evaporated with 10 drops of dilute HNO_3, the residue dissolved in dilute HCl, divided among several tubes, and tested according to the preliminary experiments for As, Sb, and Sn using the Gutzeit, Fleitmann, rhodamine-B, and flame tests which are sensitive enough to detect small amounts.

(*L*) The residue from (*K*) may contain HgS, As_2S_3, Sb_2S_3, SnS_2, and S. The color should give the student some clue to the metals present. Treat the solid with 1 ml of 6 *M* HCl, stir, and heat for 3–4 min; then centrifuge. The residue may contain black mercuric sulfide and/or yellow arsenous sulfide and sulfur. The centrate may contain $SbCl_4^-$ and $SnCl_6^{-2}$. Segregate the clear centrate in another tube and test it according to section (*O*). The HgS–As_2S_3–S mixture is washed with 1 ml of H_2O, the wash liquid rejected, then mixed with 10 drops of 6 *M* NH_4OH, 5 drops of 3% H_2O_2 and heated with stirring for 4–5 min in a bath. After this interval, add 1 ml of H_2O, stir, and centrifuge. A black residue shows HgS; the clear centrate may contain AsO_4^{-3}. Save the residue for (*M*), carry the centrate to (*N*).

(*M*) The HgS from (*L*) is washed into the tube containing the mercury residue from (*E*). Discard the wash liquid and to the solids add 8 drops of concentrated HCl and 3 drops of concentrated HNO_3, and heat and stir the tube contents in a water bath. After 3–4 min, transfer the solution to a 10-ml beaker and evaporate it slowly under the hood to a *moist residue*; do not evaporate it to dryness. Add 8 drops of H_2O and centrifuge if not clear. To the centrate add 2–3 drops of $SnCl_4^{-2}$ solution. A

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* Some (finely divided) sulfur always shows up when an alkaline sulfide is acidified. Sometimes a sponge of sulfur floats to the top leaving a clear solution. If student samples are known, however, to contain 5–20 mg/ml of each ion, this evidence is indicative that no 2B metals are present.

white to grey precipitate of mercurous chloride and mercury shows Hg^{+2} was in the unknown sample. Alternately one may use the Reinsch test, 16–4.

(*N*) The AsO_4^{-3} centrate from (*L*) is mixed with 6 drops of magnesia mixture.* A white crystalline precipitate of $(NH_4)Mg(AsO_4)$ indicates arsenic.† It is confirmed with a Gutzeit test or a Fleitmann test or these can be done directly on the unknown as spot tests. (Antimony gives the Gutzeit only, if also present.)

(*O*) The centrate of soluble chloro complexes of antimony and tin from (*L*) is boiled gently for several minutes, without splattering, to hydrolyze any CH_3CSNH_2 remaining and to volatilize any H_2S left. Dilute the solution to a total volume of about 2 ml, divide it between 2 tubes and test them as follows:

Tube 1: add a few iron filings, 2 drops of concentrated HCl, and heat. The iron will reduce the tin to Sn^{II} and the antimony to Sb, the latter appearing as black flecks. To one portion of clear reduced solution, add 1–3 drops of $HgCl_2$ and watch for the evidence of mercury reduction as noted in cation group 1 and in procedure (*M*) above. With another portion perform the tin flame test as outlined in test 16–14. (The former method is better for estimating amounts as measured by the volume of mercury precipitate.)

Tube 2: *if no tin was found*, dilute the solution to 3 ml with H_2O, add 4–5 drops of CH_3CSNH_2, and heat in a bath. An orange precipitate is Sb_2S_3 and is sufficient evidence to say antimony is in the sample. *If tin was found*, run the following two tests which work in its presence:

(*a*) Perform the rhodamine-B reaction as described in test 16–12 using a spot plate and a few drops of solution. Save the rest of the solution for part (*b*).

(*b*) To the remaining solution add 10 drops of $(NH_4)_2C_2O_4$ and 4 drops of CH_3CSNH_2 and heat in a water bath. The oxalate temporarily complexes Sn^{IV} so that Sb_2S_3 will precipitate alone.‡ In the absence of arsenic, antimony may be confirmed by the Gutzeit test directly on the unknown.

This is the end of the group 2B procedure.

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* See list of reagents, appendix A13.

† Phosphates give the same test and are assumed not present in simple unknowns. Directions in Chapter 21 provide for the detection and elimination of PO_4^{-3} as well as giving other pointers on handling the general unknown.

‡ If heating is prolonged, say beyond 5 minutes, some Sn^{II} is formed by the reducing action of H_2S and may precipitate as brown SnS.

PROBLEMS

1. An acidic solution containing only salts of group 2 metals gives a black sulfide precipitate which is partly KOH soluble. The insoluble portion is solubilized completely with dilute HNO_3, however, and when that solution is boiled down with H_2SO_4 and then diluted, no precipitate is visible and the solution is colorless. Explain the significance of these observations both as to which metals might be, and which probably are not, present. Which have not been tested?

2. Show by calculation, how many drops (20 drops = 1 ml) of 8% thioacetamide solution are needed to precipitate 10 mg of Cu as CuS.

3. If a solution is 10^{-2} *M* in $Cu(NH_3)_4^{+2}$ and 10^{-3} *M* in uncomplexed NH_3, show whether or not CuS will form if to 20.0 ml of this mixture is added 1 drop of 0.5 *M* Na_2S. Neglect volume change.

4. Show by calculation whether or not PbS will precipitate from a solution saturated with $PbSO_4$ and having a *p*H of 1.5, if treated with H_2S gas until saturated.

5. With the aid of the table of oxidation potentials, answer the following:

(*a*) Is it possible to use Zn, Cd, Sn, and/or Pb to protect Fe from corrosion? Of these, why is Zn used on galvanized fences and Sn on tin cans?

(*b*) Suggest two reducing agents which would convert BiO^+ to Bi and would be feasible for use in group 2 analysis.

(*c*) From the two tin partials given with that element's description at the beginning of this chapter, explain why a piece of metallic tin is placed in the shelf bottle of $SnCl_4^{-2}$.

(*d*) Comment on the tendency for cuprous ion to disproportionate in this way: $2Cu^+ = Cu^{+2} + Cu$ by evaluating the equilibrium constant for the reaction.

(*e*) It has been suggested that if iron is used to treat an acidified mixture of Cu^{+2} and Cd^{+2}, only copper is reduced, leaving Cd^{+2} free in solution (with Fe^{+2}) for testing. Is this separation feasible? If so, calculate the equilibrium constant for the reaction $Cu^{+2} + Fe = Cu + Fe^{+2}$ and comment on its magnitude.

6. (*a*) To an unknown suspected of containing only Bi^{III} and Cu^{+2} salts, one adds excess NH_4OH. What information does this single reagent give?

(*b*) A solution is suspected of containing only antimony salts. Why is H_2S an excellent single reagent to use for a test? What other tests would be indicated?

(*c*) A solution may contain Hg^{+2} and Cd^{+2}. What information does one elicit by adding some metallic magnesium and later, H_2S?

7. Jackson P. Slipshod gives the following method for testing an unknown solution thought to contain Hg^{+2}, Pb^{+2}, and Cd^{+2}:

> "Add a piece of copper to plate out mercury. To that solution, precipitate lead as the sulfate, then add H_2S to the centrate from the $PbSO_4$ separation, and throw out yellow CdS."
> Comment.

8. Could the *p*H for the initial group 2 precipitation conditions be correctly

indicated by any of these: methyl orange, methyl red, malachite green. See chart of indicators, Appendix A17.

9. (*Library*) Find reference to the Marsh and Bettendorf tests. Describe them briefly and contrast them to a similar test in this chapter.

10. Balance:

(*a*) $Bi(OH)_3 + Sn(OH)_4^{-2} = Bi + Sn(OH)_6^{-2}$
(*b*) $CuS + H_3O^+ + NO_3^- = Cu^{+2} + S + H_2O + NO$
(*c*) $As_2S_3 + NO_3^- + H^+ + H_2O = H_3AsO_4 + S + NO$
(*d*) $H_2S + Cr_2O_7^{-2} + H^+ = Cr^{+3} + H_2O + S$

11. Name as Werner compounds:

$Na_2[Sn(OH)_6]$, $(NH_4)_3[SbS_3]$, $[Cd(NH_3)_4]SO_4$, $K_2[Cu(CN)_3]$, $H_2[SnCl_4]$

12. (*Library*) Look up the composition and one use of each of the following materials that employ group 2 metals and their compounds:

(*a*) constantan, (*b*) German silver, (*c*) Babbitt, (*d*) dental amalgam (*e*) Wood's metal, (*f*) Bordeaux mixture, (*g*) Paris green, (*h*) Fehlings' solutions, (*i*) tartar emetic, (*j*) bluestone.

13. (*a*) Chronic arsenic poisoning in humans tends to concentrate the metal in hair roots. You are given a tuft of hair from an autopsy. How will you proceed to test for arsenic?

(*b*) You are asked by a paint company to test a rival's yellow paint to see if the pigment is lead chromate or cadmium sulfide. What will you do?

(*c*) How will you differentiate between a brass (Cu–Zn) and a bronze (Cu–Zn–Sn) by chemical means? Organize the proposal as a flow sheet.

14. Using simple procedures such as a single solvent, observation, or reaction reagent, how would you differentiate between samples of these:

(*a*) HgS and CuS, (*b*) $SnCl_4^{-2}$ and $SnCl_6^{-2}$, (*c*) CdS and SnS_2 (*d*) $AsCl_3$ and $CuCl_2$, (*e*) $BiCl_3$ and $CdCl_2$, (*f*) CdS and S, (*g*) air containing H_2S and air containing SO_2, (*h*) Pb and Cd metals, (*i*) Arsenic and antimony metals, (*j*) NH_4Cl and $NH_4(OH)$, (using a metallic ion from group 2).

15. In the group procedure, explain why these steps are taken:

(*a*) The solution is boiled down with H_2SO_4 prior to the separation of lead as $PbSO_4$. (*b*) The solution containing Sb^{III} and Sn^{IV} is divided into several portions rather than separating one element from the other and proceeding with the centrate as one does for the other elements. (*c*) H_2O_2 is added with NH_4OH in treating a mixture of As_2S_3 and HgS. (*d*) $SnCl_4^{-2}$ is used instead of $SnCl_6^{-2}$ to test for Hg^{+2}. (*e*) KOH is added to the original group 2 residue.

16. Which group 2 ion(s): (*a*) give black sulfides, (*b*) give yellow sulfides, (*c*) could be reduced in acid solution to their metallic state by using iron filings, (*d*) give a yellow sulfide with one oxidation state and a brown sulfide with another (*e*) appear in both groups 2A and 2B?

17. What single reagent will dissolve one and not the other in each pair? Which is the soluble substance in each case? (*a*) HgS and As_2S_3, (*b*) $Cu(NH_3)_4SO_4$ and CuS, (*c*) BiO(OH) and $BiCl_3$, (*d*) $Pb(OH)_2$ and $SnO_2 \cdot H_2O$, (*e*) HgS and Bi_2S_3.

18. Precipitation of As_2S_3 from acid solutions using H_2S gas frequently leads to a colloidal sulfide suspension, but this is not generally noted if CH_3CSNH_2 is used as an H_2S source. Explain the principle behind the advantage in using the organic precipitant.

19. A solution is treated under precipitating conditions for group 2 analysis and a black precipitate is obtained. This is insoluble in KOH but soluble in dilute, hot HNO_3 giving a colorless solution. When the solution is boiled down with H_2SO_4 and then diluted with H_2O, only a clear solution is obtained. What group 2 ion(s) may be present? Explain.

20. Explain these observations:

(*a*) An acid solution of Sb^{III} is diluted with water and a white precipitate forms.

(*b*) In the Cd–Cu separation using the cyanide method, a yellow color develops in the solution but no yellow precipitate.

(*c*) A metallic sample suspected of being pure tin, gives a white residue when boiled in concentrated HNO_3.

(*d*) A mixture suspected of containing Cu^{+2} and Cd^{+2} is colorless when made basic with NH_4OH. When $Na_2S_2O_4$ is added and the solution boiled, no reaction is apparent.

(*e*) A yellow group 2 sulfide is soluble in either dilute KOH or HCl.

21. Heating changes potassium stannate from a soluble to an insoluble compound. On the basis of this alone, which formula for the compound do you like best and why: $K_2[Sn(OH)_6]$ or $K_2SnO_3 \cdot 3H_2O$?

22. (*a*) Bismuth hydroxide is insoluble in 6 *M* KOH as well as in 6 *M* NH_4OH. What can one deduce concerning the amphoteric character of this compound and tendency of Bi^{III} to form complexes?

(*b*) (Library) Describe the thiourea test for bismuth.

23. $Cu_2[Fe(CN)_6]$ is soluble in NH_4OH. Which furnishes fewer Cu^{+2} ions in solution, saturated cupric hexacyanoferrate(II) or tetrammine copper(II) ion? Explain. $PbSO_4$ is soluble in NH_4Ac, and if CrO_4^{-2} is added to that solution, $PbCrO_4$ precipitates. Which lead compound is most insoluble and why? If H_2S is bubbled into a suspension of $PbCrO_4$, the mixture begins turning black. Explain.

24. A solution contains some group 2 ions. At *p*H 0.7, H_2S gives a black precipitate that partly dissolves in KOH, giving residue A and centrate **B**. A is soluble in HNO_3. Boiling this with H_2SO_4 and diluting gives a white material, C. The centrate from removal of C gives a white precipitate with NH_4OH, D, and a colorless centrate with which H_2S gives a yellow solid, E. **B** gives a yellow precipitate with dilute HCl which dissolves in excess HCl, and this, when caused to react with iron metal, yields a clear solution, F, which in turn reacts with $HgCl_2$. Identify C, D, E, and F.

25. In the discussion of group 1 in Chapter 15, two methods were used to abbreviate the procedure: a "flow sheet" and a "block outline." Prepare a block outline for group 2 by following the group 1 example and the group 2 flow sheet found in this chapter.

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17

CATION GROUP 3

Five of the group 3 metals are transition elements, so-called because the filling of the 3*d* level starting with Sc and ending with Cu in the first long horizontal row results in a transition from a 2, 8, 8 electron foundation to 2, 8, 18, while the 4*s* level holds at 1 or 2 electrons (see Chapter 3). The periodic relationships of the elements to be described are shown below.

	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	
									B	C	
									13 Al 26.98	Si	
	V	**24 Cr 52.01**	**25 Mn 54.93**	**26 Fe 55.85**	**27 Co 58.94**	**28 Ni 58.69**	Cu	**30 Zn 65.38**	Ga	Ge	
	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	

FIG. 17-1. The periodic table in the vicinity of the group 3 metals.

Aluminum

Aluminum is a strong, ductile, and malleable metal having good electric conductivity and excellent light reflectivity. The metal and its alloys are used in many applications where low density and good resistance to atmospheric corrosion are desired, such as aircraft skins and members, window frames, auto parts, cooking utensils, metal foils, and metallic paints. Alloys containing small percentages of Mn, Cu, Mg, and sometimes Cr and Zn, have good tensile properties. See Tables 21–3 and A23. These wrought alloys are widely used in airplane manufacture; they can be age-hardened and are about twice as strong as pure aluminum. The latter's sp. gr. is 2.70, its m.p. 658 C, and b.p. is 2330 C.

Aluminum is the third most abundant element, preceded only by oxygen and silicon, and these three elements are found combined in most igneous rocks, micas, feldspars, and clays. The most important mineral for metal recovery is the *hydrated oxide*, $Al_2O_3 \cdot XH_2O$, called bauxite. Iron, titanium, and silicon oxides are undesirable impurities in bauxite and are removed in the Bayer process by dissolving the aluminum oxide as aluminate ion, $Al(OH)_4^-$, in hot caustic soda, and later diluting the solution to reverse the reaction and precipitate hydrated aluminum oxide which is washed and calcined to make metal grade aluminum oxide. The purified oxide which represents about half the weight of crude ore is dissolved in cryolite, Na_3AlF_6, at high temperature and electrolyzed at about 1000 C in a Hall-Heroult or a Soederberg cell. Carbon anodes are used and the iron box of the cell is lined with carbon which serves as the cathode. Oxygen is liberated as the by-product, and molten aluminum is tapped off the bottom for casting into pigs of 99+ % Al. A large cell may produce a ton of Al and consume a half ton of anode daily.

The only *oxidation state* of Al stable in water solutions is (III), though evidence of a lower state is obtained by anodic oxidation of the metal in various solvents. For example, after the current is shut off in the electrolysis of Al in aqueous NaCl solution, H_2 is liberated at the *anode*, presumably by Al^{I} (formed in electrolysis) which reduces H^+ to the gas and is thereby oxidized to Al^{III}. The metal is strongly electropositive, though the adherent Al_2O_3 coating which is present in normal application deactivates the metal greatly. Devoid of this, Al dissolves readily in either acids (except HNO_3) or bases:

$$Al = Al^{+3} + 3e^- \qquad E^\circ = 1.66$$

$$Al + 3OH^- = Al(OH)_3 + 3e^- \qquad E^\circ_B = 2.31$$

If the surface of the metal is amalgamated to keep it active, Al can be dissolved in water to give $Al(OH)_3$ (hydrated) or in alcohols to give $Al(OR)_3$, *aluminum alkoxides*, which are strong bases. (See test 22–23 for an analogous borate ester.) Aluminum powder burns in air when heated forming a mixture of the *oxide* and *nitride*. It is capable of reducing oxides of less noble metals like iron, and use of this is made in thermite welding (Goldschmidt process) and thermite incendiaries.

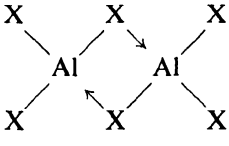
$$2Al + Fe_2O_3 = Al_2O_3 + 2Fe + H_r$$

The heat of reaction H_r easily renders the iron in the molten state. When heated with halogens or sulfur, aluminum forms the *halides* and *sulfide* AlX_3 and Al_2S_3; the latter hydrolyzes in H_2O to give H_2S and $Al(OH)_3$.

Aluminum hydroxide ($K_{SP} = 5 \times 10^{-33}$) is amphoteric, dissolving in acids to form salts when it functions as a base, and in strong bases to form aluminates when it functions as an acid:

$$Al(OH)_3 + 3H^+ + 3NO_3^- = 3H_2O + Al^{+3} + 3NO_3^-$$
$$Al(OH)_3 + Na^+ + OH^- = Na^+ + Al(OH)_4^- .$$

Aluminum hydroxide is not soluble in NH_4OH nor does Al^{+3} form an ammine complex, although *ammoniates* such as $AlCl_3 \cdot 6NH_3$ (corresponding to *hydrates* $AlCl_3 \cdot 6H_2O$) are known. The *nitrate*, *sulfate*, and *fluoride* of Al are clearly electrovalent compounds as shown by their high melting points and conductance in aqueous solution, but the other halides of Al are largely covalent. Of these, aluminum chloride is industrially important as a catalyst in some organic reactions; it, for example, promotes the change from a straight-chain to branched-chain structures in alkanes, the latter having higher octane ratings. The aluminum *halides* are hydroscopic and decompose when heated to dehydrate them, giving Al_2O_3 plus the halogen acid. The molecular weights in the vapor state correspond to a doubled molecule presumably held together through halogen bridge bonding:



Complexes in solution range from AlX^{+2} to AlX_6^{-3}. K_{ins} for AlF_6^{-3} is 1.44×10^{-20}.

Aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$ and the double sulfate, *potassium aluminum sulfate* (alum), $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ are two important commercial compounds of the metal and are prepared from reaction between clays and sulfuric acid. The compounds are both used because Al^{III} hydrolyzes to give an acidic solution and also because (hydrated) $Al(OH)_3$ precipitates.

$$Al^{+3} + 6H_2O = Al(H_2O)_6^{+3} = Al(OH)_3(H_2O)_3 + 3H^+$$

Thus one use of aluminum sulfate is in baking powders where its acidity causes $NaHCO_3$ to release CO_2, which raises dough; another use is in settling suspended matter in municipal water treatment by adsorption and mechanical entrapment with the flocculant aluminum hydroxide precipitate.

Qualitatively, Al^{+3} is identified by the characteristic gelatinous appearance of its hydroxide, and, in lower concentration, by formation of a red lake with the organic reagent, aluminon (test 17–6 this chapter, and Example 16, Chapter 12). *Quantitative determination* is similar; large quantities are precipitated with NH_4OH and ignited and weighed as the oxide, or precipitated with oxine (special experiment 7, part 6). Small quantities are measured colorimetrically using aluminon.

Chromium

This metal is hard and brittle and has a high luster. It has two crystal forms, a hexagonal form stable below 800 C, and a cubic form stable at higher temperatures. Of the elements in periodic group VIB, chromium is most abundant and easiest to win from the ore. The chief mineral is chromite, $Cr_2O_3 \cdot FeO$ which is reduced by heating with coke to give an iron-chromium alloy that is added as such to iron melts to give chromium steels. These steels contain 14–30% Cr. Two common ones are: 18% Cr, 8% Ni, remainder iron (called 18-8 stainless) for applications like the construction of food handling machinery; and 15% Cr, 60% Ni, remainder iron (called nichrome) and used in heating elements. Such alloys are tough and difficult to fabricate but have good corrosion resistance. Considerable Cr_2O_3 is used to make furnace linings and green paints. Cr metal is also used as a protective and decorative coating on other metals, as in auto fixtures. The sp. gr. of Cr is 7.1, the m.p. is 1540 C, and the b.p. is 2475 C.

The *oxidation states* of chromium are (II), (III), (IV)?, (V), and (VI). Chromium may also be said to have a (0) oxidation state in *chromium carbonyl*, $Cr(CO)_6$, a covalent compound of considerable stability. Donation by CO of a total of 12 electrons gives an electron configuration about Cr like Kr, the next rare gas. Mo and W also form hexacarbonyls. The metal dissolves slowly in acid to give *chromous* ion, Cr^{II}, which is readily oxidized to the *chromic* state, Cr^{III}. The chromic ion has a strong tendency toward 6-coordination with ions like halide and cyanide and is present in water solution as characteristically violet-colored $Cr(H_2O)_6^{+3}$. Three partials are

$$Cr = Cr^{+2} + 2e^- \qquad E^\circ = 0.91$$

$$Cr = Cr^{+3} + 3e^- \qquad E^\circ = 0.74$$

$$Cr^{+2} = Cr^{+3} + e^- \qquad E^\circ = 0.41$$

Heated Cr metal reacts with O_2 to give Cr_2O_3, with N_2 to yield CrN, with halogens to give CrX_3 (except in the case of I_2 where the latter's lack of oxidizing strength gives only CrI_2), and with sulfur to give CrS for the same reason. *Chromous compounds* somewhat resemble corresponding ferrous compounds but are not important. Adding base to solutions of chromic salts precipitates *hydrated chromic oxide*, written $Cr(OH)_3$ ($K_{SP} = 7 \times 10^{-31}$), although no definite formula may be assigned. This hydroxide is amphoteric and dissolves in either strong acids or bases, the latter giving *chromites* that have variable composition depending upon base strength:

$$Cr(OH)_3 + 3H^+ = Cr^{+3} + 3H_2O$$

$$Cr(OH)_3 + 3OH^- = Cr(OH)_6^{-3}$$

Concentrated NH_4OH solutions give $Cr(NH_3)_6^{+3}$. In addition to the oxide and hydrous oxide (hydroxide), the *phosphate* of Cr^{III} is also only slightly soluble.

Cr^{VI} compounds are industrially important. The *chromates*, CrO_4^{-2}, and *dichromates*, $Cr_2O_7^{-2}$, are the forms in which hexavalent chromium is known. Cr^{VI} is a powerful oxidizing agent in acid solution.

$$2Cr^{+3} + 7H_2O = Cr_2O_7^{-2} + 14H^+ + 6e^- \qquad E^\circ = -1.36$$

Advantage is taken of this in analytical chemistry in titration of Fe^{+2} to Fe^{+3}, and in commerce for the tanning of hides. $Na_2CrO_4 \cdot 10H_2O$ is made by fusing chromite ore with soda ash and extracting the mass with water. $Na_2Cr_2O_7 \cdot 2H_2O$ is prepared from that solution by acidification with H_2SO_4.

The chromic-chromate-dichromate-perchromate transformations are illustrated in the group 3 analytical procedure. In basic solution, green $Cr(OH)_3$ is converted to $Cr(OH)_4^-$ and oxidized to yellow CrO_4^{-2} by H_2O_2, since at high pH, the potentials allow hydrogen peroxide to convert Cr^{III} to Cr^{VI}, a reaction that goes the other way in dilute acid solution.

$$2Cr(OH)_4^- + 2OH^- + 3H_2O_2 = 2CrO_4^- + 8H_2O$$

Acidification of this mixture with HNO_3, followed by addition of H_2O_2 and butanol, C_4H_9OH, gives orange $Cr_2O_7^{-2}$, then the unstable *perchromic acid* which dissolves in and colors the alcohol layer blue:

$$2CrO_4^{-2} + 2H^+ = Cr_2O_7^{-2} + H_2O$$

$$H_2Cr_2O_7 + 4H_2O_2 = 2CrO_5 + 5H_2O$$

The color changes are used in qualitative testing to detect chromium.

A covalently bonded Cr^{VI} compound is *chromyl chloride*, CrO_2Cl_2, a liquid which is soluble in CCl_4, CS_2, etc., and used in certain organic oxidations. It is prepared by heating a dichromate, alkali metal chloride, and sulfuric acid together. Chloride is identified via this reaction due to the distinctive red color of CrO_2Cl_2. Chromyl chloride boils at 116 C without decomposition but is easily hydrolyzed to $H_2O + Cl_2 + CrCl_3$.

Quantitatively, large amounts of chromium are put into solution by sodium carbonate—sodium peroxide fusion, followed by acidification. Addition of KI to the $Cr_2O_7^{-2}$ yields an equivalent amount of I_2, which is titrated with standard $Na_2S_2O_3$. Small amounts ($<$ 10 ppm) of hexavalent Cr are run colorimetrically with *s*-diphenylcarbazide.

Iron

Iron is the most important of the structural metals, and, fortunately for mankind, it is the fourth most abundant element in the earth's crust and is concentrated in several huge deposits. The sp. gr. of Fe is 7.86, its m.p. is 1539 C, and b.p. is 2800 C. The human body is about 0.005% by weight iron, and igneous rocks are about 5.0% by weight iron. Gradual weathering of rocks (primarily calcium, magnesium, and iron silicates) has resulted in deposition of oxides of iron from which the metal is obtained by coke reduction, as explained in Chapter 13. These minerals include hematite, Fe_2O_3, magnetite, Fe_3O_4, and limonite, $2Fe_2O_3 \cdot 3H_2O$. Iron shows three distinct solid forms plus another which differs only in magnetism from one of the other three. The α-, β-, and δ- forms are all body-centered cubical lattices, whereas γ-iron is face centered; α and β are similar except that α is magnetic and none of the others are. Little is known about δ-iron since it is stable only in a narrow range of high temperatures. The relationship is:

$$\alpha \overset{770\text{ C}}{\rightleftharpoons} \beta \overset{928\text{ C}}{\rightleftharpoons} \gamma \overset{1411\text{ C}}{\rightleftharpoons} \delta \overset{1530\text{ C}}{\rightleftharpoons} \text{Liquid} \overset{3235\text{ C}}{\rightleftharpoons} \text{gas}$$

Uses for iron and its alloys are too numerous and obvious to mention, but it may be repeated here that the most important alloys are those with carbon (the steels) because the normally soft iron is greatly hardened by carbon, and steels are capable of wide variation of properties by heat treatment.

The *oxidation states* of iron are (II), (III), (IV), and (VI); they are respectively illustrated by Fe^{+2} *ferrous*, Fe^{+3} *ferric*, FeO_3^{-1} *perferrite*, and FeO_4^{-2} *ferrate*. Of these the perferrites have been prepared only by high-temperature reactions of melts like $Fe(NO_3)_3 + Sr(NO_3)_2$, whereas the ferrates, which are also strong oxidants, are made in basic solutions by anodic oxidation of iron or by chlorination of a suspension of *hydrous ferric oxide*. In addition to these four oxidation states, a (0) state is also observed in a few compounds like *iron pentacarbonyl*, $Fe(CO)_5$, a liquid boiling at 102 C and prepared by the action of carbon monoxide on powdered iron. The compound is poisonous and its formation accounts for the disintegration of metal around automobile exhausts. For purposes here, only the common (II) and (III) states will be considered. Related couples in acid solution are:

$$Fe = Fe^{+2} + 2e^- \qquad E^\circ = 0.44$$
$$Fe^{+2} = Fe^{+3} + e^- \qquad E^\circ = -0.77$$

Iron metal is therefore attacked by acids and is capable of reducing Fe^{+3} to Fe^{+2}. Strong oxidizing agents like $Cr_2O_7^{-2}$ and HNO_3 passivate iron metal by giving it an oxide surface. Iron also dissolves in basic solution where *ferrous hydroxide* is readily converted to ferric which is insoluble and helps displace the equilibrium:

$$Fe + 2OH^- = Fe(OH)_2 + 2e^- \qquad E_B^\circ = 0.88$$
$$Fe(OH)_2 + OH^- = Fe(OH)_3 + e^- \qquad E_B^\circ = 0.56$$

Ferrous hydroxide is noted to be a much better reducing agent than Fe^{+2}. *Ferrous compounds* are usually light green, since that is the color of Fe^{+2}. *Ferrous sulfate heptahydrate* (copperas), $FeSO_4 \cdot 7H_2O$, is the most common ferrous salt. It is made by the oxidation of the natural iron sulfide, *pyrite* or fool's gold, FeS_2. Ferrous sulfate is used to make "iron blues," which are pigments produced by reaction of Fe^{+2} with ferrocyanide and followed by oxidation to Prussian blue with dichromate (see p. 403, Chapter 22). These pigments are used to make inks (see special experiment 7) and other chemicals. *Ferrous sulfide*, FeS, is preparable by direct combination of the heated elements; it yields H_2S when acidified. *Ferrous ammonium sulfate* (Mohr's salt), $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, is used as a standard in quantitative analysis.

Ferric compounds are normally obtained when ferrous compounds are oxidized and vice versa. Ferric oxide (hydrated), written as *ferric hydroxide*, $Fe(OH)_3$, forms readily from $Fe(OH)_2$ under the influence of air oxidation. Dissolving the red-brown $Fe(OH)_3$ in acids yields ferric salts. An exception is HI: its reducing action gives FeI_2 as the final product. Fe^{III} forms many soluble complexes: FeX_6^{-3} (with halogens), $Fe(C_2O_4)_3^{-3}$, $Fe(CN)_6^{-3}$, $Fe(SCN)_6^{-3}$, etc., some of which are illustrated under the sections on anions. Depending upon concentrations, intermediate amounts of coordination are possible, $Fe(SCN)^{+2}$, $Fe(SCN)_2^+$, etc. *Ferric oxide*, Fe_2O_3, may be prepared in different shades of red and is used as a pigment; *ammonium hexacyanoferrate(III)*, $(NH_4)_3[Fe(CN)_6]$, is the source of blue color in blue print paper, and *ferric chloride*, $FeCl_3$, is used as an acid etchant for metals.

Table 17-1. Equilibrium Constants for Some Iron(II) Reactions

Reactions (in order of decreasing $[Fe^{+2}]$)	K	Formula Weight
$Fe(OH)_2 = Fe^{+2} + 2OH^-$	1.8×10^{-15}	89.87
$FeCO_3 = Fe^{+2} + CO_3^{-2}$	2.11×10^{-11}	115.86
$FeS_{(\alpha)} = Fe^{+2} + S^{-2}$	4×10^{-17}	87.91
$FeSe = Fe^{+2} + Se^{-2}$	$\sim 10^{-26}$	134.81
$Fe(CN)_6^{-4} = Fe^{+2} + 6CN^-$	$\sim 10^{-35}$	211.91

Table 17-2. Equilibrium Constants for Some Iron(III) Reactions

Reactions (in order of decreasing $[Fe^{+3}]$)	K	Formula Weight
$Fe(SCN)^{+2} = Fe^{+3} + SCN^-$	1.04×10^{-3}	113.93
$FePO_4 = Fe^{+3} + PO_4^{-3}$	1.5×10^{-18}	150.83
$Fe(OH)_3 = Fe^{+3} + 3OH^-$	6×10^{-38}	106.87
$FeF_5^{-2} = Fe^{+3} + 5F^-$	5×10^{-16}	150.85
$Fe_2S_3 = 2Fe^{+3} + 3S^{-2}$	$\sim 10^{-88}$	207.88
$Fe(CN)_6^{-3} = Fe^{+3} + 6CN^-$	$\sim 10^{-42}$	211.91

Ferrous and ferric iron can be differentiated simply by their color in water solution or the color produced with ions like SCN^-, $Fe(CN)_6^{-3}$, and $Fe(CN)_6^{-4}$ as illustrated in test 17-1. *Ferric ferrocyanide* is called Prussian blue, *ferrous ferricyanide* is Turnbull's blue, *ferric ferricyanide* is Berlin green (though it is brownish colored), and *ferrous ferrocyanide* has no common name and is white, or if air oxidized, light blue.

There are many sensitive organic reagents that are used in colorimetry for both qualitative and *quantitative analysis*; two good ones are 1,10-phenantholine and α,α'-dipyridyl. The usual macro quantitative method for iron is one in which Fe^{+3} is reduced to Fe^{+2} with either Zn metal or Sn^{II} and then reoxidized by titration in acid solution with MnO_4^-, $Cr_2O_7^{-2}$, or Ce^{IV}.

Cobalt

This is a silvery metal with a slight bluish color that is harder and stronger than either Fe or Ni and is magnetic below 1150 C. Its sp. gr. is 8.9, the m.p. is 1493 C, and b.p. is 3520 C. The principal minerals are cobaltite CoAsS, smaltite $CoAs_2$, and cobalt bloom, $3CoO \cdot As_2O_5 \cdot 8H_2O$. These must go through several refining processes to recover cobalt metal from the metallic impurities which include Ag, Fe, Ni, and Cu. A mixture of NiO + CoO is obtained after several roasting steps, and this is handled by the Mond process in which reduction with CO + H_2 at 300 C gives the metals. Nickel is then removed from the powdered metallic mixture by causing it to react with CO and form *nickel carbonyl,* $Ni(CO)_4$, which is volatile. The $Ni(CO)_4$ is pumped through a tower packed with nickel pellets where it decomposes reversibly at 180 C. Cobalt does not react with carbon monoxide.

Cobalt metal is used in some important applications by itself and as an alloying metal. When bombarded in atomic piles it acquires and retains radioactivity better than any other common metal and is used as a radiation substitute for radium in cancer therapy. It may also be used in bomb cases containing nuclear explosives, since the explosion would produce radio cobalt vapor that might remain dangerous for years and would increase the casualty range with its radioactive "fallout." Cobalt is added to Cr—Ni—Mo—C steels up to 12% by weight to give a product useful in cutting hard materials such as heat-treated steels. Cobalt powder is used as a binding agent in making sintered tungsten and titanium carbides, such as carbaloy, which are used in drawing and extrusion dies. The stellite alloys containing about 1.25% C, 65% Co, 28% Cr, and 4% W are used in cutting tools because of their wear and oxidation resistance, ability to keep the edge at high temperatures, and low friction coefficient with respect to most metals.

The *oxidation states* of Co are (I), (II) *cobaltous,* (III) *cobaltic,* and (IV). Of these the only simple ion stable in water solution is Co^{+2} (hydrated). Co^{I} and Co^{IV} are rare, and Co^{+3} is a powerful enough oxidizing agent to liberate O_2 from H_2O and is only capable of existence in aqueous solution in the form of complexes such as $Co(NH_3)_6^{+3}$. Some potential values of interest are:

$$Co = Co^{+2} + 2e^- \qquad E^\circ = 0.28$$

$$Co^{+2} = Co^{+3} + e^- \qquad E^\circ = -1.84$$

$$Co(NH_3)_6^{+2} = Co(NH_3)_6^{+3} + e^- \qquad E_B^\circ = -0.1$$

$Co(H_2O)_6^{+2}$ is pink. When a little strong base is added, a bluish $Co(OH)_2$ precipitates; more base changes this to a pinkish $Co(OH)_2$ and air gradually oxidizes it to black $Co(OH)_3$. Cobaltous ion gives black CoS with alkaline sulfides. As freshly precipitated, it is slowly soluble in dilute HCl and is called the α-form, but after standing it changes structure to the β-form which is considerably less soluble. *Cobaltous chlorides* in which the coordination number of cobalt is 6, are pink, whereas those with 4-coordination are blue. Both Co^{II} and Co^{III} form many Werner compounds readily coordinating NH_3, H_2O, CN^-, X^-, NO_2^-, etc. See Chapter 4 for structures. The coordination number is usually 6 and the geometry is octahedral.

Cobalt compounds have limited use; for example, $CoCl_2$ is used with dessicants like silica gel as an indicator, since, when it changes from its blue color to the pink of $[Co(H_2O)_6]Cl_2$, it indicates that the dessiccant's absorptive capacity is low. CoO is used in ceramic glazes to give a blue color, as one might guess from the bead tests described in experiment 5, Chapter 23. *Cobalt napthenates* are used as paint and varnish driers.

The blue borax bead is good qualitative evidence of Co, as is the formation of yellow $K_3Co(NO_2)_6$, test 17–9.

TABLE 17–3. EQUILIBRIUM CONSTANTS FOR SOME COBALT(II) REACTIONS

Reactions (in decreasing order of $[Co^{+2}]$)	*K*	Formula Weight
$Co(NH_3)_6^{+2} = Co^{+2} + 6NH_3$	1.25×10^{-5}	161.12
$Co(OH)_2 = Co^{+2} + 2OH^-$	2.5×10^{-16}	92.96
$CoCO_3 = Co^{+2} + CO_3^{-2}$	8×10^{-13}	118.95
$CoS_{(\alpha)} = Co^{+2} + S^{-2}$	5×10^{-22}	91.00
$CoS_{(\beta)} = Co^{+2} + S^{-2}$	1.9×10^{-27}	91.00

Quantitatively, Co may be determined colorimetrically with SCN^--acetone and extraction of the color, or larger amounts can be determined electrolytically after removing any iron as a phosphate precipitate and separating Co from any Ni by precipitation (and later resolution) using α-nitroso-β-naphthol. The subsequent electrolysis is done from NH_4OH solution.

Nickel

Nickel is a silvery metal which is malleable and ductile and yet stronger than iron. It does not oxidize as readily as iron and is magnetic below 345 C. The sp. gr. is 8.9, the m.p. is 1452 C, and the b.p. is 2800 C. It is used in many corrosion-resistant alloys as monel, hastelloy, stainless steel, and in the important magnetic alnico alloys. See appendix A23. Nickel is also used as a plating metal and as a catalyst for hydrogenations, such as the conversion of cottonseed oil to solid cooking fats.

The main minerals are pentalandite ($2FeS \cdot NiS$), nickelite, and millerite. The latter two are nominally NiS. Nickel is separable by the Mond process described under **Cobalt** or once isolated as NiS it is reducible by heating with coke. Purification is frequently by electrolysis.

The chemistry of Ni is similar to that of Fe and Co though nickel is less active.

$$Ni = Ni^{+2} + 2e^- \qquad E^\circ = 0.25$$

The nickel *oxidation states* are (0), (I), (II), (III), and (IV). These are illustrated respectively by *nickel carbonyl*, $Ni(CO)_4$, *potassium tricyanonickelate(I)*, $K_2[Ni(CN)_3]$, *nickelous sulfate hexahydrate*, $NiSO_4 \cdot 6H_2O$, *nickel trioxide*, Ni_2O_3, and *nickelic oxide*, NiO_2. Not much is known about any of these states except the dipositive one, since the others are produced only under special conditions. NiO_2 is used in the Edison battery, $NiO_2 + Fe + 2H_2O = Ni(OH)_2 + Fe(OH)_2$—reaction is in KOH solution. Most other compounds of the unfamiliar states are of but theoretical interest and for discussion here, the chemistry of nickel is that of Ni^{+2} and its compounds. Among these the *oxide* NiO, *hydroxide* $Ni(OH)_2$, *sulfide* NiS, *carbonate* $NiCO_3$, *chromate* $NiCrO_4$, *oxalate* NiC_2O_4, and *phosphate* $Ni_3(PO_4)_2$ are not appreciably water soluble although they will dissolve in mineral acids. NiS, like CoS, will not precipitate in acidic solution and once formed, is slow to dissolve in dilute HCl; a separation from other group 3 precipitates is sometimes made on that basis. NiS has three forms each possessing a different solubility product constant (Table 17–4). The α-form predominates in alkaline sulfide precipitations but changes to the less soluble β- or γ-form upon standing or if acid is added.

Hydrated Ni^{+2} salts are green and dehydrated ones are yellow. Nickelous ion, like the cobaltous ion, forms many complexes (though they are not as stable), such as $Ni(CN)_4^{-2}$, $Ni(H_2O)_4^{+2}$, and $Ni(NH_3)_4^{+2}$. In these, Ni^{+2} has the argon shell plus eight electrons in the $3d$ group. Coordination of 4 groups, each contributing two electrons, establishes a $3d$, a $4s$, and two $4p$ orbitals resulting in a square planar spatial arrangement characteristic of dsp^2 hybridization. Ni^{+2} also forms complexes with 6-coordinated groups, as $Ni(NH_3)_6^{+2}$, in which the $3d$, $4s$, and $4p$ quantum levels are filled by electron donation of six pairs of electrons from coordinated groups.

Nickel and cobalt are generally isolated from other group 3 ions, then tested in the presence of each other, so tests for Ni^{+2} which are not interferred with by Co^{+2} and vice versa are important analytically. Thus SCN^--acetone, α-nitroso-β-naphthol, and KNO_2—HAc react with Co^{+2} but not with Ni^{+2}. Dimethylglyoxime-NH_3 precipitates Ni^{+2} but not Co^{+2}.

The characteristic red *nickel-dimethylglyoxime chelate* is used *quantitatively* simply by filtering it off, drying at 110 C, and weighing. Nickel is assayed volumetrically using standard KCN, which forms $Ni(CN)_4^{-2}$ in a solution made slightly basic with NH_4OH; AgI is used as the indicator

TABLE 17-4. EQUILIBRIUM CONSTANTS FOR SOME NICKEL(II) REACTIONS

Reactions (in order of decreasing $[Ni^{+2}]$)	K	Formula Weight
$NiCO_3 = Ni^{+2} + CO_3^{-2}$	1.36×10^{-7}	118.70
$Ni(OH)_2 = Ni^{+2} + 2OH^-$	1.6×10^{-16}	92.71
$Ni(NH_3)_4^{+2} = Ni^{+2} + 4NH_3$	1×10^{-8}	126.81
$Ni(NH_3)_6^{+2} = Ni^{+2} + 6NH_3$	1.8×10^{-9}	160.87
$NiS_{(\alpha)} = Ni^{+2} + S^{-2}$	1×10^{-22}	90.75
$NiS_{(\beta)} = Ni^{+2} + S^{-2}$	1×10^{-26}	90.75
$NiS_{(\gamma)} = Ni^{+2} + S^{-2}$	2×10^{-28}	90.75
$Ni(CN)_4^{-2} = Ni^{+2} + 4CN^-$	$\sim 10^{-22}$	162.73

since when all the Ni^{+2} is complexed as the cyanide, the turbidity due to AgI disappears with the next drop of CN^-.

$$AgI + 2CN^- = Ag(CN)_2^- + I^-$$

Nickel may also be determined by electrolysis in NH_4OH solutions previously freed of copper and cobalt.

Manganese

This metal has a reddish tint and is moderately soft if pure, but as normally obtained by carbon reduction of the dioxide it is hard due to the presence of Mn_3C in solid solution. Electrolytic reduction gives pure metal. The sp. gr. is 7.2, the m.p. is 1244 C, and the b.p. is 2087 C. Manganese is used in at least three important general alloy types: (1) medium manganese structural steels containing 0.75–1.75% Mn, which are as strong as plain carbon steels yet contain less carbon and hence are more ductile (2) manganese bronzes, which are Cu-Zn brasses to which are added 0.1–5.0% Mn, 0.8–4.0% Fe, and 0.1–1.5% Sn to increase hardness and strength and decrease dezincification and grain growth and (3) Hadfield steels, containing up to 14% Mn, which have unusual wear resistance due to a work hardening of the surface yet exhibit retention of toughness in the rest of the structure. Hadfield steels find application in rail switches, earth moving equipment, conveyors, crushing machinery, etc., where wear is apt to be excessive.

The important mineral is pyrolusite, MnO_2, which is usually mixed with iron ores for common reduction to make ferromanganese, about 75% Mn and 25% Fe, and Spiegeleisen, roughly the reverse composition. Both alloys are added to iron melts in the preparation of steels. Low-grade ores containing CaO, Fe_2O_3, SiO_2, Al_2O_3, and MnO_2 are concentrated by the recently announced Nossen process in which the powdered ore is reduced at about 800 C to give MnO. The mass is extracted with HNO_3, solubilizing Mn and Co and leaving the rest, from which iron can be obtained magnetically. The solution is concentrated and HNO_3, $Ca(NO_3)_2$ (for fertilizer), and MnO_2 are recovered by heating the concentrate. About 0.8 million tons of Mn metal are used yearly in the U.S. for steel making, and another 0.1 million tons of MnO_2 are consumed in the chemical and dry cell battery industries. Pyrolusite, interestingly enough, is found on the ocean floor as well as in more conventional deposits. These so-called "manganese nodules" have not yet been exploited.

The *oxidation states* of Mn are (I) as $K_5[Mn(CN)_6]$, *potassium hexacyanomanganate*(I); (II) as $MnSO_4$, *manganous sulfate*; (III) as $Mn(OH)_3$, *manganic hydroxide*; (IV) as MnO_2, *manganese dioxide*; (V) as Na_3MnO_4, *sodium manganate*(V); (VI) as $CaMnO_4$, *calcium manganate*, and (VII) as $KMnO_4$, *potassium permanganate*. Of these, Mn^{II} and Mn^{III} have basic characteristics, Mn^{IV} is amphoteric, and the three higher states are acidic. *Mn^{III}* and *Mn^{V} compounds* are not stable toward disproportionation. Mn^{VI} is stable only in basic solution and Mn^{I} is known only in complex cyanides. Mn^{II} is a reducing agent and Mn^{VII} is an oxdizing agent.

Manganous ion, Mn^{+2} is the most familiar manganese ion in solution and most of its compounds are light pink. Bases precipitate $Mn(OH)_2$ which does not dissolve in excess base but is soluble if the concentration of NH_4^+ is high. Air oxidizes the hydroxide to a brown *hydrous oxide of Mn^{III}*, which is usually represented as $Mn(OH)_3$. Heating any of these hydroxides in air gives Mn_3O_4. Manganese metal dissolves in acids to yield salts plus hydrogen, and is slowly soluble in bases giving the hydroxide and hydrogen:

$$Mn = Mn^{+2} + 2e^- \qquad E^\circ = 1.18$$

$$Mn + 2OH^- = Mn(OH)_2 + 2e^- \qquad E_B^\circ = 1.55$$

Pink MnS is precipitated from Mn^{+2} solutions by alkaline sulfides and it is soluble in dilute acids. Other slightly soluble Mn^{+2} compounds are the *carbonate*, *cyanide* (soluble in excess due to complex formation), *oxalate*, and *phosphate*. None of these is of commercial interest.

MnO_2 is the only important Mn^{IV} compound. It is used in dry cell batteries ($Zn = Zn^{+2} + 2e^-$ and $2MnO_2 + 4H_2O + 2e^- = 2Mn(OH)_3 + 2OH^-$) and as a drier in paints. MnO_2 dissolves slowly in mineral acids to give Mn^{IV} salts, but these are not stable and change to Mn^{II} with oxidation of the anion. MnO_2 fused with a base like KOH or Na_2CO_3 to which has been added a strong oxidizing agent like $KClO_3$ gives green manganates as K_2MnO_4. Acidification brings about disproportionation:

$$3MnO_4^{-2} + 4H^+ = 2MnO_4^- + MnO_2 + 2H_2O$$

In basic solution, in the presence of strong oxidizing agents, manganates are oxidized to permanganates. $KMnO_4$, the most common of these, is prepared by fusing MnO_2 with KOH and oxidizing the manganate in KOH solution by bubbling in chlorine. Related half cell data are:

$$Mn^{+2} + 2H_2O = MnO_2 + 4H^+ + 2e^- \qquad E^\circ = -1.23$$

$$MnO_2 + 4OH^- = MnO_4^{-2} + 2H_2O + 2e^- \qquad E^\circ = -0.60$$

$$MnO_4^{-2} = MnO_4^- + e^- \qquad E^\circ = -0.56$$

The couple

$$Mn^{+2} + 2H_2O = MnO_4^- + 8H^+ + 5e^- \qquad E^\circ = -1.51$$

s a familiar one in redox titrimetry. Oxidations using MnO_4^- are generally run in sulfuric acid solution. Typical reducing agents quantitatively determined with standardized $KMnO_4$ are Fe^{+2}, H_2O_2, $H_2C_2O_4$, HNO_2, Sn^{II},. Mo^{III}, U^{IV}, VO^{+2}, As^{III}, and Ti^{III}. In these Mn^{+2} and the other products are not highly colored, so MnO_4^- acts as its own indicator, the first drop in excess coloring the solution. If oxidations are carried out in neutral or basic solution, brown MnO_2 precipitates and the end point is not clear. With neutral solutions in the presence of Ba^{+2}, reaction goes only to Mn^{VI} as $BaMnO_4$ precipitates, a reaction used to determine some organic reductants like alcohols, aldehydes, and cyanides which otherwise present difficulty, due to side reactions, if run in acid solutions.

TABLE 17-5. EQUILIBRIUM CONSTANTS FOR SOME MANGANESE(II) REACTIONS

Reactions (in order of decreasing $[Mn^{+2}]$)	K	Formula Weight
$Mn(OH)_2 = Mn^{+2} + 2OH^-$	1×10^{-19}	88.96
$Mn_3(PO_4)_2 = 3Mn^{+2} + 2PO_4^{-3}$	10^{-22}	354.78
$MnCO_3 = Mn^{+2} + CO_3^{-2}$	8.8×10^{-11}	114.94
$MnS = Mn^{+2} + S^{-2}$	8×10^{-14}	87.00
$MnC_2O_4 = Mn^{+2} + C_2O_4^{-2}$	1.1×10^{-15}	126.96

Manganese is found qualitatively by oxidation, as previously mentioned, to MnO_4^- whose purple color is distinctive, or to MnO_4^{-2} whose green color is easily recognized in fusion mixtures.

Quantitatively, manganese is oxidized to MnO_4^- and small amounts are found colorimetrically. Larger amounts are handled by titrating with a standardized solution of reducing agent such as sodium arsenite.

Zinc

Zinc is malleable and ductile in the range 100–150 C but somewhat brittle otherwise. Its sp. gr. is 7.14, m.p. is 419.4 C, and b.p. is 907 C. The metal is used as a protective coating on iron fences, sheeting, and pipes. It is deposited by dipping in molten zinc (galvanizing), by baking on a layer of zinc powder (sherardizing), or by electrolysis in alkaline baths. Zinc is also used in several important alloys; brass is the one produced in greatest tonnages. Zinc dust is also used in certain metallurgical reductions to displace more noble metals from solution.

Of the six oxide, sulfide, and carbonate ores in demand today as zinc sources, sphalerite, sometimes called black jack, ZnS, and zincite, ZnO, are most widely distributed. The ores are concentrated and roasted to ZnO. The metal is then obtained by two general processes: (1) carbon reduction and distillation of zinc by either the older batch, Belgian horizontal-retort method, or the continuous vertical-retort method, or (2) electrolytically at 35 C from a dilute H_2SO_4-$ZnSO_4$ solution, using an Al cathode and Pb anode. The zinc obtained in the latter method is remelted and cast into slabs for further processing; the more pure zinc from the former method may be redistilled to greater than 99.99% purity. The usual impurities are cadmium (which zinc strongly resembles), lead, and iron.

Experiments have indicated that zinc has *oxidation states* of (0), (I), (II), and (III), but almost all of zinc chemistry is that of dipositive zinc as the zinc ion, Zn^{+2}, and as the zincate ion. The latter varies in composition with base strength, is readily hydrolyzed by dilution, and written variously as ZnO_2^{-2}, $HZnO_2^-$, $Zn(OH)_3^-$, and $Zn(OH)_4^{-2}$. Zinc metal is a good reducing agent and dissolves in acid or base:

$$Zn = Zn^{+2} + 2e^- \qquad E^\circ = 0.76$$

$$Zn + 2OH^- = Zn(OH)_2 + 2e^- \qquad E_B^\circ = 1.25$$

The powdered metal burns readily in air to the *oxide* which is basic, $Zn(OH)_2$ is a crystalline material unlike the "hydroxides" of Al, Fe, Ti. Cr, Zr, etc. It is formed when Zn^{+2} and a dilute base react or ZnO is shaken with H_2O, and is soluble either in excess strong base forming zincate ion, or in ammonium hydroxide, forming tetrammine zinc ion, $Zn(NH_3)_4^{+2}$. The sp^3 bond type in the latter leads to tetrahedral geometry. ZnO is used in white paints and as a filler in rubber compounding. Zincate-strong base solutions are used to plate metals like Al with Zn prior to Cu plating.

Zinc salts are made by dissolving Zn or ZnO in acids. The *halides* are the most water soluble and are also appreciably soluble in organic solvents in which they are sometimes employed (as is Al_2Cl_6) for catalytic effects. $ZnCl_2$ is used as a flux in soldering because of its ability to dissolve metal oxide films. ZnS is precipitated in group 3 by alkaline sulfides and is readily soluble in dilute acids. It is prepared on an industrial scale, $\mathbf{ZnSO_4 + BaS \overset{\Delta}{=} BaSO_4 + ZnS}$; the mixture of products is called lithopone, a white paint pigment. Other sparingly soluble zinc compounds besides those in Table 17-6 are the *phosphate*, $Zn_3(PO_4)_2$, and *ferrocyanide*, $Zn_2Fe(CN)_6$, all of which are white.

TABLE 17-6. EQUILIBRIUM CONSTANTS FOR SOME ZINC REACTIONS

Reactions (in order of decreasing $[Zn^{+2}]$)	K	Formula Weight
$ZnC_2O_4 = Zn^{+2} + C_2O_4^{-2}$	1.5×10^{-9}	137.40
$ZnCO_3 = Zn^{+2} + CO_3^{-2}$	2×10^{-10}	125.39
$Zn(OH)_2 = Zn^{+2} + 2OH^-$	5×10^{-17}	99.40
$Zn(NH_3)_4^{+2} = Zn^{+2} + 4NH_3$	3.4×10^{-10}	133.50
$ZnS = Zn^{+2} + S^{-2}$	1×10^{-20}	97.44
$ZnSe = Zn^{+2} + Se^{-2}$	$\sim 10^{-31}$	144.34
$Zn(CN)_4^{-2} = Zn^{+2} + 4CN^-$	1.2×10^{-18}	169.42

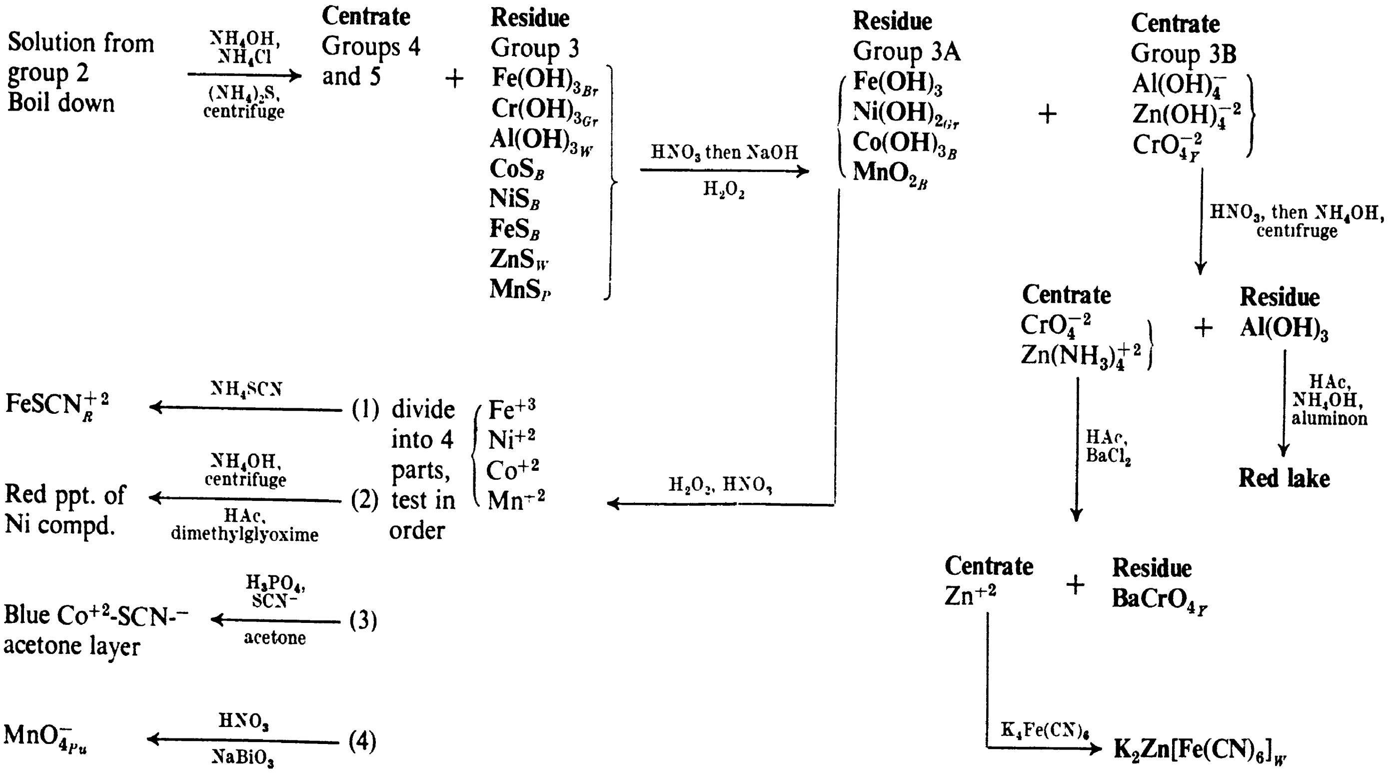
Qualitatively, Zn^{+2} is detected as the sulfide or ferrocyanide after other group 3 metals have been removed. *Quantitatively*, Zn^{+2} is often titrated with standard $Fe(CN)_6^{-4}$ using UO_2^{+2} as an external indicator, or it is precipitated as $Zn(NH_4)PO_4$ and ignited and weighed as $Zn_2P_2O_7$, *zinc pyrophosphate*.

Group 3 Analysis—General Description

The ions of groups 1 and 2 are first removed as described in the two preceding chapters. The solution is buffered with $NH_4OH + NH_4Cl$ and $(NH_4)_2S$ is added. In this alkaline sulfide solution, Al, Cr, and Fe^{+3} precipitate as hydrous oxides and the other group 3 ions, including Fe^{+2}, precipitate as sulfides. Centrifugation of this mixture separates group 3 in the residue and retains groups 4 and 5 in the centrate.

The residue is dissolved in nitric acid and separated into two subgroups by the addition of excess NaOH. These are called subgroup 3A (the "nickel group") and subgroup 3B (the "aluminum group"). Subgroup 3A is a residue of $Fe(OH)_3$, $Ni(OH)_2$, $Co(OH)_2$, and $Mn(OH)_2$. Subgroup 3B is a solution of amphoteric metals as complex hydroxides, $Al(OH)_4^-$, $Cr(OH)_4^-$, and $Zn(OH)_4^-$. Adding H_2O_2 to the mixture does not dissolve

FLOW SHEET—GROUP 3



or precipitate any metals but does oxidize* $Co(OH)_2$ to $Co(OH)_3$, $Mn(OH)_2$ to MnO_2, and $Cr(OH)_4^-$ to CrO_4^{-2}, and the mixture is then centrifuged to separate the subgroups.

Continuing first with subgroup 3A, one dissolves the solids in a mixture of hot, dilute HNO_3 and H_2O_2 to give a solution of Fe^{+3}, Ni^{+2}, Co^{+2}, and Mn^{+2}. The solution is divided into four parts and each tested for a different ion. Iron is tested with SCN^-, the evidence being the red ferric thiocyanate color; nickel is tested with dimethylglyoxime as described in Chapter 12 (after precipitating iron and manganese with NH_4OH), a positive test being a bright red precipitate; cobalt is tested with SCN^- and acetone (after complexing iron with H_3PO_4), a positive reaction being a blue color in the organic layer; and manganese is tested by oxidation with $HNO_3 + NaBiO_3$ to give purple permanganate ion, MnO_4^-. These spot tests are distinctive enough so that a systematic separate scheme for subgroup 3A is not necessary.

Subgroup 3B is acidified with HNO_3 and then made slightly basic with NH_4OH whereupon aluminum precipitates as the hydrous oxide, leaving CrO_4^{-2} and $Zn(NH_3)_4^{+2}$ in the centrate after centrifuging. Aluminum is confirmed by solution and reprecipitation in the presence of aluminon. The chromate-tetraammine zinc solution is buffered and chromate removed by precipitation with Ba^{+2} to give yellow, insoluble $BaCrO_4$. The zinc ions in the centrate are then shown present by precipitation with ferrocyanide of white $K_2Zn[Fe(CN)_6]$.

This procedure is but one of many workable schemes and the student should read the article by Tenbusch and Brewer listed in the references at the end of this chapter for others.

PRELIMINARY TESTS WITH GROUP 3 IONS

Test solutions contain 10 mg/ml of the metallic ions.

Test 17–1. Some Reagents for Group 3 Analysis. As time permits, try each of the following in *separate* tests with a few drops of each group 3 test soln., including both Fe^{+2} and Fe^{+3}: little NH_4OH, excess NH_4OH, little 6 M NaOH, excess NaOH, excess NaOH + H_2O_2, $(NH_4)_2S$, KSCN, $K_4[Fe(CN)_6]$, and $K_3[Fe(CN)_6]$. Summarize the results in a table including formulas and characteristics of the products. Note which tests might help confirm ions in the unknown and what interferences one might encounter in a mixt. of several ions. Your data can be of value in seeking confirmatory tests on the unknown.

Test 17–2. Group 2 and Group 3 Sulfide Precipitations. In solns. about 0.3 M in H^+, the $[S^{-2}]$ is sufficient to ppt. group 2 sulfides but not large

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* The potentials in basic solution are such that peroxide is capable of oxidations like these. In the next step with acid solution, H_2O_2 acts as a reducing agent, however.

enough to ppt. group 3 sulfides, nor is $[OH^-]$ large enough to ppt. group 3 hydroxides. On this basis is the separation between these groups effected.

To illustrate, put 5 drops of Cd^{+2} soln., 5 drops of Fe^{+2} soln., 5 drops of H_2O, 1 drop of 6 M HCl, and 5 drops of thioacetamide in a test tube and heat it in a water bath. Only yellow CdS ppts. Consult the K_{SP} values and see why this is expected. Add 2 drops of 6 M NaOH to neutralize the acid and increase the $[S^{-2}]$. What is the black ppt. now forming?

Test 17-3. Separation of a 3A 3B Mixture. Make a mixt. of 4 drops of Al^{+3} test soln., 4 drops of Fe^{+3}, and 10 drops of H_2O. Review the behavior of these ions with excess strong base as noted in Test 17-1. Add 3 drops of 6 M NaOH to the mixt. and stir. What is the residue and what is in soln.? Centrifuge, remove the centrate, and neutralize it with 2 M HAc. What is the ppt. that forms? Write the equations and explain how this method effected the separation (later used in the unknown procedure) between typical ions of the subgroups.

Test 17-4. Conversion of $Cr(OH)_3$ to $Cr(OH)_4^-$, CrO_4^{-2}, $Cr_2O_7^{-2}$ and CrO_5. These transformations are described under **Chromium** in this chapter and in part H, Chapter 22. Try the reactions and account for the color changes by writing equations. Start by preparing some chromic hydroxide and carry the sample through the operations indicated.

Test 17-5. Oxidation States of Mn.

(*a*) *Mn^{+2} to MnO_4^-.* Mix in a crucible 2 drops of Mn^{+2} test soln., 10 drops of H_2O, 2 drops of concd. H_3PO_4, 6 drops of dil. HNO_3, and warm. Now add a few mg of one of the following oxidizers: $NaBiO_3$, sodium bismuthate; $(NH_4)_2S_2O_8$, ammonium peroxydisulfate; $Na_3H_2IO_6$, trisodium paraperiodate. Warm the mixt. again. Note the red color of permanganate against the white background. The concn. limit is 0.1 ppm Mn.

(*b*) *Mn^{+2} to MnO_2.* Mix 4 drops of Mn^{+2} soln., 10 drops of H_2O, and 2 drops of 6 M NaOH. The ppt. is $Mn(OH)_2$ and it will gradually turn dark due to atmospheric oxidation to hydrated manganese dioxide, sometimes written $MnO(OH)_2$. This can be hastened by adding 6 drops of 3% H_2O_2. Centrifuge and save the residue for (*c*).

(*c*) *MnO_2 to MnO_4^{-2}.* This is our first *bead test* and the instructor will demonstrate it first. Prepare a carbonate bead by fusing some Na_2CO_3 on a hot Pt wire. (Nichrome wire is not recommended as a substitute in this particular test.) Reheat the bead, touch it to the MnO_2 prepd. in (*b*), and reheat. Now touch it to a crystal of $KClO_3$ and reheat. The green color is due to the manganate ion, MnO_4^{-2}.

As an alternate confirmation of the MnO_2 ppt., one can convert it to MnO_4^- by the combination of reagents in (*a*).

Test 17-6. Aluminon Test. Aluminon is a common name for an org. reagent used to colorimetrically detect aluminum in concns. lower than can be visibly pptd., as $Al(OH)_3$. Dilute 1 drop of Al^{+3} test soln. to 10 ml and put 2 ml of that in a test tube. Add a drop of 1 M HAc, 4 drops of NH_4Ac, 3 drops of aluminon, and mix. Compare the color to that of a blank made by using simply 2 ml of dist. water with buffer and reagent. See Example 16, Chapter 12, p. 197. Fe^{+3} and Cr^{+3} interfere with this test by giving similar reactions.

Test 17–7. Thenard's Test for Al. This is our first *blowpipe test* and the instructor will demonstrate it first. Put a spatula full of $Al(OH)_3$, which you have prepd., on a charcoal block, add a drop of 0.05 *M* Co^{+2} soln., and direct a Bunsen flame to the mixt. with a blowpipe. A delicate blue (Thenard's blue) in the well-ignited residue is indicative of Al, due probably to the presence of cobalt aluminate, $Co(AlO_2)_2$.

Alternately the test can be run on either some rolled up filter paper or on asbestos fiber held on a Pt or nichrome wire. The matrix is impregnated with the test chemicals and ignited in the Bunsen flame directly. Under the same conditions, Zn^{+2} gives a green color and Mg^{+2} a pink color. A blank should also be run since Co^{+2} gives a little color of its own.

Test 17–8. Cobalt Bead Test. See part 1, special experiment 4. Prepare first a small sample of CoS, then a borax bead. Fuse a *little* of the sulfide on the bead and notice the color produced after several minutes heating. It may be due to cobalt metaborate, $Co(BO_2)_2$, or the complex salt $Na_2[Co(BO_2)_4]$.

Test 17–9. $K_3Co(NO_2)_6$. To 3 drops of Co^{+2} test soln., add 5 drops of H_2O, a drop of 6 *M* HAc, 3 drops of KNO_2, and warm the tube in a water bath. The yellow, slowly forming ppt. is potassium hexanitrocobaltate(III). This is a good test for cobalt in the presence of nickel.

Test 17–10. Co^{+2}-Acetone Test. (*a*) Make a dil. Co^{+2}–Fe^{+3} mixt. Add a drop of KSCN and note the red color of the ferric-thiocyanate ions. Decolorize to a light pink by dropwise addns. of 6 *M* H_3PO_4 and good mixing, then add 3 drops in excess. Fe^{+3} is complexed (see test 22–17, part *b*) by this means. Now add another drop of KSCN, then carefully put 5 drops of acetone, $(CH_3)_2C{=}O$, in the tube to form a layer on top. The blue color, possibly $Co(SCN)_2[O{=}C(CH_3)_2]_2^{-2}$, proves the presence of cobalt. The concn. limit is 10 ppm Co.

(*b*) The student may optionally wish to try variations of the test using for example sodium potassium tartrate to complex the iron and a higher ketone like methyl isobutyl ketone to coordinate cobalt.

Test 17–11. Co^{+2} and Ni^{+2} Compared, Using Dimethylglyoxime. Dilute 4 drops of Co^{+2} test soln. to 1 ml in a tube, and in another tube prepare a similar diln. of Ni^{+2}. To each add 3 drops of 0.5 *M* NH_4Cl, a drop of 3 *M* NH_4OH, and 3 drops of dimethylglyoxime. Compare the results with reference to example 1, Chapter 12, p. 193 for the equation. The concn. limit is about 3 ppm Ni. Fe^{+2} gives a red color with the reagent and should be oxidized to Fe^{+3} with H_2O_2 if present.

Test 17–12. Co^{+2} and Ni^{+2} Compared, Using α-Nitroso-β-naphthol. Make dilns. as in test 17–11. To each add a drop of 6 *M* HAc and 4 drops of organic reagent and heat the tubes in a water bath. Note results and see paragraph 6, Chapter 12, for equation.

Test 17-13. Rinmann's Test for Zn. Repeat test 17-7 using a little ZnS or $Zn(OH)_2$ in place of $Al(OH)_3$. The color produced is probably due to $CoZnO_2$ and is called Rinmann's green.

Test 17-14. Dithizone Test for Zn^{+2}. See special experiment 10, Chapter 23, and example 2, Chapter 12.

Analysis of Known Mixtures

A known group 3 sample may be analyzed prior to analysis of the unknown, or several simple mixtures as in test 17-3 may be tried to see if one has in mind the separations needed, as well as short cuts, in which some ions may be tested directly in the presence of others. If no further preliminary study of this nature is undertaken, the student, having his notebook writeup completed, proceeds to the unknown sample and follows the procedure for group 3 analysis. Some of the confirmatory and spot tests from the preliminary tests may be used also at his discretion.

Interfering Ions

Of the anions discussed in Chapter 22, BO_2^-, F^-, $C_2O_4^{-2}$, and PO_4^{-3} hinder analysis by complexing some group 3 cations and/or prematurely precipitating group 4 cations. Directions are given in Chapter 21 for circumventing these difficulties but they are not present unless so stated by the instructor.

ANALYTICAL REACTIONS OF GROUP 3 CATIONS

A. Reactions with $NH_4Cl + NH_4OH$

(1) $Fe^{+3} + 3NH_4OH \overset{(NH_4^+)}{=} Fe(OH)_{3_{Br}} + 3NH_4^+$

(2) $Cr^{+3} + 3NH_4OH \overset{(NH_4^+)}{=} Cr(OH)_{3_{Gr}} + 3NH_4^+$

(3) $Al^{+3} + 3NH_4OH \overset{(NH_4^+)}{=} Al(OH)_{3_{W}} + 3NH_4^+$

(4) $Co^{+2} + 6NH_4OH \overset{(NH_4^+)}{=} Co(NH_3)_6^{+2} + 6H_2O$

$$4Co(NH_3)_6^{+2} + 2H_2O + O_2\ (\text{air}) = 4Co(NH_3)_{6_{Br}}^{+3} + 4OH^-$$

(5) $Ni^{+2} + 6NH_4OH \overset{(NH_4^+)}{=} Ni(NH_3)_{6_{Bu\ V}}^{+2} + 6H_2O$

(6) $Fe^{+2} + 2NH_4OH \overset{(NH_4^+)}{=} Fe(OH)_{2_{Gr}} + 2NH_4^+$

$$4Fe(OH)_2 + 2H_2O + O_2\ (\text{air}) = 4Fe(OH)_3$$

(7) $Zn^{+2} + 4NH_4OH \overset{(NH_4^+)}{=} Zn(NH_3)_{4_{Cl}}^{+2} + 4H_2O$

(8) $Mn^{+2} + NH_4OH \overset{(NH_4^+)}{=}$ No reaction

B. Reaction of the Above upon $(NH_4)_2S$ Addition

(9) $2Fe(OH)_3 + 6NH_4^+ + 3S^{-2} = 2FeS_B + 6NH_4OH + S_Y$ (some)

$2Fe^{+3} + 3S^{-2} = Fe_2S_{3_B}$ (also in cold solution)

$Fe_2S_3 + 6H_2O = Fe(OH)_3 + 3\mathit{H_2S}$ (when heated)

(10) $Cr(OH)_3 + 2NH_4^+ + S^{-2} =$ No reaction

(11) $Al(OH)_3 + 2NH_4^+ + S^{-2} =$ No reaction

(12) $2Co(NH_3)_6^{+3} + 3S^{-2} = 2CoS_B + 12NH_3 + S_Y$

(13) $Ni(NH_3)_6^{+2} + S^{-2} = NiS_B + 6NH_3$

(14) $Zn(NH_3)_4^{+2} + S^{-2} = ZnS_W + 4NH_3$

(15) $Mn^{+2} + S^{-2} = MnS_P$

C. Acid Action on Sulfides and Hydroxides

(16) $Fe(OH)_3 + 3H^+ = Fe^{+3} + 3H_2O$

$FeS + 4H^+ + NO_3^- = Fe^{+3} + \mathit{NO} + S + 2H_2O$

(17) $Cr(OH)_3 + 3H^+ = Cr^{+3} + 3H_2O$

(18) $Al(OH)_3 + 3H^+ = Al^{+3} + 3H_2O$

(19) $3CoS + 8H^+ + 2NO_3^- = 3Co^{+2} + 2\mathit{NO} + 3S + 4H_2O$

(20) $3NiS + 8H^+ + 2NO_3^- = 3Ni^{+2} + 2\mathit{NO} + 3S + 4H_2O$

(21) $3ZnS + 8H^+ + 2NO_3^- = 3Zn^{+2} + 2\mathit{NO} + 3S + 4H_2O$

D. Reaction with Excess NaOH

(22) $Fe^{+3} + 3OH^- = Fe(OH)_3$

(23) $Cr^{+3} + 4OH^- = Cr(OH)_4^-$

(24) $Al^{+3} + 4OH^- = Al(OH)_4^-$

(25) $Co^{+2} + 2OH^- = Co(OH)_{2_{Bu}} = Co(OH)_{2_P}$

(26) $Ni^{+2} + 2OH^- = Ni(OH)_{2_{Gr}}$

(27) $Fe^{+2} + 2OH^- = Fe(OH)_{2_{Gr}}$

(28) $Zn^{+2} + 4OH^- = Zn(OH)_4^{-2}$

(29) $Mn^{+2} + 2OH^- = Mn(OH)_{2_{P-W}}$

E. Reaction of the Above with H_2O_2 in Basic Solution

(30) $\mathrm{Fe(OH)_3 + H_2O_2 =}$ No reaction

(31) $\mathrm{2Cr(OH)_4^- + 3H_2O_2 + 2OH^- = 2CrO_{4_Y}^{-2} + 8H_2O}$

(32) $\mathrm{Al(OH)_4^- + H_2O_2 =}$ No reaction

(33) $\mathrm{2Co(OH)_2 + H_2O_2 = 2Co(OH)_{3_B}}$

(34) $\mathrm{Ni(OH)_2 + H_2O_2 =}$ No reaction

(35) $\mathrm{2Fe(OH)_2 + H_2O_2 = 2Fe(OH)_3}$

(36) $\mathrm{Zn(OH)_4^{-2} + H_2O_2 =}$ No reaction

(37) $\mathrm{Mn(OH)_2 + H_2O_2 = MnO_{2_B} + 2H_2O}$

F. Subgroup 3A Resolution in $HNO_3 + H_2O_2$

(38) $\mathrm{Fe(OH)_3 + 3H^+ = Fe^{+3} + 3H_2O}$

(39) $\mathrm{2Co(OH)_3 + H_2O_2 + 4H^+ = 2Co^{+2} + 6H_2O} + O_2$

(40) $\mathrm{Ni(OH)_2 + 2H^+ = Ni^{+2} + 2H_2O}$

(41) $\mathrm{MnO_2 + H_2O_2 + 2H^+ = Mn^{+2} + 2H_2O} + O_2$

G. Subgroup 3B with Excess HNO_3

(42) $\mathrm{2CrO_4^{-2} + 2H^+ = Cr_2O_{7_{Or}}^{-2} + H_2O}$

(43) $\mathrm{Al(OH)_4^- + 4H^+ = Al^{+3} + 4H_2O}$

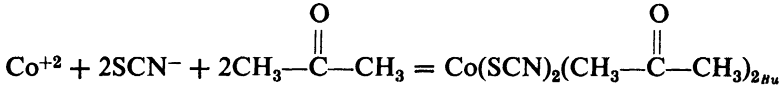
(44) $\mathrm{Zn(OH)_4^{-2} + 4H^+ = Zn^{+2} + 4H_2O}$

H. Iron

(45) $\mathrm{Fe^{+3} + SCN^- = FeSCN_R^{+2}}$

(46) $\mathrm{4Fe^{+3} + 3Fe(CN)_6^{-4} = Fe_4[Fe(CN)_6]_{3_{Bu}}}$

I. Cobalt

(47) 

$$\mathrm{Co^{+2} + 2SCN^- + 2CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 = Co(SCN)_2(CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3)_{2_{Bu}}}$$

(48) $\mathrm{Co^{+2} + 3K^+ + 7NO_2^- + 2HAc}$

$\mathrm{= K_3[Co(NO_2)_6]_Y} + NO + \mathrm{H_2O + 2Ac^-}$

(See also paragraph 6, Chapter 12, p. 194.)

J. Nickel

No additional reactions. (See also example 1, Chapter 12.)

K. Manganese

$$2Mn^{+2} + 14H^{+} + 5BiO_3^{-} = 2MnO_{4_{Pu}}^{-} + 5Bi^{+3} + 7H_2O \tag{49}$$

$$2MnO_2 + 10H^{+} + 3BiO_3^{-} = 2MnO_4^{-} + 3Bi^{+3} + 5H_2O \tag{50}$$

L. Chromium

$$Cr(OH)_4^{-} + H^{+} = Cr(OH)_3 + H_2O \tag{51}$$

$$Ba^{+2} + CrO_4^{-2} = BaCrO_{4_{Y}} \tag{52}$$

(See also part **H**, Chapter 22.)

M. Aluminum

$$Al(OH)_4^{-} + H^{+} = Al(OH)_3 + H_2O \tag{53}$$

(See also paragraph 16, Chapter 12.)

N. Zinc

$$2K^{+} + Zn^{+2} + Fe(CN)_6^{-4} = K_2Zn[Fe(CN)_6]_{W} \tag{54}$$

(See also example 2, Chapter 12.)

PROCEDURE FOR GROUP 3 ANALYSIS

(*A*) *If using a solution known to contain only the metals of group* 3, dilute 1 ml of sample with 2 ml of H_2O. Add 8 drops of 2 *M* NH_4Cl, and put the tube in a hot-water bath. After several minutes add 15 *M* NH_4OH dropwise with good stirring, and continue addition until the solution becomes distinctly alkaline as evidenced by a red color with phenolphthalein when a drop of solution is transferred with the stirring rod to a drop of indicator on the spot plate. Now add 8 to 10 drops of $(NH_4)_2S$ reagent, continue to stir, and keep warm for another 2 to 3 minutes; then rinse off the stirring rod and centrifuge. The centrate is discarded and the residue retained for group 3 analysis, (*C*) below.

If at this point in the general unknown analysis, phosphate and borate require removal according to directions given in Chapter 21, the instructor will so indicate.

(*B*) *If the sample is a general unknown*, the centrate from paragraph (*C*), Chapter 16, is the solution used. As this already contains some ammonium acetate and unhydrolyzed thioacetamide, the procedure will be slightly different from (*A*), above. Heat the solution in a water bath, add 4 drops of NH_4Cl, and then, with stirring, 15 *M* NH_4OH until alkaline. After a few minutes, add 2 drops of $(NH_4)_2S$, and see if any further precipitation takes place. If so, add drops of sulfide reagent until precipitation is complete. Wash down the stirring rod and tube walls with a few drops of H_2O, centrifuge, and remove the centrate and save it for groups 4 and 5. Wash the residue with a hot mixture of 1 ml of H_2O and 4 drops of NH_4Cl, centrifuge, and discard the wash liquid. The residue is analyzed starting with (*C*).

(*C*) The residue from (*A*) or (*B*) may consist of any mixture of $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, CoS, NiS, FeS, ZnS, and/or MnS. Add to it 1 ml of 6 *M* HNO_3, and stir while warming in the hot-water bath. If the precipitate is not dissolved, except for a little sulfur,* which usually aggregates and floats as a small spongy mass, add another 10 drops of acid and continue heating. Remove the sulfur and rinse the solution into a 20-ml beaker with the aid of a few drops of H_2O. Evaporate the solution slowly under the hood to a volume of about 6–8 drops. Avoid splattering and avoid evaporation to dryness. Rinse the solution into a test tube with the aid of several $\frac{1}{2}$ ml portions of water. Heat in a water bath and add drops of 6 *M* NaOH until alkaline, then 8 drops more. Finally, put in 10 to 12 drops of 3% H_2O_2, mix, and continue to keep the tube hot† for 4 to 5 minutes longer. Centrifuge. Put the centrate in a 20-ml beaker and save for (*E*). Wash the residue 2 or 3 times with about 1 ml of hot H_2O each time, combining the first wash extract with the centrate and discarding subsequent washings. Analyze the residue according to the next paragraph.

(*D*) The residue from (*C*) is group 3A and may contain any combination of $Fe(OH)_3$, $Ni(OH)_2$, $Co(OH)_3$, and MnO_2. With 30 to 40 drops of 6 *M* HNO_3 rinse the mixture into a 20-ml beaker. Heat carefully with a low flame, then add 4 to 6 drops of 3% H_2O_2 and boil the solution carefully. A little more HNO_3 and H_2O_2 may be added if the residue does not dissolve completely in a few minutes. Let the solution cool, add 2 ml of water and divide the solution among 4 tubes:

Tube 1. Add 3 drops of SCN^- solution. A dark red color as in test 17–4 shows iron is present. A faint pink is reported as a *trace* of Fe.

Tube 2. If iron was present, completely precipitate it with 15 *M* NH_3, centrifuge, and just neutralize the centrate with 6 *M* HAc. Add 6 drops of dimethylglyoxime to this solution and a drop of 6 *M* NH_4OH and mix. A bright red precipitate proves nickel was in the sample.

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* As in nitric acid solutions of group 2 sulfides, small amounts of sulfides may be occluded in the sulfur residue and color it darkly. The loss will be small and is neglected here.

† Continued heating not only helps coagulation but also hastens decomposition of excess H_2O_2, which would reduce CrO_4^{-2} in (*E*) when acidified. In basic solution hydrogen peroxide oxidizes Cr^{III} to Cr^{VI}, but in acidic solution the reverse occurs.

Review test 17–12. If iron was not in Tube 1, neutralize with HAc and NH_4OH and proceed as above with the organic reagent, followed by a drop of NH_4OH.

Tube 3. If iron was present, add 3 drops of SCN^- and as in test 17–10 decolorize the iron thiocyanate with excess 6 *M* H_3PO_4. Add another drop of SCN^- solution, then without shaking the mixture add 5 drops of acetone. A blue organic layer is proof that cobalt is present.

If iron was not found in Tube 1, H_3PO_4 is omitted, and SCN^- and acetone are added initially. The blue color when Co^{+2} is present is the same.

Tube 4. Add 3 drops of concentrated H_3PO_4, 3 of concentrated HNO_3, heat, and add a bit of solid $NaBiO_3$. A red to purple color as in test 17–5 shows manganese is present.

This is the end of the 3*A procedure.*

(*E*) The centrate from (*C*) may contain any combination of $Al(OH)_4^-$, $Zn(OH)_4^{-2}$, and/or CrO_4^{-2}. Boil the mixture for a minute. Then add concentrated HNO_3 until the mixture is acidic, transfer it to a test tube, and add concentrated NH_4OH until it is strongly basic again. A yellow color indicates CrO_4^{-2} is present, and a white flocculant precipitate is $Al(OH)_3$.* Centrifuge and remove the centrate to another tube for analysis in paragraph (*G*). Save the residue for (*F*).

(*F*) Wash the residue with 2 ml of hot H_2O and discard the washings. Redissolve the residue in a few drops of 6 *M* HAc, add 1 ml of H_2O, 4 drops of aluminon, and heat in the water bath. When hot, add a few drops of 3 *M* NH_4OH to make it neutral or barely basic. A red precipitate confirms aluminum as in test 17–6.

(*G*) The centrate from (*E*) contains CrO_4^{-2} only if it is yellow but may also contain colorless $Zn(NH_3)_4^{+2}$. If it is colorless, neutralize it with 6 *M* HAc and add 2 drops excess; then put in 6 drops of $K_4Fe(CN)_6$. A whitish precipitate shows zinc is present as in test 17–1.

If the centrate from *E* is yellow, just neutralize it with 6 *M* HAc. Now put in drops of $BaCl_2$ until precipitation of $BaCrO_4$ is complete and centrifugation should yield a colorless centrate. Carry the centrate to

(*H*) The yellow residue shows the presence of chromium in the sample. This element may be confirmed according to test 22–21.

(*H*) Treat the centrate with 2 drops of 6 *M* HAc and 6 drops of $K_4Fe(CN)_6$. As before, a whitish residue indicates zinc.

This is the end of the group 3*B procedure.*

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* A *trace* of gelatinous silicic acid from the dissolution of glass by alkali is usually visible here. Al^{+3} from the sample should give a *strong* test. Silicic acid gives only a white color in the aluminon test.

PROBLEMS

1. One has a greenish suspension of $Fe(OH)_2$ in water at *p*H 7. Air is bubbled through and after a while the suspension is noted to have turned brown and the solution *p*H dropped to 6. Explain with equations.

2. There is a generalization that in the ferrous and ferric compounds formed with ferro- and ferricyanide, dark color is only noted in the compounds containing iron of both valences. What experimental evidence can you offer here?

3. Write equations to show how one could start with chromite ore and a few common chemicals and prepare two industrially important products: potassium dichromate and Prussian blue.

4. Outline a separation of Fe^{+3} and Cr^{+3} based on the amphoterism of the latter.

5. Show by calculation whether or not FeS can precipitate from a hot mixture of 1 drop of 5% CH_3CSNH_2, 2 drops of 6 *M* NaOH, and 1 drop of 0.01 *M* $FeSO_4$ in a total volume of 2 ml.

6. Complete:

(*a*) $\underset{H^+}{\overset{OH^-}{\leftrightarrows}} Cr(OH)_3 \underset{OH^-}{\overset{H^+}{\rightleftharpoons}}$

(*b*) $Cr_2O_7^{-2} + H^+ + H_2O_2 =$

(*c*) $Na_2O_2 + Cr(OH)_4^- + H_2O =$

7. J. P. Slipshod proposes the following group 3 shortcuts for analysts in a hurry:

(*a*) "If an unknown may contain only Zn^{+2} and Fe^{+3}, addition of $Fe(CN)_6^{-4}$ will give a white precipitate with zinc. After centrifuging it out, the centrate gives a red color for iron with SCN^-.

(*b*) "In a Co^{+2}–Ni^{+2} mixture, a borax bead test is run on a portion, giving a grey color for Ni^{+2}, and to the other portion is added $(NH_4)_2S$, giving a black precipitate of CoS which shows cobalt is present.

(*c*) "In a Cr^{+3}–Al^{+3} mixture, add hot NaOH to solubilize amphoteric aluminum and leave $Cr(OH)_3$. The centrate is mixed with aluminon giving a red color, and the residue is dissolved in H_2SO_4 which gives a blue color of CrO_5 in butyl alcohol."

Mention wherein these procedures are open to question.

8. How would you test a metal foil to see if it is tin or aluminum?

9. HNO_3, but not HCl, may be shipped in aluminum tank cars. Explain.

10. Many other group 3 procedures are used besides the one given in this chapter. One precipitates the group as done here, then dissolves all but NiS and CoS in dilute HCl. The centrate from that separation is treated with concentrated NH_4OH in which Zn^{+2} and Cr^{+3} are complexed and are soluble. The hydroxide residue is separated and treated with NaOH in which $Al(OH)_3$ dissolves.

With regard to the fractions separated, the CoS–NiS mixture is dissolved in more concentrated, hot HCl, and then neutralized and analyzed with the organic reagents. The Zn–Cr ammonia complexes are reacted with Na_2O_2 to give $Zn(OH)_4^{-2}$ and CrO_4^{-2}, the latter being precipitated with Ba^{+2}, the former just acidified and precipitated with ferrocyanide. Draw a flow sheet for this and include iron and manganese in the scheme as they would react, and include a separation and confirmation of them.

11. Using all the information you have on group 3, propose a separation scheme of your own invention for those seven ions and present it as a flow sheet.

12. (*Library*) Copy or prepare a flow sheet on group 3 from another qualitative text and compare it with the one in this book. Try to criticize one point in each as being unsatisfactory by virtue of its technical difficulty, possible incomplete separation, or other reason.

13. Give equations for application of the Goldschmidt process to chromite ore.

14. A rust inhibitor for radiators is supposed to contain potassium chromate. What action does this compound have on iron and how would one test for CrO_4^{-2} in a mixture of simple salts? How could one tell by inspecting the radiator drain water that iron corrosion had been going on?

15. Aluminum is chemically quite active and the E° value for $Al = Al^{+3} + 3e^-$ is high. Why don't airplanes made with a great deal of almost pure Al skin corrode badly in moist air? Why does pure Al corrode less readily than its alloys? Trimethyl aluminum, $(CH_3)_3Al$, has been used as a rocket fuel. Cite one advantage of it. How might it be synthesized? If burned with liquid O_2, what are the probable products?

16. (*a*) A group 3 unknown is suspected to contain only Mn^{+2} and Co^{+2}. What quick methods are available for testing the suspicion?

(*b*) Repeat (*a*) for a sample suspected to contain only Fe^{+3} and Zn^{+2}.

(*c*) Repeat for a sample thought to contain Ni^{+2}, Cr^{+3}, and Al^{+3}.

17. There is a little aluminum in some glass, and strong basic solutions stored in glass are known to dissolve it slowly. How could one analyze a sample of 6 *M* NaOH for Al? In what form would the aluminum be?

18. What group 3 ions may be present in each of the following:

(*a*) A solution known to contain cations of group 3 only is colorless.

(*b*) A group 3 unknown gives a blackish precipitate with $(NH_4)_2S$ and when that is dissolved in hot HCl, a light green solution results.

(*c*) A group 3 solution gives a black precipitate and yellow supernatant liquid when reacted with $NaOH + H_2O_2$. The precipitate is soluble in $H_2SO_4 + H_2O_2$ to yield a solution which has a faint pink tint.

(*d*) A mineral is a black powder. It is dissolved in HCl and when excess NH_4OH is added a brown flocculent precipitate comes down.

(*e*) What color would one observe after dissolving a piece of 18–8 stainless steel in HCl? What would be the result of adding excess NaOH to that solution?

19. $Co(OH)_3$ is formed in basic solution by air oxidation of $Co(OH)_2$. When the mixture is acidified with HCl, the odor of chlorine gas is detectable. Explain.

20. A solution of Cr^{+3} is acidified with H_2SO_4 and a piece of Zn is added. The color gradually changes from dark green to blue. Explain, and include oxidation potential data for support.

21. Draw a flowsheet for the preparation of a pig of bronze (Cu–Zn–Sn)

starting with chalcopyrite, zincite, and cassiterite ores and any other materials necessary.

22. Dimethylglyoxime will give a color with as little as 3 γ of Ni. If 10 mg of alloy are dissolved and tested with the reagent, what is the minimum percentage by weight Ni in the sample that can be detected? (Ans. 0.03%)

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18

CATION GROUP 4

Magnesium may be analytically segregated with this group or with group 5 depending upon the group 4 precipitating conditions (illustrated in Chapter 8 by calculations). In the methods described here, Mg^{+2} is put with group 5 and discussed there despite its obvious relationship to other "alkaline earth" metals of periodic group IIA. Beryllium chemistry is described and illustrated with experiments in Chapter 20. Radium is not dealt with here, but other than its rarity and radioactivity it is quite similar to Ba.

IA	IIA	IIIB	
Li	Be		
Na	Mg		
K	**20** **Ca** **40.08**	Sc	
Rb	**38** **Sr** **87.63**	Y	
Cs	**56** **Ba** **137.36**	La	
Fr	Ra	Ac	

FIG. 18-1. The periodic table in the vicinity of the group 4 metals.

Barium

Barium is a soft, silvery metal of very limited use. Its sp. gr. is 3.75, its m.p. is 717 C, and b.p. is 1640 C. The main mineral is barites, $BaSO_4$. A mixture of $BaSO_4$ and ZnS is called lithopone and is the basis for some white paints.

While a subchloride and subhydride of barium, BaCl and BaH, have been reported, the only stable compounds are those in which the oxidation state is (II).

Barium has the same order of high chemical activity as the alkali metals,

$$\mathbf{Ba} = Ba^{+2} + 2e^- \qquad E^\circ = 2.90$$

It easily decomposes water to yield $H_2 + Ba(OH)_2$. The metal tarnishes rapidly in air and forms at elevated temperatures a *hydride* with H_2, BaH_2; an *oxide* and *peroxide* with O_2, BaO and BaO_2; and a *nitride* with N_2, Ba_3N_2. These compounds react with water to yield, in order, $Ba(OH)_2 + H_2$; $Ba(OH)_2$; $Ba(OH)_2 + O_2$; $Ba(OH)_2 + NH_3$. *Barium hydroxide* is a stronger base than either $Sr(OH)_2$ or $Ca(OH)_2$ and is the most difficult to dehydrate to the oxide. The peroxide is also the most stable of those formed by the alkaline earths, as is typical of other barium compounds.

Among other compounds of barium, the *acetate*, *bromide*, *chloride*, *chlorate*, *iodide*, and *nitrite* are quite soluble; the *fluoride*, *hydroxide*, and *nitrate* somewhat less soluble; and the salts listed in Table 18–1 are very slightly soluble. *Barium sulfide* is not formed in water solution since the solid reacts with H_2O giving $H_2S + Ba(HS)_2 + Ba(OH)_2$. As typical of large metallic ions, Ba^{+2} forms complexes weakly.

TABLE 18–1. EQUILIBRIUM CONSTANTS FOR SOME BARIUM REACTIONS

Reactions (in order of decreasing [Ba^{+2}])	K	Formula Weight
$Ba(OH)_2 \cdot 8H_2O = Ba^{+2} + 2OH^- + 8H_2O$	5.0×10^{-3}	315.50
$BaF_2 = Ba^{+2} + 2F^-$	2.4×10^{-5}	175.36
$BaC_2O_4 \cdot 2H_2O = Ba^{+2} + C_2O_4^{-2} + 2H_2O$	1.5×10^{-8}	261.41
$BaCO_3 = Ba^{+2} + CO_3^{-2}$	1.6×10^{-9}	197.37
$BaSO_4 = Ba^{+2} + SO_4^{-2}$	1.5×10^{-9}	233.42
$BaSO_3 = Ba^{+2} + SO_3^{-2}$	9.5×10^{-10}	217.42
$BaCrO_4 = Ba^{+2} + CrO_4^{-2}$	8.5×10^{-11}	253.37
$BaSeO_4 = Ba^{+2} + SeO_4^{-2}$	2.8×10^{-11}	280.32
$Ba_3(PO_4)_2 = 3Ba^{+2} + 2PO_4^{-3}$	6×10^{-39}	602.04

Quantitatively, Ba^{+2} is determined by weighing it in the form of $BaSO_4$. One qualitative test is the yellow-green flame and another is the fact that $BaCrO_4$ is much less soluble than other group 4 chromates.

Strontium

This metal, like the other alkaline earths, is silvery white but harder and more brittle than Ba. It has no use as an engineering metal. Its sp. gr. is 2.6, the m.p. is 771 C, and the b.p. is 1384 C. The principal minerals are strontionite, $SrCO_3$, and celestite, $SrSO_4$. $Sr(NO_3)_2$ and $Sr(ClO_3)_2$ are used to impart a red flame color in fireworks and $Sr(OH)_2$ is employed in certain sugar refining processes, but uses of strontium compounds are generally quite limited.

There are no stable Sr^1 compounds so we may say that the *oxidation state* of this element is (II) only. It decomposes H_2O giving $Sr(OH)_2 + H_2$, its powerful reducing character obvious from the high positive potential:

$$Sr = Sr^{+2} + 2e^- \qquad E^\circ = 2.89$$

The metal burns brightly in air to give only the *oxide* SrO, which reacts with H_2O to form the strong base $Sr(OH)_2$ whose saturated water solution, however, is only 0.074 M at 25 C. The metal also forms a *hydride* SrH_2 with H_2 and *nitride* Sr_3N_2 with N_2 at higher temperatures.

The same solubility generalizations given for Ba^{+2} compounds hold for those of Sr^{+2}. The *chromate* is more soluble in the case of Sr, but it can be precipitated if alcohol is added to the water solution, a procedure used in the unknown sample manipulation described later. Strontium compounds impart a bright red color to the bunsen flame (see special experiment 5), which is useful as a qualitative test.

TABLE 18–2. EQUILIBRIUM CONSTANTS FOR SOME STRONTIUM REACTIONS

Reactions (in order of decreasing $[Sr^{+2}]$)	K	Formula Weight
$Sr(OH)_2 \cdot 8H_2O = Sr^{+2} + 2OH^- + 8H_2O$	3.2×10^{-4}	265.77
$Sr(HPO_4) = Sr^{+2} + HPO_4^{-2}$	2×10^{-4}	183.62
$Sr(HCO_3)_2 = Sr^{+2} + 2HCO_3^-$	1.83×10^{-6}	209.67
$SrCrO_4 = Sr^{+2} + CrO_4^{-2}$	3.6×10^{-5}	203.64
$SrSO_4 = Sr^{+2} + SO_4^{-2}$	7.6×10^{-7}	183.69
$SrF_2 = Sr^{+2} + 2F^-$	7.9×10^{-10}	125.63
$SrC_2O_4 \cdot H_2O = Sr^{+2} + C_2O_4^{-2} + H_2O$	5.61×10^{-8}	193.67
$SrCO_3 = Sr^{+2} + CO_3^{-2}$	7×10^{-10}	147.64
$Sr_3(PO_4)_2 = 3Sr^{+2} + 2PO_4^{-3}$	1×10^{-31}	452.84
$Sr_3(AsO_4)_2 = 3Sr^{+2} + 2AsO_4^{-3}$	2×10^{-49}	540.71

Quantitatively, Sr^{+2} is precipitated and weighed as $SrSO_4$ after Ba^{+2} is removed as the chromate and Ca^{+2} as the oxalate.

Calcium

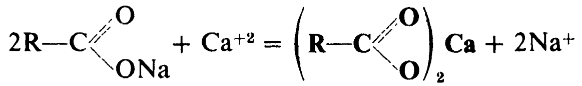
Calcium is silvery and brittle. Its sp. gr. is 1.55, its m.p. is 851 C, and b.p. is 1487 C. As a metal, it is used in lead alloys for electric cable sheathing and as a degasifier in steel making. Common minerals are dolemite, $CaCO_3 \cdot MgCO_3$, gypsum, $CaSO_4 \cdot 2H_2O$, apatite, $(CaF)Ca_4(PO_4)_3 \pm Cl$, aragonite and calcite, two forms of $CaCO_3$, and fluorite, CaF_2. Ca is the third most abundant metal in the earth's crust. It is obtained by methods typical of the alkaline earths, namely electrolysis of its molten chloride–fluoride mixture in a graphite crucible (anode), using an iron cathode.

The only stable *oxidation state* is (II), though some Ca^{I} compounds have been formed under special conditions. The metal is very active chemically as a reducing agent:

$$Ca = Ca^{+2} + 2e^- \qquad E^\circ = 2.87$$

and it also combines with H_2, O_2, and N_2 when heated in those atmospheres yielding CaH_2, CaO, and Ca_3N_2, respectively.

Ca^{+2} is found in natural brines and waters, as well as in many rocks, and with Mg^{+2} constitutes the "*hardness*" in the water. These ions react with conventional soaps, which are sodium and potassium salts of long-chain aliphatic acids, to precipitate the calcium and magnesium soaps:



$$2R{-}C\begin{matrix}{\nearrow}O\\ \searrow ONa\end{matrix} + Ca^{+2} = \left(R{-}C\begin{matrix}{\nearrow}O\\ \searrow O\end{matrix}\right)_2 Ca + 2Na^+$$

This process softens the water but of course is not the best way to do so. The softening of water is of prime importance particularly in heat exchange equipment since calcium salts may precipitate by chemical reaction

$$Ca(HCO_3)_2 \overset{\Delta}{=} CaCO_3 + H_2O + CO_2$$

or simply by evaporation at the container walls. These deposits insulate boiler tubes, resulting in burn outs, since higher heats are needed to maintain normal operation. *Calcium bicarbonate* in the reaction above is known as "*temporary hardness*," since water bearing it may be partially softened by heating. Other calcium salts are not removed in similar fashion. Two additional softening methods are worthy of mention: first, the *zeolite process* in which a complex silicate-aluminate exchanges $2Na^+$ for each Ca^{+2} and can be regenerated for further softening by utilizing mass action with a strong brine (NaCl) solution; and second, the general process in which softening chemicals are added to the water, such as borates, silicates, and phosphates which are capable of forming soluble complexes with Ca^{+2}.

There are quite a few important calcium compounds. The carbonate is calcined to give lime, CaO, which in a water slurry is called slaked lime, $Ca(OH)_2$. Saturated $Ca(OH)_2$ is 0.021 *M* at 25 C. *Calcium carbonate* is an important raw material also in the cement and glass industries and as a fluxing material in several metallurgical processes, including iron smelting.

The CO_2 obtained from roasting $CaCO_3$ is used with NH_3 and NaCl in the Solvay process for the production of Na_2CO_3 and $NaHCO_3$. The residue of CaO is slaked and used to recover NH_3 from the Solvay by-product NH_4Cl. *Calcium chloride* produced from that step finds use (*a*) on gravel roads where it keeps down dust by removing moisture from the air (mono, di, tetra, and hexa hydrates are known) (*b*) as a refrigeration plant brine, and (*c*) as a deicing salt for winter roads. Gypsum (*calcium sulfate dihydrate*) is used as a soil conditioner, in plaster, cement and plaster board, and to make plaster of Paris, the hemihydrate:

$$2CaSO_4 \cdot 2H_2O \overset{\Delta}{=} (CaSO_4)_2 \cdot H_2O + 3H_2O$$

Calcium sulfide is made by heating gypsum with coke. It is reversibly oxidized by air and is not too soluble in water even though it is appreciably hydrolyzed to $H_2S + Ca(HS)_2$. A mixture of "lime-sulfur" and water, if boiled, produces a mixture of *calcium polysulfides* which is used to treat over-alkaline soils. Simple lime-sulfur mixtures are used as fungicidal dusts on fruit trees and garden crops; lime–copper sulfate–water is Bordeaux mixture, used for the same purpose.

Calcium phosphate, $Ca_3(PO_4)_2$, is the main constituent in teeth and bone and also occurs in large natural deposits which are mined for fertilizer and phosphorus chemical manufacture. By reacting phosphate rock with H_2SO_4, various slowly soluble fertilizers are obtained, "super phosphate of lime," for instance, is approximately $Ca(H_2PO_4)_2 \cdot 2CaSO_4 \cdot 2H_2O$.

Qualitatively, Ca^{+2} is segregated and identified as the slightly water-soluble *oxalate* which is solublized in HCl to give a red-orange flame test.

TABLE 18–3. EQUILIBRIUM CONSTANTS FOR SOME CALCIUM REACTIONS

Reactions (in order of decreasing $[Ca^{+2}]$)	*K*	Formula Weight
$CaCrO_4 = Ca^{+2} + CrO_4^{-2}$	7.1×10^{-4}	156.09
$Ca(IO_3)_2 \cdot 6H_2O = Ca^{+2} + 2IO_3^- + 6H_2O$	1.73×10^{-6}	497.98
$Ca(OH)_2 = Ca^{+2} + 2OH^-$	1.3×10^{-6}	74.10
$CaSO_4 \cdot 2H_2O = Ca^{+2} + SO_4^{-2} + 2H_2O$	2.4×10^{-5}	172.17
$Ca(HPO_4) = Ca^{+2} + HPO_4^{-2}$	2×10^{-6}	136.08
$CaC_4H_4O_6 \cdot 2H_2O = Ca^{+2} + C_4H_4O_6^{-2} + 2H_2O$	7.7×10^{-7}	224.20
$CaF_2 = Ca^{+2} + 2F^-$	1.7×10^{-10}	78.08
$CaCO_3$ (aragonite) $= Ca^{+2} + CO_3^{-2}$	6.9×10^{-9}	100.09
$CaCO_3$ (calcite) $= Ca^{+2} + CO_3^{-2}$	4.7×10^{-9}	100.09
$CaC_2O_4 \cdot H_2O = Ca^{+2} + C_2O_4^{-2} + H_2O$	1.3×10^{-9}	146.12
$Ca_3(PO_4)_2 = 3Ca^{+2} + 2PO_4^{-3}$	1.3×10^{-32}	310.20

Quantitatively it is precipitated in similar fashion, then either ignited to the *carbonate* or dissolved in dilute H_2SO_4, and the oxalic acid liberated is titrated with standard permanganate (see Oxalate, p. 391). Calcium in hard water is titrated with versene (Chapter 4) using murexide indicator, and "total hardness" ($Ca^{+2} + Mg^{+2}$) is titrated using versene and eriochrome black-T indicator.

Group 4 Analysis—General Description

Ions of the first three analytical groups are first precipitated as described in the preceding chapters. The centrate is evaporated to dryness, HNO_3 added, the mixture re-evaporated to destroy NH_4^+ salts,* then diluted and buffered, and $(NH_4)_2CO_3$ is added. When the concentrations are correct, Mg^{+2} does not precipitate but $BaCO_3$, $SrCO_3$, and $CaCO_3$ do. The mixture is centrifuged and group 5 ions (Mg^{+2}, Na^+, K^+, and NH_4^+) remain in the centrate to be later analyzed for group 5.

The white residue of group 4 carbonates is dissolved in HAc. The solution is buffered with NH_4Ac, and K_2CrO_4 is added. This precipitates only Ba^{+2}, as yellow $BaCrO_4$. It is removed by centrifugation, dissolved in HCl, and barium is reprecipitated as white $BaSO_4$, which is insoluble in HCl or NaOH and is confirmatory for Ba^{+2}. The Sr^{+2}–Ca^{+2}–CrO_4^{-2} centrate is made alkaline with NH_4OH, additional CrO_4^{-2} added, and then ethyl alcohol, C_2H_5OH. In the mixed water–alcohol solvent, yellow $SrCrO_4$ is not soluble and precipitates, leaving after centrifuging a centrate containing Ca^{+2} as the only metal ion. The strontium chromate is dissolved in HCl, and the solution gives a characteristic red flame test confirming Sr^{+2}. The Ca^{+2} centrate is boiled to expel alcohol, then just acidified, and $(NH_4)_2C_2O_4$ added, giving a white precipitate of calcium oxalate that may be dissolved in HCl and the Ca^{+2} is confirmed in that solution by a red-orange flame test.

The procedure with the sample as described is summarized as a flow sheet on page 312. An alternate group 4 procedure based on the use of ferrocyanide is also given.

PRELIMINARY TESTS WITH GROUP 4 IONS

Test solutions contain 10 mg/ml of the group 4 ions.

Test 18-1. Flame Tests and the Spectroscope. See special experiment 5, Chapter 23.

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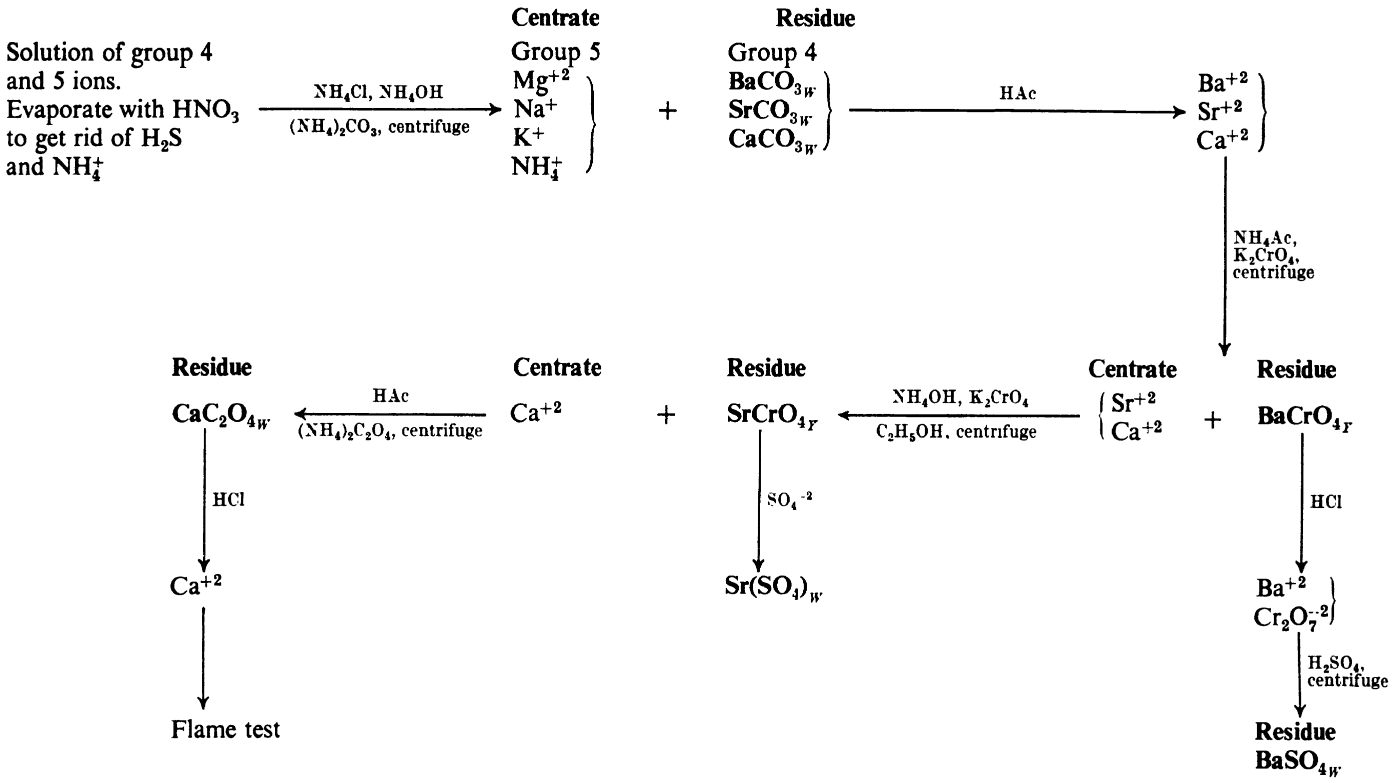
* NH_4^+ regulates both CO_3^{-2} and OH^- and a known amount is added later:

$$NH_4^+ + OH^- = NH_4OH$$

$$NH_4^+ + CO_3^{-2} = NH_3 + HCO_3^-$$

Flow Sheet—Group 4



Test 18–2. Some Group 4 Precipitating Agents. Using 6–10 drops of each group 4 test soln., try a few drops of the following in *separate* tests. Record formulas and colors of any ppts. that form, and note which reagents might be used in differentiating among the test ions: K_2CrO_4, Na_2HPO_4 + a few drops of NH_4Cl and NH_4OH, $NaOH$, $(NH_4)_2SO_4$, $(NH_4)_2C_2O_4$, NaF, and finally $NaBF_4$ + a few drops of NH_4OH.

Test 18–3. The Ca^{+2}-Sr^{+2} Separation via the Solubility of $Ca(NO_3)_2$. Calcium and strontium are difficult cations to separate. Two methods are given in the procedure, two in special experiment 11, Chapter 23, and three more below.

All the group 4 nitrates are water-solub. but in methyl alcohol (CH_3OH) the solubility at 25 C in mg of salt per ml of alcohol are: $Ca(NO_3)_2$ 520, $Sr(NO_3)_2$ 0.6, $Ba(NO_3)_2$ 0.4. Make a mixt. of 5 drops of Ca^{+2} and 5 drops of Sr^{+2} solns., add 10 drops of $(NH_4)_2CO_3$, warm, and centrifuge. Discard the liq., add a few drops of dil. HNO_3 to dissolve the residue, and rinse it into a small beaker. Evaporate the soln. just to dryness, cool, and add a ml of CH_3OH. Stir well, and rinse into a tube with a few more drops of alcohol. Centrifuge and save both soln. and residue. Add another ml of alcohol to the residue, stir well, centrifuge, and combine solns. in a beaker.

Evaporate the alcohol *just* to dryness. Add a ml of H_2O, 2 drops of NH_4OH, and 6–8 drops of $(NH_4)_2C_2O_4$. A fine, white ppt. is CaC_2O_4.

To the residue from the alcohol treatment, add a ml of H_2O, 3 drops of NH_4OH, 6–8 drops of $(NH_4)_2SO_4$, and warm the tube. A slow forming, white ppt. is $SrSO_4$.

The above separation may also be made using C_2H_5OH, ethyl alcohol, or 83% (fuming) HNO_3 instead of CH_3OH as a solvent.

Test 18–4. The Ca^{+2}-Sr^{+2} Separation via $Ca(S_2O_3)_2^{-2}$. Make a mixt. of Ca^{+2}–Sr^{+2} as before. Add an equal vol. of satd. $(NH_4)_2SO_4$ and about 100 mg of $Na_2S_2O_3 \cdot 5H_2O$. Heat in a bath for a few min., centrifuge, and save both residue and soln.

The soln. contains the Ca complex. Add 10 drops of H_2O, 6–8 drops of $(NH_4)_2C_2O_4$, and warm in a bath. The white ppt. is CaC_2O_4. It may be dissolved in HCl and a flame test tried.

The residue is $SrSO_4$, contaminated with a little $CaSO_4$, and is not tested further.

Test 18–5. The Ca^{+2}-Sr^{+2} Separation Using $K_4[Fe(CN)_6]$. Put 10 drops of Ca^{+2} in one tube and 10 of Sr^{+2} in another. Add 10 drops of H_2O and about 50 mg of solid NH_4Cl to each and stir to dissolve it. Now add 3 drops of $K_4[Fe(CN)_6]$ to each and note that only Ca^{+2} gives a ppt., $K_2Ca[Fe(CN)_6]$.

Repeat the test omitting the NH_4Cl and put the tubes in the hot-water bath. Note the same reaction at a slower rate.

If the Sr^{+2} concn. is large, it too will give these tests, though more slowly. Ba^{+2} and Mg^{+2} in large concn. also give the tests, but diln. of the soln. will minimize these interferences.

Make a Ca^{+2}–Sr^{+2} mixt. and ppt. Ca^{+2} as above. Remove the liq. and add $(NH_4)_2SO_4$ to ppt. Sr^{+2}. This separation is used in the alternate unknown procedure.

Analysis of a Known Mixture

The class may be directed to analyze a known mixture containing group 4 or a mixture of group 4 and 5 cations before proceeding to the unknown. If not, then the unknown is begun according to the procedure which follows the group equations.

ANALYTICAL REACTIONS OF GROUP 4 CATIONS

A. Carbonate Precipitations and Resolutions

Let M^{+2} be any group 4 metal ion:

(1) $M^{+2} + CO_3^{-2} = \mathbf{MCO}_{\mathbf{3}_W}$

(2) $MCO_3 + 2HAc = M^{+2} + 2Ac^- + H_2O + \mathit{CO}_2$

B. Barium

(3) $Ba^{+2} + CrO_4^{-2} = \mathbf{BaCrO}_{\mathbf{4}_Y}$

(4) $\mathbf{2BaCrO_4} + 2H^+ = 2Ba^{+2} + Cr_2O_7^{-2} + H_2O$

(5) $Ba^{+2} + SO_4^{-2} = \mathbf{BaSO}_{\mathbf{4}_W}$

C. Strontium

(6) $Sr^{+2} + CrO_4^{-2} = \mathbf{SrCrO}_{\mathbf{4}_Y}$ (in C_2H_5OH—H_2O)

(7) $\mathbf{2SrCrO_4} + 2H^+ = 2Sr^{+2} + Cr_2O_7^{-2} + H_2O$

D. Calcium

(8) $Ca^{+2} + C_2O_4^{-2} = \mathbf{CaC_2O}_{\mathbf{4}_W}$

PROCEDURE FOR GROUP 4 ANALYSIS

(*A*) *If the sample is the centrate from the separation of group* 3, it is evaporated to 0.5 ml, centrifuged to remove any precipitate of sulfur, then put in a small crucible or beaker and evaporated to dryness. When cool, 1 ml of concentrated HNO_3 is added and the mixture evaporated in the hood and heated dry until no more fuming of NH_4^+ salts is evident. The residue is dissolved in a mixture of 4 drops of 6 *M* HCl and 16 drops of H_2O and rinsed into a 4-in. tube. The crucible is rerinsed with an additional milliliter of H_2O which is added to the previous solution. Centrifuge the mixture if not clear and save the centrate.

Add 100 mg of solid NH_4Cl, then concentrated NH_4OH until alkaline (use a stirring rod to transfer a drop to a drop of phenolphthalein on a spot plate), and then add a drop more. Add 12 drops of $(NH_4)_2CO_3$ and put the tube in a *warm*-water* bath. Stir a few times over the next 3–5 minutes, then centrifuge, saving the centrate for group 5 analysis and the residue for group 4, paragraph (*C*).

(*B*) *If the sample never contained ions of the first three groups and includes only group* 4 *or groups* 4 *and* 5 start with 1 ml of it. If it contains NH_4^+ (test 19–8) evaporate with HNO_3 as above. If NH_4^+ is not present, proceed. Add 1 ml of H_2O, 200 mg of NH_4Cl, and 2 drops of concentrated NH_4OH. Then add 12 drops of $(NH_4)_2CO_3$ and place the tube in a *warm*-water* bath. Stir a few times over the next 3–5 minutes, then centrifuge. If the sample is to be analyzed for group 5 ions, save the centrate for that purpose, otherwise discard it. Save the residue for group 4 analysis as continued in paragraph (*C*).

(*C*) Stir the residue from (*A*) or (*B*) with a mixture of 8 drops of H_2O and 2 drops of $(NH_4)_2CO_3$, centrifuge, and discard the wash liquid. The residue is any combination of $BaCO_3$, $SrCO_3$, and/or $CaCO_3$. Add 1 ml of H_2O and 3 drops of 6 *M* HAc with stirring. If the solid does not dissolve completely, add another drop of acid. Add a drop of phenolphthalein and dilute NH_4OH until a pink color is obtained, then a drop of K_2CrO_4. No yellow precipitate indicates Ba^{+2} is absent and one proceeds to (*E*). If a precipitate forms, add additional drops of chromate to insure complete $BaCrO_4$ precipitation. Centrifuge, save the residue for (*D*), and the centrate for (*E*).

(*D*) Dissolve the residue with a mixture of 4 drops of dilute HCl and 16 drops of H_2O. Now put in 4 drops of $(NH_4)_2SO_4$ and heat the tube in a water bath for 5 minutes. Centrifuge and wash the white precipitate free of orange dichromate color with a mixture of 1 drop of dilute H_2SO_4 in 1 ml of H_2O. The white, fine, crystalline precipitate is $BaSO_4$ and confirms Ba^{+2}. It is insoluble in hot HCl.

(*E*) The centrate from (*C*) contains CrO_4^{-2} and may also have present Sr^{+2} and Ca^{+2}. Add 5 drops of dilute NH_4OH, 3 drops of K_2CrO_4, and heat it in a boiling-water bath. When hot add dropwise, with stirring, 40 drops of 95% ethyl alcohol. Remove the tube, cool it in a beaker of cold water, and stir occasionally. A yellow precipitate is probably $SrCrO_4$. Centrifuge, save the precipitate for (*F*), the centrate for (*G*). If no precipitate appears, Sr^{+2} is absent and the solution is carried to (*G*).

(*F*) Dissolve the precipitate from (*E*) in a milliliter of H_2O, warm, and

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* Too much heating decomposes ammonium carbonate rapidly:

$$(NH_4)_2CO_3 \overset{\Delta}{=} 2NH_3 + H_2O + CO_2$$

add 10 drops of $(NH_4)_2SO_4$. A fine, white precipitate is $SrSO_4$. If no precipitate forms in this step after having a yellow precipitate in the previous step, the yellow precipitate was K_2CrO_4 and Sr^{+2} is absent.

Alternately, the $SrCrO_4$ precipitate may be solubilized in HCl and a flame test run. A red flame, contaminated with some violet from K^+, confirms Sr.

(*G*) Transfer the solution from (*E*) to a 20-ml beaker and under the hood evaporate it *slowly* to about 10 drops with a direct, moving flame, being careful to avoid splattering. If the alcohol vapor catches fire, it is allowed to simply burn off. The heating is stopped, and when the beaker cools its contents are rinsed into a tube with 1.5 ml of H_2O. Add enough 6 *M* HAc to just decolorize the phenolphthalein, then 1 drop in excess. Now heat the tube in a boiling-water bath and when hot add 10 drops of $(NH_4)_2C_2O_4$. Allow the tube to remain hot for 8–12 minutes. A white precipitate is CaC_2O_4, and no precipitate indicates the absence of Ca^{+2}. The precipitate may be isolated, dissolved in a few drops of 6 *M* HCl, and a flame test run; a red-orange color confirms calcium.

This is the end of the group 4 *procedure.*

ALTERNATE PROCEDURE FOR GROUP 4 ANALYSIS

An alternate method for the group 4 separations is desirable because of the trouble the Ca–Sr separation gives.

(*H*) Precipitate the group as directed in (*A*) or (*B*), isolate $BaCrO_4$ as in (*C*), and confirm it in (*D*). Save the Ca^{+2}–Sr^{+2} centrate for *I*.

(*I*) Add $(NH_4)_2CO_3$ until precipitation is complete. Centrifuge and discard the centrate. Dissolve the residue of $CaCO_3$ and $SrCO_3$ in 6 drops of 6 *M* HAc; add 20 drops of H_2O and 5 drops of 6 *M* NH_4OH. Add half a spatula full of solid NH_4Cl. Shake the tube to dissolve the solid. Add 6 drops of $K_4[Fe(CN)_6]$, shake, and allow the tube to stand a minute. Centrifuge. The residue is potassium calcium ferrocyanide (test 18–5). Save the centrate for (*J*).

(*J*) Add 10 drops of H_2O and 6 drops of $(NH_4)_2SO_4$ and stand the tube in a hot-water bath. A white precipitate is $SrSO_4$.

PROBLEMS

1. List as many similarities, then as many differences, as you can in the chemistries of the group 4 metals. What trends does one detect with increasing atomic number? Suppose that radium had not been discovered yet. Predict

some characteristics for the metal and a few of its compounds. (See also problem 6 and Chapter 3.)

2. On the facts gleaned from the preliminary experiments and reading alone, suggest an original procedure for the analysis of a solution known to contain only group 4 soluble salts, and give it in outline or flow-sheet form.

3. J. P. Slipshod has made a few cuff notes on group 4 shortcuts:

(*a*) "To differentiate between samples of Ba and Ca metals, drop both into an aqueous brine solution of 1.7 sp. gr. Barium being heavier will be observed to slowly sink.

(*b*) "Since the K_{SP} of CaF_2 is the lowest of the series and the K_{SP} of $BaCrO_4$ is less than that of $SrCrO_4$, to analyze an unknown add F^- and centrifuge out the CaF_2; then add CrO_4^{-2} and obtain solid $BaCrO_4$, leaving Sr^{+2} in the last centrate, and the group is separated completely in two steps.

(*c*) "To a solution 10^{-3} *M* in each metal ion, add enough SO_4^{-2} to keep its concentration 10^{-6} *M*. This precipitates $BaSO_4$. Add more SO_4^{-2} and maintain it at 10^{-4} *M* to precipitate all the Sr^{+2}, leaving Ca^{+2} in solution to identify by a flame test. In this, one reagent does everything."

Where possible, prepare a quantitative critique of these methods.

4. What single reagent, test, or observation would enable one to distinguish between:

(*a*) $CaCl_2$ and $SrCl_2$ (*b*) $BaCO_3$ and $BaSO_4$ (*c*) $Sr(NO_3)_2$ and $SrCO_3$ (*d*) $BaCrO_4$ and $BaCr_2O_7$ (*e*) $CaCO_3$ and CaC_2O_4?

5. A solution is 10^{-3} *M* in NH_4OH, 10^{-1} *M* in NH_4^+ and 10^{-2} *M* in Mg^{+2}. Will $Mg(OH)_2$ precipitate? Explain why Mg does not precipitate in group 4 as the analysis is conducted here.

6. From the data given in this text for the first 5 alkaline earths, prepare a graph of °C vs. atomic number and sketch the melting and boiling point curves. Extrapolate the trends to number 88, radium, to predict those physical properties of the rarest IIA metal. (Ans. Values estimated by this method are 960 C and 1140 C.)

7. (*a*) Why won't $BaCrO_4$ precipitate at low *p*H?

(*b*) Since HAc dissolves carbonates how does it compare in acid strength with H_2CO_3? Explain.

8. Why does not one use CO_2 gas (as H_2S gas may be used in earlier groups) to precipitate the group 4 ions instead of $(NH_4)_2CO_3$?

9. (*a*) Dilute HAc will dissolve $SrCrO_4$ but not $BaCrO_4$. Why?

(*b*) Would you expect HCN to dissolve CaC_2O_4? Why?

10. A group 4 unknown gives a white precipitate with ammonium carbonate, another sample of the unknown gives no reaction with potassium chromate, and a third portion gives a white precipitate with dilute sulfuric acid. What conclusions can one make? If further tests are needed to analyze the sample, explain why and what they should be.

11. Draw a complete flow sheet for the alternate, (ferrocyanide) procedure for group 4 analysis and give the reaction equations for each ion in each step.

12. (*Library*) Find reference to the use of potassium rhodizonate in group 4 analysis. Give reactions, interferences, and sensitivity.

13. Anhydrous calcium chloride shaken with benzene (C_6H_6) containing a trace of water dries the organic liquid by forming hydrates. If shaken with alcohol containing a little water, however, one gets only a pasty suspension, water is not removed, and some of the salt goes into solution. What explanation can you offer for the difference?

14. How could one prepare:

(*a*) $BaCO_3$ from $BaCl_2$ (*b*) $BaCr_2O_7$ from $BaCrO_4$ (*c*) $BaCl_2$ from $BaSO_4$ (*d*) $Ca(NO_3)_2$ from calcite (*e*) $SrSO_4$ from $SrCrO_4$? Give the equations.

15. The solubility of $Sr(OH)_2$ is such to give a solution 0.148 N in OH^-, as determined by titration with standard acid. Show that this leads to a calculation of the K_{SP}.

16. One text suggests that the student use saturated $CaSO_4$ or $SrSO_4$ as a reagent for Ba^{+2}. What would be the result according to pertinent tabular data?

REFERENCES

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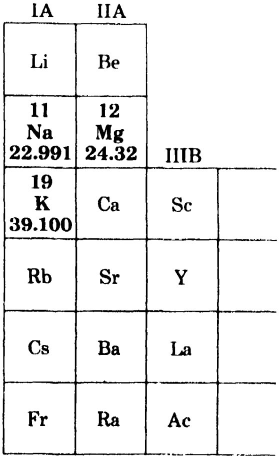
2. R. B. Hahn, *J. Chem. Educ.*. **30**, 349 (1953). (HNO_3 for the Ca-Sr mixture)
3. G. L. Beyer and W. Rieman *Anal. Chem.*, **19**, 35 (1947). (Ba-Sr)
4. S. Kallmann, *Anal. Chem.*, **20**, 449 (1948). (Ca, Ba, Sr)

19

CATION GROUP 5

The members of what is known as cation group 5 in qualitative analysis come from the first two periodic table groups as shown in the figure. Ammonium ion is the only cation described on these pages that is not a metallic ion, but in many of its reactions it acts like one. Lithium is discussed in Chapter 20. It and rubidium, cesium, and francium would also be members of group 5, but, the last three, and particularly short-lived, synthetic, radioactive Fr, are not common in occurrence, or of much other than theoretical interest.



IA	IIA	IIIB	
Li	Be		
11 **Na** **22.991**	**12** **Mg** **24.32**		
19 **K** **39.100**	Ca	Sc	
Rb	Sr	Y	
Cs	Ba	La	
Fr	Ra	Ac	

FIG. 19-1. The periodic table in the vicinity of the group 5 metals.

Magnesium

Mg is a silvery metal and the most important of the alkaline earths as an element for structural uses. It is the third most naturally abundant metal of engineering importance (preceded only by Al and Fe), and Mg^{+2} is preceded in quantity present only by Cl^- and Na^+ in sea water.

Mg is produced from sea water and from its minerals, carnellite, $MgCl_2 \cdot KCl \cdot 6H_2O$, magnesite, $MgCO_3$, dolemite, $MgCO_3 \cdot CaCO_3$, and brucite, $MgO \cdot H_2O$. Sea water is treated by the Dow process with calcined (CaO) and slaked ($Ca(OH)_2$) oyster shells to precipitate $Mg(OH)_2$, which is filtered off and dissolved in HCl. The $MgCl_2$ solution is concentrated by evaporation to give solid $MgCl_2 \cdot 2H_2O$ which is melted and electrolyzed to give the metal and chlorine; the latter, a valuable by-product, is used partly to displace Br_2 from sea water, and partly to make more HCl. The plants in operation each use 20,000 gallons of sea water a minute and 2,500 tons of shells a day.

Isolation of Mg from dolomitic limestones is accomplished by the ferrosilicon process described in Chapter 13.

Magnesium metal is used in light alloys with aluminum (the Dow metals) and is all-important in aircraft manufacture. It is harder than aluminum and its strength/weight ratio is as good as the best Al alloys, but it is more chemically active and needs more surface protection. Having a specific gravity of only 1.74, Mg is the least dense structural metal. Its m.p. is 650 C and its b.p. is 1126 C. It is also used in incendiary bombs, flares, photoflash bulbs, and as a degasifier in the manufacture of radio tubes and in the refining of certain metals; it removes oxygen from Cu and Ni melts, rids Pb of Bi by forming insoluble Mg_3Bi, desulfurizes Ni alloys, and reduces $TiCl_4$ to Ti, for example.

The *oxidation states* are (I) and (II) but only derivatives of the latter are stable and important. The metal is a powerful reducing agent:

$$Mg = Mg^{+2} + 2e^- \qquad E^\circ = 2.37$$

It burns brightly in air forming the *oxide*, MgO, and *nitride*, Mg_3N_2. Addition of water to this mixture yields the slightly soluble *hydroxide*, $Mg(OH)_2$ and NH_3. Salts of Mg^{+2} are little hydrolyzed, so $Mg(OH)_2$ must be a strong base but its alkalinity is considerably curtailed by its insolubility. It is soluble in NH_4^+, however, a fact used to retain Mg^{+2} in the group 5 cation solution, whereas group 4 precipitates.

$$Mg\,(OH)_2 + 2NH_4^+ = 2NH_4OH + Mg^{+2}$$

Milk of magnesia is a suspension of $Mg(OH)_2$ in water. The metal also reacts with halogens to form *halides*, and when heated with sulfur it gives MgS which readily hydrolyzes in hot water to $Mg(OH)_2 + H_2S$. Metallic Mg is used in some reactions with organic compounds, the most important of which is the formation of alkyl and aryl magnesium halides known as *Grignard reagents*, which undergo many reactions of synthetic and analytical importance:

$$Mg + RX = RMgX$$

Anhydrous magnesium sulfate is not known but several hydrates are (heating them gives a basic sulfate) and these are quite soluble;

$MgSO_4 \cdot 7H_2O$ is epsom salts. Many magnesium compounds form hydrates and these aquo complexes, with oxygen attached to Mg^{+2}, are quite stable. $Mg(ClO_4)_2$, *magnesium perchlorate*, is one of the best dehydrating agents known.

Mg^{+2} does not give a visible flame test but is readily detected in group 5 by precipitation as white, crystalline $Mg(NH_4)PO_4$, or by use of an organic reagent described later (test 19–2).

TABLE 19–1. EQUILIBRIUM CONSTANTS FOR SOME MAGNESIUM REACTIONS

Reactions (in order of decreasing $[Mg^{+2}]$)	*K*	Formula Weight
$MgC_2O_4 = Mg^{+2} + C_2O_4^{-2}$	8.6×10^{-5}	112.35
$MgF_2 = Mg^{+2} + 2F^-$	8×10^{-8}	62.32
$MgCO_3 \cdot 3H_2O = Mg^{+2} + CO_3^{-2} + 3H_2O$	$\sim 1 \times 10^{-5}$	138.38
$MgNH_4PO_4 = Mg^{+2} + NH_4^+ + PO_4^{-3}$	2.5×10^{13}	137.38
$Mg(OH)_2 = Mg^{+2} + 2OH^-$	8.9×10^{-12}	58.34
$Mg_3(AsO_4)_2 = 3Mg^{+2} + 2AsO_4^{-3}$	$\sim 10^{-35}$	350.78

Quantitatively, Mg is determined by precipitation as $MgNH_4PO_4$, followed by ignition to and weighing as $Mg_2P_2O_7$, *magnesium pyrophosphate*. In hard water, Mg^{+2} is analyzed as described in the last paragraph on calcium, Chapter 18, p. 311, and also colorimetrically, using titan yellow with which Mg^{+2} forms a colored lake.

Sodium

Sodium is a metal soft enough to be cut with a knife. It has a pinkish tinge and because it reacts rapidly with moisture and oxygen is stored in airtight containers or under inactive liquids such as kerosene. Its sp. gr. is 0.97, its m.p. is 97.5 C, and b.p. is 892 C. The source of Na is sodium chloride as obtained from natural brines, sea water, or salt deposits. The metal is produced by electrolysis at about 650 C in the Downes cell containing a molten $NaCl$–Na_2CO_3 mixture. Cl_2 is the by-product. If aqueous NaCl is electrolyzed the result is $NaOH + Cl_2$. Metallic sodium is used (*a*) in atomic reactors and sodium-filled valves of high temperature engines to aid heat transfer (*b*) in organic chemistry for certain reductions and base-catalyzed reactions (*c*) to make sodium cyanide, and (*d*) to alloy with lead in the manufacture of tetraethyl lead for gasoline:

$$4NaPb + 4C_2H_5Cl \overset{\Delta}{=} (C_2H_5)_4Pb + 4NaCl + 3Pb$$

Additional utilization of the metal is (*e*) as a metal descaler, following heat treatment and (*f*) as a reductant of $TiCl_4$ and $ZrCl_4$ to produce those metals. U.S. output of Na metal is 145 thousand tons yearly.

All the alkali metals are strong reducing agents and the only known *oxidation state* is (I):

$$\mathbf{Na} = Na^+ + e^- \qquad E^\circ = 2.71$$

Sodium metal will burn in air when heated forming the yellowish *peroxide* Na_2O_2. The latter reacts with water yielding *sodium hydroxide* and oxygen.

One interesting reaction of sodium (as well as other alkali metals) is with liquid ammonia. Blue solutions are formed which become bronze colored with increasing metal concentration and have very high electric conduction. The reaction is

$$x\mathrm{NH_3} + \mathbf{Na} \rightleftharpoons Na^+ \text{ (solvated)} + e^- \text{ (solvated)}$$

The negative particle is the electron, showing the ease with which group IA metals ionize. The metal also reacts with hydrogen to give *sodium hydride*, NaH, which is used in metal descaling, with sulfur to form the *sulfide* Na_2S and *polysulfides*, and with halogens to give *halides*, NaX. Sodium chemicals are produced and used in large tonnages. Sodium hydroxide, one of the strongest bases and industrially the most important, is made in Castner cells. A concentrated NaCl solution is electrolyzed at a mercury cathode with which Na metal amalgamates and then reacts with water to make NaOH. The by-product is chlorine. Sodium hydroxide, or caustic soda, is used to make soap by reaction with fats and is also reacted with Cl_2 to make *sodium hypochlorite*, NaOCl, a bleach. Other uses of NaOH are in the manufacture of rayon by the xanthate process where cellulose is dissolved in a CS_2–NaOH mixture, and in petroleum and paper processes. Anhydrous *sodium sulfate* is called salt cake, while the decahydrate, $Na_2SO_4 \cdot 10H_2O$, is known as Glauber's salt. Both are made from NaCl and sulfuric acid. These salts are used in the paper industry to make pulp and as a raw material to produce *sodium sulfide* via carbon reduction. Na_2S is used to make sulfur-containing dyes and for removing hair from hides. The intermediate in salt cake manufacture is *sodium bisulfate*, $NaHSO_4$, known also as niter cake. It is used as a mild acid in dye baths, metallurgical fluxes, and industrial cleaning preparations. Sodium bisulfite is made from a suspension of sodium carbonate in water by passing SO_2 through it. The dried product has the formula $Na_2S_2O_5$ and is called *sodium metabisulfite* or *sodium pyrosulfite*. It is used as a bleach in textile manufacture, in food preservatives, and in tanning as a reducing agent for chromium solutions. *Sodium sulfite*, Na_2SO_3, is produced by boiling the bisulfite solution with more Na_2CO_3.

This may be converted to *sodium thiosulfate*, $Na_2S_2O_3$, by heating sulfur with its concentrated solution. *Sodium nitrate*, $NaNO_3$, is made from sodium hydroxide and nitric acid; *sodium nitrite*, $NaNO_2$, is made from the reaction mixture, $Na_2CO_3 + NO + O_2$. The by-products are CO_2 and some $NaNO_3$. *Sodium silicates* of various ratios of Na_2O/SiO_2 are made by fusing Na_2CO_3 with sand in a furnace. Silicates are used in paste-board adhesives, soaps, textile sizing, fireproofing, strong alkali cleaners, and ceramic glazes. *Sodium tetraborate* (borax), $Na_2B_4O_7 \cdot 10H_2O$, is a naturally occurring salt used in cleaners, soaps, and in making other borates. Reaction with sodium peroxide and hydrogen peroxide, for example, gives *sodium perborate*, $NaBO_3$, which is a bleach and a mild oxidizing agent used in cleaners and some mouth washes. *Sodium amide*, $NaNH_2$, is made from ammonia and sodium metal. It is used to prepare some organic compounds because of its strong reducing and base strengths, and to make *sodium cyanide*, NaCN. The last reaction inferred is between $NaNH_2$ and C and the by-product is H_2. Sodium cyanide is used as a complexing agent in gold mining, as a case-hardening agent for steels, in organic reactions to introduce the —CN group, and in electroplating where it complexes metal ions for slow electrolytic release. *Sodium carbonate*, Na_2CO_3, also called soda ash, and the decahydrate, sal soda or washing soda, $Na_2CO_3 \cdot 10H_2O$, are made from the ammonia-soda or the Solvay process, which dates back to 1869. In this important commercial operation, ammonia is reacted with carbon dioxide to make $(NH_4)_2CO_3$, ammonium carbonate. It in turn is reacted with more CO_2 in water solution to yield the bicarbonate, NH_4HCO_3, which reacts with NaCl to give $NaHCO_3 + NH_4Cl$. The $NaHCO_3$ is heated to produce $Na_2CO_3 + CO_2 + H_2O$. *Sodium bicarbonate* is produced separately from a saturated solution of Na_2CO_3 and CO_2. $NaHCO_3$ is used in manufacturing baking powders, carbonated drinks, and fire extinguishers.

In qualitative analysis, one of the most sensitive and reliable tests is the yellow color of the Na^+ flame. Many reagent grade chemicals contain enough Na^+ to give this test. *Quantitative analysis* using wet chemical methods is hampered by lack of redox possibilities and by the fact that most sodium compounds are fairly soluble. The usual gravimetric precipitate is the *sodium zinc uranyl acetate hexahydrate*, $NaZn(UO_2)_3Ac_9 \cdot 6H_2O$. See test 19–6.

Potassium

Potassium is a silvery metal with a bluish tint. It is similar to sodium in chemical action and methods of production, though there is little demand for the metal as such. The sp. gr. is 0.86, the m.p. is 63.5 C, and the b.p. is 779 C. The sources of potassium are natural brines and salt deposits. The principal mineral is sylvinite, a mixture of sylvite, KCl, and halite, NaCl.

Potassium is a very strong reducing agent:

$$K = K^+ + e^- \qquad E^\circ = 2.93$$

Like sodium, potassium metal burns in air to form a mixture of *oxide*, K_2O, and *peroxide*, K_2O_2; reacts with hot H_2 to form the salt-like *hydride*, KH; reacts with liquid NH_3 to give blue solutions containing ammoniated potassium ions and electrons; reacts with sulfur to give *sulfides*, with halogens to give *halides* and with H_2O to give H_2 and the strong base KOH.

Potassium chloride is the potassium compound in greatest demand primarily as a fertilizer component* and as a cheap starting material for the preparation of other K compounds. Aqueous KCl is electrolized to make KOH + Cl_2; the KOH is used chiefly to make *potassium* (*soft*) *soaps* and other chemicals. *Potassium nitrate* for use in black powder, fuses, fertilizers, and glass is made by metathesis from $NaNO_3$ + KCl. *Potassium acid tartrate*, $KHC_4H_4O_6$, for baking powders is a by-product from wine vats. *Potassium sulfate* for fertilizers is made by the interaction of the mineral burkeite, $Na_2CO_3 \cdot 2Na_2SO_4$, with KCl. *Potassium carbonate*, used in making glass, is made by carbonation of a mixture of $MgCO_3$ + KCl followed by hot-water treatment to decompose the product, $MgKH(CO_3)_2 \cdot 4H_2O$, giving $MgCO_3$ again plus K_2CO_3. The alloy NaK is a liquid at room temperature in the range 40–90 wt % K. It is prepared by reaction between Na and KCl at 840 C and used as a heat transfer liquid and as a reducing agent in some organic reactions. It reacts with glass at high temperatures, however, and its reaction with polyhalogenated hydrocarbons is explosive. K metal sells for about $2.50 per lb and Na for $0.15 per lb at the present time.

A good qualitative test for K^+ is the flame test (see special experiment 5). There are also a few slightly soluble potassium compounds whose precipitation is used both qualitatively and *quantitatively*. These are *dipotassium sodium hexanitrocobaltate*, $K_2Na[Co(NO_2)_6]$; (NH_4^+, Rb^+, and Cs^+ give precipitates also with $Na_3[Co(NO_2)_6]$), *potassium perchlorate*, $KClO_4$, and $K_2[SiF_6]$, *potassium fluosilicate*.

Ammonium

The ammonium ion, NH_4^+, is made by reaction of H^+ with ammonia, NH_3, the combination resulting from dative bonding by the unshared electron pair from N. *Ammonia* is made by the Haber process or its

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* A fertilizer marked for example "10-10-5", contains by weight, "10% N, 10% available P_2O_5, and 5% K_2O soluble in distilled water." according to governmental agriculture agencies' definitions.

higher pressure modification called the Claude process, both of which cause direct combination of the elements. The former uses temperatures in the range 500–600 and pressures of 100–200 atmospheres over an iron oxide catalyst.

The *oxidation state* of N in NH_3 and NH_4^+ is (– III). This radical is commonly considered in cation analysis because of the frequent occurrence of ammonium salts and the similarity of behavior of NH_4^+ and metallic ions, particularly K^+. The apparent metallic character of NH_4^+ is illustrated in its reduction at low temperatures by sodium amalgam whereby free ammonium radicals are formed, and alloy with mercury as would a metal.

$$NH_4^+ + e^- = NH_4$$

The amalgam explosively releases NH_3 and H_2 on heating.

Ammonia gas dissolves in water sufficiently to give at laboratory conditions a solution containing 28–30% NH_3 or about 60% NH_4OH and having a specific gravity of about 0.90. Ammonium hydroxide is a weak base. *Ammonium carbonate* $(NH_4)_2CO_3$, is made by reacting CO_2 gas with aqueous ammonia. *Ammonium sulfate*, $(NH_4)_2SO_4$, for fertilizers is made from reaction between aqueous ammonium carbonate and a suspension of gypsum. *Ammonium dihydrogen phosphate*, $NH_4H_2PO_4$, and *diammonium hydrogen phosphate*, $(NH_4)_2HPO_4$, are made by absorption of ammonia in phosphoric acid. These salts are used in fireproofing wood and textiles and in fertilizers. *Ammonium nitrate*, NH_4NO_3, is prepared by reaction between NH_3 and HNO_3 and is utilized in fertilizers and in explosives which also contain T.N.T. *Ammonium halides* are made from the halogen acids and NH_3; *ammonium sulfide*, $(NH_4)_2S$, is made from H_2S and NH_3 and *ammonium polysulfides*, $(NH_4)_2S_x$, are prepared by dissolving sulfur in $(NH_4)_2S$ solution.

TABLE 19–2. EQUILIBRIUM CONSTANTS FOR SOME GROUP 5 REACTIONS

Reactions (in order of decreasing [group 5 ion])	K	Formula Weight
$KClO_4 = K^+ + ClO_4^-$	8.9×10^{-3}	138.55
$Na_2[SiF_6] = 2Na^+ + [SiF_6]^{-2}$	1.7×10^{-4}	188.07
$NaHCO_3 = Na^+ + HCO_3^-$	1.2×10^{-3}	84.01
$K_2[PtCl_6] = 2K^+ + [PtCl_6]^{-2}$	1.4×10^{-6}	486.16
$Na_2H_2Sb_2O_7 = 2Na^+ + H_2Sb_2O_7^{-2}$	1.3×10^{-6}	403.54
$K_3[Co(NO_2)_6] = 3K^+ + [Co(NO_2)_6]^{-3}$	$\sim 10^{-11}$	452.29
$(NH_4)_3[Co(NO_2)_6]$ $= 3NH_4^+ + [Co(NO_2)_6]^{-3}$	$\sim 10^{-11}$	389.11

Analytically, NH_4^+ is detected by heating with a strong base to drive out NH_3, which is identified by odor, or alternately, K_2HgI_4 (Nessler's reagent), may be added to the mixture to obtain a yellow to brown color. *Quantitative analysis* is made by distilling the NH_3 into a known volume of standard acid and back titrating unreacted acid with standard base (the Kjeldahl method), or by absorption of the ammonia in boric acid followed by titration of NH_4BO_2 with standard acid (the Winkler modification). Ammonium salts sometimes interfere with other analyses and are removed by heating with HNO_3 or simply by heating; temperatures in excess of about 300 C are sufficient to either decompose or vaporize (sublime) them.

Group 5 Analysis—General Description

No systematic separation directions are needed to aid in identifying the ions of this cation group since spot tests are available for the detection of each member in the presence of the others.

If only group 5 is to be analyzed in a general mixture, it is first tested for NH_4^+ by warming with dilute NaOH and noting the odor of NH_3. Next the first four cation groups are removed using group 3 precipitating conditions followed by addition of a mixture of $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$ to complete the separation by removing group 4. The centrate then consists of group 5 ions and excess NH_4^+, and is processed as described below.

If the sample is known to contain only group 4 and 5 cations, NH_4^+ is again tested for on a separate portion and the main portion is reacted with the sulfate-oxalate mixture to precipitate group 4, and the centrate is used for group 5. *If the sample contains only group 5 cations*, NH_4^+ is tested first again, then spot tests are made for the rest of the group members.

If NH_4^+ is found, or is introduced in the SO_4^{-2}—$C_2O_4^{-2}$ treatment, it is best to remove it by evaporation with HNO_3, as ammonium ion also gives a positive test with one of the few reagents for K^+. After baking, the residue is dissolved in H_2O and the solution is ready to be used for tests of other ions. See the preliminary tests for these.

PRELIMINARY TESTS WITH GROUP 5 IONS

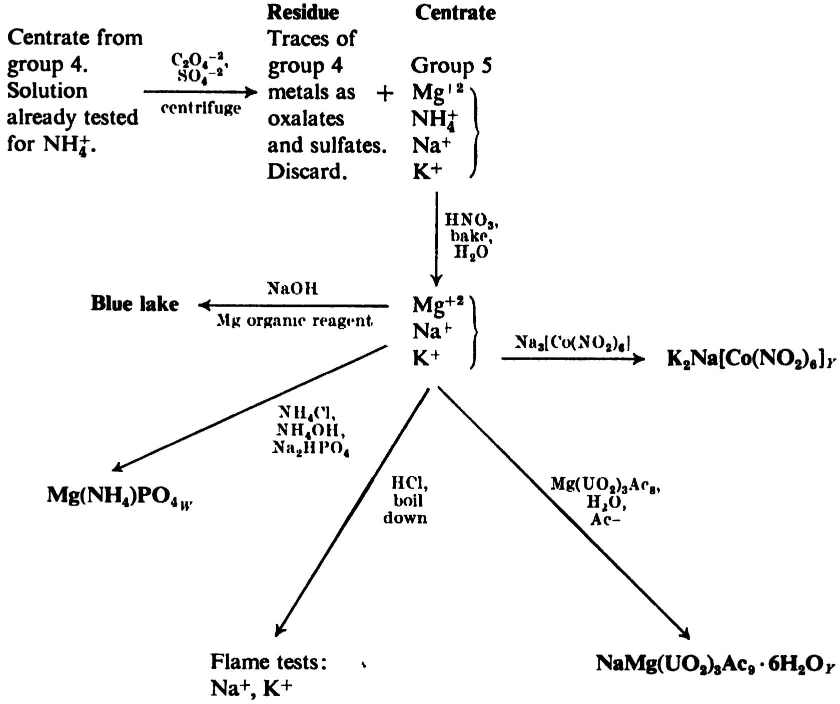
Solutions contain 10 mg/ml of the group 5 ions.

Test 19-1. Flame Tests and the Spectroscope.

See special experiment 5.

Test 19-2. p-Nitrobenzeneazoresorcinol for Mg^{+2}. Put a drop of Ca^{+2} test soln in one spot plate depression, a drop of Sr^{+2} in another, a drop of

FLOW SHEET—GROUP 5



Ba^{+2} in another, and a drop of Mg^{+2} in another. Add to each 2 drops of H$_2$O, 1 drop of 6 M NaOH or KOH, and a drop of the org. reagent. Mix each spot with a stirring rod, and note and record the differences. See example 15, Chapter 12, p. 197. Is this reagent useful as a spot test for Mg^{+2} in a group 4 and 5 mixt. of ions?

Test 19–3. Precipitating Agents for Mg^{+2}. Repeat the tests given in 18–2, and note any similarities and differences between magnesium and the other alkaline earth ions.

Test 19–4. Miscellaneous Group 5 Reagents. With reference to problem, 1, this chapter, try one or more reagents made available by the instructor, and include data from the literature concerning sensitivity, etc. *Note the dangers inherent in the use of H$_2$SiF$_6$ and HClO$_4$; both cause bad burns, and perchlorates are explosive.*

Test 19–5. Blowpipe Test for Mg^{+2}. Using the techniques described in part 2 of special experiment 4, and test 17–7, put a spatula full of Mg(OH)$_2$ (Mg^{+2} + NH$_4$OH) on a charcoal block, add a drop of 0.05 M Co^{+2} soln., and direct the oxidizing flame to it with a blowpipe. A pink color possibly due to

$MgCoO_2$ develops. Alternately the test may be run using asbestos fiber or wadded filter paper in place of charcoal, and heating is done directly in the Bunsen flame.

✓***Test 19–6. Magnesium (or Zinc) Uranyl Acetate for Na^+.*** Boil down 1 ml of Na^+ soln. to about one third its original vol., cool, and add an equal vol. of $Mg(UO_2)_3Ac_8$. What is the slowly forming, yellowish, cryst. ppt.? Potassium does not interfere if it is present in quantity less than four times that of sodium. The reagent also ppts. ferrocyanide and phosphate, but these are presumed absent or removable by methods given in Chapter 21. Zinc uranyl acetate and some other double acetates work equally well in Na^+ pptn., but all are appreciably water sol., hence the concn. of the sample. Li^+ gives a similar ppt.

✓***Test 19–7. Sodium Cobaltinitrite for K^+ and NH_4^+.*** (*a*) Solns of $Na_3[Co(NO_2)_6]$ are not too stable and should be prepd. fresh (0.1 g of reagent in 0.5 ml of H_2O). Shelf reagent should be checked with K^+ test soln. as follows: 1 drop of 1 *M* HNO_3 and 5 drops of reagent are added to 10 drops of soln. contg. 0.5–5 mg of K^+ and the mixt. allowed to stand 1–5 min to ppt. yellow $K_2Na[Co(NO_2)_6]$. The unknown is run in the same way. The reaction with NH_4^+ is similar and should be tried. Note any diff. in color of ppts. Write reaction equations. Give Werner names to all complex compds.

(*b*) *Preparation of the Reagent* (*Optional*). Dissolve 5 g of $NaNO_2$ in 6 ml of hot H_2O. Cool to 50 C, add 1.6 g of powd. $Co(NO_3)_2 \cdot 6H_2O$, and stir. Add 1 ml of glacial HAc, mix, and allow to stand an hour, swirling occasionally to aid release of nitrogen oxides. Then add 6–10 ml of alcohol and swirl several times during next 10 min. Filter the orange product with suction and wash it with 5 ml of alcohol. Spread the filter paper to dry. Bottle the dry product and make soln. from it as needed. Reactions are

$$Co(NO_3)_2 \cdot 6H_2O + 6NaNO_2 = Na_4[Co(NO_2)_6] + 6H_2O + 2NaNO_3$$

$$Na_4[Co(NO_2)_6] + HNO_2 + HAc = NaAc + H_2O + \mathit{NO} + Na_3[Co(NO_2)_6]$$

Test 19–8. Displacement of NH_3 from NH_4^+. A strong base will liberate a weaker one from its salts. Put 6 drops of NH_4^+ soln. in a small beaker, add 10 drops of H_2O, and 3 drops of 6 *M* NaOH. Warm. *Remove the flame*, stir the soln., then *cautiously* note the odor of ammonia above the container. (This test should not be carried out in a tube using an open flame for heat, otherwise the soln. may splatter out. *Immediately wash off any hot NaOH spilled on the skin with plenty of water and very dil. HAc.*) Further indication of NH_3 release may be had by holding a moistened piece of indicator paper above the heating soln., and noting evidence of a basic reaction. Rapid heating and boiling gives a false indicator test due to tiny droplets of soln. (contg. NaOH) being driven out.

✓***Test 19–9. Nessler's Test for NH_4^+ and NH_3.*** (*a*) Dil. a drop of NH_4^+ test soln. with 2 ml of water, and to a few drops of that, add 2–3 drops of Nessler's soln. A yellow to brown color of HO—Hg—NH—HgI is a positive test. The method can be used in quant. colorimetry in the range 0–3 ppm NH_4^+ or NH_3.

(*b*) *Preparation of the Reagent* (*Optional*). Dissolve 0.03 moles of $HgCl_2$ (mol. wt 271.5) in 90 ml of hot H_2O and, with stirring, add to it a hot soln. contg. 0.06 moles of KI (mol. wt 166) in 30 ml of H_2O. Filter the red HgI_2 by suction and wash twice using 30 ml of H_2O each time. Stir the moist product into 8 ml of hot H_2O contg. 0.059 moles of KI. Put the container in a water bath and keep it hot for 20 min. Stir occasionally, allowing about a fourth of the vol. to evap. Centrifuge or decant the mixt. and discard any residue. Put the centrate in an evapg. dish and store over $CaCl_2$ in a (vacuum) desiccator. This will give a moist crystalline mass of potassium tetraiodomercuriate(II) dihydrate, $K_2[HgI_4]\cdot 2H_2O$. Further drying can be done by pressing between sheets of filter paper and more desiccation over $CaCl_2$. The product is bottled and used to make Nessler's solution by dissolving a few crystals in about a ml of 3 *M* KOH.

Test 19–10. Lithium as a Group 5 Ion. Review lithium chemistry in Chapter 20 and optionally perform the tests. Note how one would detect Li^+ in this cation group if it were included in a general unknown.

Analysis of a Known Mixture

Proceed to the unknown sample unless directed to do a known sample over group 5. The notebook should be completed to this point.

ANALYTICAL REACTIONS OF GROUP 5 CATIONS

A. Magnesium

1. $$Mg^{+2} + NH_4OH + HPO_4^{-2} = Mg(NH_4)PO_{4_w} + H_2O$$

2. $$Mg^{+2} + 2OH^- = Mg(OH)_{2_w}$$

3. $$MgO + CoO \overset{\Delta}{=} MgCoO_{2_p}$$

4. Mg^{+2} + *p*-nitrobenzeneazoresorcinol = Blue lake (Chapter 12)

B. Sodium

1. $$Na^+ + Mg^{+2} + 3UO_2^{+2} + 9Ac^- + 6H_2O = NaMg(UO_2)_3Ac_9\cdot 6H_2O_y$$

C. Potassium

1. $$2K^+ + Na^+ + Co(NO_2)_6^{-3} = K_2Na[Co(NO_2)_6]_y$$

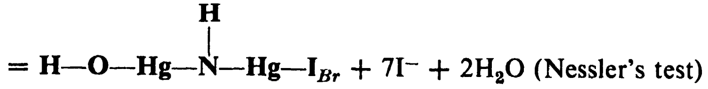
D. Ammonium

1. $$2NH_4^+ + Na^+ + Co(NO_2)_6^{-3} = (NH_4)_2Na[Co(NO_2)_6]_y$$

2. $$Co(NO_2)_6^{-3} + H_2O = 2Co^{+2} + 2H^+ + 11NO_2^- + NO_3^-$$
$$2NH_4^+ + 2NO_2^- = 2N_2 + 4H_2O$$

3. $$NH_4^+ + OH^- = NH_4OH = NH_3 + H_2O$$

4. $NH_3 + 2HgI_4^{-2} + 3OH^-$



$$= H{-}O{-}Hg{-}\overset{\overset{\textstyle H}{|}}{N}{-}Hg{-}I_{Br} + 7I^- + 2H_2O \text{ (Nessler's test)}$$

PROCEDURE FOR GROUP 5 ANALYSIS

(*A*) *If the sample is a simple unknown containing only group* 5 *ions*, test for NH_4^+ as described in test 19–8. If NH_4^+ is *not* found, proceed with other portions of sample to test described in (*E*). If NH_4^+ *is* detected, concentrate 1–1.5 ml of sample to 0.5 ml by boiling in a 20-ml beaker and proceed to (*C*).*

(*B*) *If the sample is the centrate from previous analysis*, NH_4^+ is present, because NH_4OH or its salts were added at one time or another and will have to be decomposed. There are also possibly some group 4 ions left by incomplete precipitation that must be removed so they will not precipitate as phosphates and render the later Mg^{+2} test inconclusive. These interferences are handled in the next paragraphs.

Boil down the solution available for group 5 in a 20-ml beaker to a volume of about 1 ml, add a drop of $(NH_4)_2SO_4$ and a drop of $(NH_4)_2C_2O_4$, and heat the mixture in a water bath for several minutes. Let it cool after removal, add 10 drops of H_2O, stir, then centrifuge any residue and discard it unless its volume is appreciable and prior group 4 analysis was not satisfactory. (This residue can be solubilized via Na_2CO_3 transposition, as explained in Chapter 21, and returned to the beginning of the group 4 procedure for another try.)

(*C*) To the solution from (*A*) or (*B*), add 6 drops of concentrated HNO_3 and evaporate the mixture carefully in the hood using a moving flame under the beaker, and when dry, allow it to cool and add 6 more drops of the HNO_3 and evaporate again and heat until no more fumes are visible. The NH_4^+ salts are now gone.†

(*D*) Cool the beaker and its baked contents from (*C*), add 1 ml of H_2O, and warm briefly to resolubilize the salts that are left. Divide the solution

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* Mg^{+2} may be tested for without elimination of NH_4^+, and whether NH_4^+ is found or not, one may perform 19-2 directly. The flame tests for Na^+ and K^+ may also be run at this time although the volatile ammonium salts tend to minimize the K^+ color particularly, and small amounts of K^+ in the presence of large amounts of NH_4^+ could be missed, so K^+ is always tested for as provided later.

† No residue indicates no Mg^{+2}, K^+, or Na^+ salts were in the sample. Carbon from organic matter and silica from the glassware may be visible, but these of course will not redissolve in H_2O.

equally among four tubes, and proceed as directed in the next four sections.

(*E*) With reference to the four solutions from (*D*) or (*A*):

Tube 1: remove several drops to a spot plate and run test 19–2 for Mg^{+2}, if this was not done as mentioned in footnote.

Tube 2: add 2 drops of concentrated HCl and run flame tests according to special experiment 6, Chapter 23. Use the filter technique if looking for K^+ in the presence of Na^+.

Tube 3: evaporate to about half volume, cool, and run test 19–6 for Na^+. This precipitation allows one to estimate sodium content. The flame test is so sensitive that trace Na^+ impurities in analytical grade chemicals may give a positive reaction. While the flame is visible from solutions as dilute as 2 ppm Na^+, the solution must contain Na^+ at a concentration of better than 300 ppm to yield the triple acetate precipitate (without using alcohol to decrease its solubility, which is an unreliable procedure since it may cause the reagent itself to come out of solution).

Tube 4: evaporate to about half volume, cool, and test for K^+ according to test 19–7 (*a*).

This is the end of the group 5 procedure.

PROBLEMS

1. (*Library*) Some reagents also used in the qualitative analysis of group 5 ions, but not detailed here, are potassium dihydrogen pyroantimonate, perchloric acid, dipicrylamine, chloroplatinic acid, tartaric acid, hydrofluosilicic acid, and titan yellow. Find references to these and list for each the reaction equation, evidence that constitutes a positive test, interferences, sensitivity, and any other data that appears significant.

2. An ice plant is using ammonia refrigeration. You are asked to locate a pinhole ammonia gas leak in a complex of pipes. What method do you suggest?

3. Ammonia leaks are sometimes located by burning a sulfur-containing candle, a positive test being the appearance of dense white fumes. Explain the basis for this method. Would humidity of the air have any effect?

4. If one does not perform the HNO_3 evaporation on the group 4 centrate before running the group 5 analysis, what error might be introduced?

5. One evaporates a 50.0 ml sample of irrigation water to a small volume and precipitates K^+ in it as $KClO_4$, using perchloric acid. Show that,

$$\text{ppm K} = (\text{mg KClO}_4)(5.63)$$

6. Mg is sometimes determined in natural waters as follows: 100.0 ml of H_2O

is evaporated to a small volume, Mg^{+2} is precipitated as $(NH_4)MgPO_4$ and ignited to $Mg_2P_2O_7$ which is weighed. Show that

$$\text{ppm Mg} = (\text{mg } Mg_2P_2O_7)(2.184)$$

7. (*Library*) The Nelson and Castner-Kellner cells are industrially employed to make caustic soda. Find reference to these, sketch each, and explain their operations briefly.

8. From the descriptions in this text, give balanced equations for the commercial production of each of the following: CH_3MgBr, Na, NaOH, NaH, Na_2O_2, NaOCl, $Na_2SO_4 \cdot 10H_2O$, Na_2S, $NaHSO_4$, Na_2SO_3, $NaNO_3$, $Na_2S_2O_3$. Give a use for each one.

9. As in problem 8: $NaNO_2$, Na_2SiO_3, $NaBO_3$, $NaNH_2$, NaCN, $Na_2CO_3 \cdot 10H_2O$, $(NH_4)_2CO_3$, $NaHCO_3$, KOH, K_2SO_4, K_2CO_3, and KNO_3.

10. A colorless, aqueous solution gives no reaction with $(NH_4)_2CO_3 + NH_3$, and in a separate test gives no flame test and no odor when heated with KOH. What conclusions can one make?

11. What simple tests can one apply to differentiate between: (*a*) KCl and NH_4Cl (*b*) $Mg(NO_3)_2$ and $NaNO_3$ (*c*) $(NH_4)_2NaCo(NO_2)_6$ and $K_2NaCo(NO_2)_6$ (*d*) halite and sylvinite (*e*) $Mg(NH_4)PO_4$ and $MgHPO_4$.

12. (*a*) Calculate the pounds of N, P, and K in 100 pounds of a "10-10-5" fertilizer. Express each as a per cent.

(*b*) A sample of liquid fertilizer (an aqueous solution of chemicals) has a sp. gr. of 1.2. It sells for \$2.00/gal and is a 10-10-5 preparation using 80% by wt H_3PO_4 (\$10.00/100 lbs) as a P source, KCl (\$4.00/100 lbs) as a K source, and urea, $(H_2N)_2CO$, (\$10.00/100 lbs) as an N source. If the gallon bottle, label, labor, and other fixed expenses are \$0.27/gal, calculate the profit realized in preparing 1000 gal of solution packaged in gallon bottles.

13. A group 5 solution gives a white gelatinous precipitate and (simultaneously) a sharp odor when NaOH is added. What do these observations indicate? What confirmatory tests for ions suspected to be present should be run on separate portions of sample? On what ions in group 5 have no data been gathered by this single test? How should one test for them?

14. Table salt "cakes" on rainy days due to the presence of traces of hygroscopic $MgCl_2$. How could one test such a sample for Mg^{+2}?

15. Could any of the group 4 or 5 ions listed for analysis be oxidized to a higher state in acid solution by MnO_4^-? Could any be reduced to a lower state in acid solution by Sn^{II}? Explain briefly any generalizations you can make here.

16. (*a*) Why is it convenient to put Mg^{+2} in group 5 rather than let it precipitate in group 4?

(*b*) What is the lowest *p*H at which it is theoretically possible to precipitate $Mg(OH)_2$ from 1 *M* Mg^{+2}?

(*c*) Why doesn't Mg precipitate in one of the first three analytical groups?

(*d*) Methyl bromide CH_3Br, reacts with Mg metal in anhydrous ether to give the Grignard reagent methyl magnesium bromide. This solution is poured over dry ice (CO_2) and the reagent opens one carbon—oxygen bond and adds across it as a positive magnesium bromide ion and a negative methyl ion. When water is mixed with that product, magnesium hydroxy bromide and acetic acid are formed. Write balanced equations for this illustration of a Grignard synthesis.

17. The solubility of $K_2[SiF_6]$ is about 6×10^{-3} moles/liter. Place it in Table 19–2.

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20

SOME LESS FAMILIAR ENGINEERING METALS

This chapter outlines the chemistry of eight metals that bear similarities to some already described, but these metals are generally unfamiliar to the beginner. This does not mean that they are necessarily more rare in natural occurrence. Zr, Ti, V, W, and Li are all more abundant in the earth's crust than Sn, Zn, Co, Pb, As, Sb, B, Cd, Hg, and Bi, but their metallurgy makes them difficult to obtain in a pure state. In recent years due to demands in the fields of high-temperature engines, high-speed aircraft, electronics, and atomic energy, a tremendous impetus has been given metallurgical research, and metals which were laboratory curiosities a few years ago are today produced and used in large tonnages. For example, zirconium, the twelfth most abundant metal in the earth, sold for $300 a pound in 1945 and a grand total of 20 pounds were produced in the United States that year. In 1954, because of its desirability as a structural material in atomic reactors, about 200,000 pounds of zirconium were produced, the price dropped to about $14 a pound, and its metallurgy is now better known than that of many metals that have been used for years.

Chemically speaking, the selection of elements in this chapter is not particularly representative. Lithium is similar to sodium and magnesium, already discussed; beryllium is similar to magnesium and aluminum; molybdenum and tungsten are related in properties to chromium; titanium and zirconium have like reactions and oxidation states, etc.

It is felt, however, that because of their engineering and metallurgical importance these metals warrant sufficient emphasis along applied lines for inclusion here.

IA	IIA	IIIB		IVB	VB	VIB	VIIB	
3 Li 6.940	4 Be 9.013							
Na	Mg							
K	Ca	Sc		22 Ti 47.90	23 V 50.95	Cr	Mn	
Rb	Sr	Y		40 Zr 91.22	Nb	42 Mo 95.95	Tc	
Cs	Ba	La	*	Hf	Ta	74 W 183.92	Re	
Fr	Ra	Ac	†					

* Lanthanides	Ce	Pr	Nd	Pm	Sm	
† Actinides	Th	Pa	92 U 238.07	Np	Pu	

FIG. 20-1. The periodic table in the vicinity of the "less familiar metals."

Tungsten

Tungsten is a gray, hard metal that is slowly attacked by acids or bases. The main ores are wolframite, (Fe, Mn)WO_4, and scheelite, $CaWO_4$. These are refined chemically in several ways; the Shoppler process, for example, employs fusion with Na_2CO_3, leaching with water, filtration, and acidification to produce the *trioxide*, WO_3. This is reducible with C or H_2 to give the metal at about 1250 C. H_2 is the preferred reductant since the objectionable formation of brittle tungsten carbide cannot be controlled with carbon reduction. The method produces tungsten powder, which is then compacted and electrically fused. The high melting point of the metal precludes casting. The workability of the fused stock is good and it may be rolled and formed in the usual ways. W sells for about $4.50 a pound now.

The metal is used in alloy steels as a hardening agent and a developer of fine-grain structure leading to a densely packed material. Tungsten carbides, WC and W_2C, are among the hardest known alloys and are used in cutting tools. Alloys with Fe, Co, Cr, C, V, and Si are common, all of them being adapted to service where hardness and high melting point are of prime importance: chisels, punches, dies for hot work, lamp filaments, etc. Typical alloys are carbaloy, nominally 90% WC, 10% Co, and stellite no. 6, nominally 6% W, 39% Cr, and 55% Co.

Tungsten has *oxidation states* (0), (II), (III), (IV), (V), and (VI). The main oxide therefore is WO_3. WO_3 is not appreciably soluble in acids but will dissolve in bases to form tungstates like $Na_2(WO_4)$, *sodium orthotungstate*, as well as tungstates of more complex structure. Acidification of these hot solutions yields yellow *tungstic acid*, H_2WO_4, and of the cold solutions yields a white hydrate, $H_2WO_4 \cdot H_2O$, which changes slowly to the other form. The tendency for tungsten-oxygen radicals to condense is so great that there are very few simple ions of this type in solution. Tungsten(III) is known only as chloro complexes in solution, derivatives of the acid $H_3W_2Cl_9$. Depending upon concentration and pH, literally hundreds of complex tungsten acids may form and are obviously extremely difficult to isolate and study. Tungsten(IV) is known in solution in chloro and octacyano complexes. Tungsten(V) is stable in solution only as complexes such as $W(CN)_8^{-3}$.

Orthophosphoric acid with normal (WO_4^{-2}) tungstates gives *heteropoly tungstophosphates* such as $H_3P(W_3O_{10})_4 \cdot xH_2O$, where the W_3O_{10} radical has substituted for four oxygen atoms in orthophosphate. A wide range of radicals* of this type are known, combinations being often represented as oxide ratios:

$$P_2O_5 : WO_3 = 1:24,\ 1:22,\ 1:21,\ 1:20,\ 1:16,\ 1:12,\ 1:7$$
$$As_2O_5 : WO_3 = 1:16,\ 1:6,\ 1:3$$
$$SiO_2 : WO_3 = 1:12,\ 1:10$$

Compounds containing W in the cation, like WF_6, WCl_6, and WBr_6 (the only hexabromide known), are not of much importance, since they are quickly hydrolyzed in water. In acid solution, active metals like Zn and Sn reduce tungstates to blue compounds called "*tungsten blues.*" This is a useful color reaction for the qualitative detection of tungsten. (Molybdenum gives a similar reaction.) The tungsten blue structures vary with preparation; formulas as $(WO_2)_2WO_4 \cdot xH_2O$ and $W_8O_{23} \cdot xH_2O$ have been suggested. Reduction of tungstates by hydrogen gives a series of "*tungsten*

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* In one nomenclature system, numbers follow names to help differentiation among the many compounds. $(NH_4)_3[P(W_{12}O_{40})]$ is called ammonium tungstophosphate (3.12.40).

bronzes" whose approximate formula is $WO_2 \cdot xWO_3$, in which x varies from 1 to about 7. These materials are highly colored, some being bronze, and all are moderately good electric conductors but are chemically inert.

Some analysts put W in a special cation group with SiO_2 and a few other substances that precipitate in advance of cation group 1 when the sample is acidified. If carried along without prior separation it will appear in group 1 and may be separated from the other members of the group by treating the mixture of chlorides and hydrolysis products with alkaline sulfide, in which tungsten alone forms a soluble complex, WS_4^{-2}. Acidification of the centrate produces brown WS_3, which hydrolyzes in hot water to H_2WO_4.

W is *quantitatively determined* in steels by dissolving the sample in hot aqua regia which converts W to $H_2WO_4 \cdot H_2O$. This is filtered off and ignited below 750 C (WO_3 is volatile above that) and weighed as the oxide.

Molybdenum

This element is a silvery metal which can be ductile and malleable depending upon temperature and microstructure. Like Ti, Fe, W, etc., Mo undergoes an allotropic transformation, but with molybdenum the change takes place near room temperature. The main ores are molybdenite, MoS_2, and wulfenite, $PbMoO_4$. These are converted at high temperature to MoO_3, from which the metal is obtained by aluminothermy or electric furnace reduction with C, Si, or H_2. Powdered Mo so obtained is compacted and sintered electrically, then, using a sintered bar as one electrode and a cooled copper crucible for the other (Mo does not alloy with Cu), the Mo is resistance melted at about 2700 C under vacuum or in a rare gas atmosphere. Air reacts with Mo at elevated temperatures to give both *oxides* and *nitrides* and must be excluded during melting. The process is typical metallurgy for a number of high-melting metals. Conditions like 1100 amperes at 20 volts melting about 30 pounds of Mo an hour are common.

Electrolytic molybdenum of greater than 99.9% purity has recently been reported produced on a laboratory scale by the National Bureau of Standards. K_2MoCl_6 and mixtures of alakli metal halides are fused and electrolysis is carried out at about 600 C under argon.

The metal is used mostly as an alloying element in steels to which it imparts good air hardening properties that are important in keeping large castings from cracking. With nickel, alloys containing up to 30% Mo have been prepared for use where corrosion is apt to be severe, as in acid-containing reactors. Molybdenum is also used, up to about 4%, as a less critical substitute for tungsten in high-speed steels. Such steels carry descriptive names like mo-cut, mo-tung, mo-van, etc. Molybdenum has been employed in heating elements for furnaces but cannot be used at high temperatures without suitable ceramic coatings, such as BeO, which protect the metal from forming MoO_3 with the air. Molybdic oxide sublimes and does not give a protective coating to the metal. The largest use of *molybdic oxide*, MoO_3, is as a catalyst in "reforming" gasoline fractions to increase the octane rating by producing branch chain hydrocarbons from straight chain ones. An intercrystalline mixture of lead chromate and *lead molybdate* is called "molybdenum orange," one of the few important inorganic pigments for paints and inks. *Sodium molybdate*, Na_2MoO_4, is used in the order of a few ounces per acre of soil to treat for molybdenum deficiency which manifests itself in plants by hindering their utilization of nitrogen. *Molybdenum disulfide*, MoS_2, is an unusually good dry lubricant in that it can be used at temperatures as high as 1000 C in a nonoxidizing atmosphere as well as at very low pressures. Its lubricating ability is not affected by high pressure. Molybdenum metal is worth about $2 a pound today.

Molybdenum has *oxidation numbers* (0), (II), (III), (IV), (V), and (VI). The metal is soluble in acids but gives, with HNO_3, H_2MoO_4 from which white MoO_3 precipitates. This oxide is soluble in bases, forming *molybdates* of various formulas like Na_2MoO_4 and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. *Molybdic acid*, $H_2MoO_4\cdot H_2O$, like tungstic acid, is capable of many condensation reactions* from which such ions as $Mo_3O_{11}^{-4}$, $HMo_6O_{21}^{-5}$, $H_9Mo_{24}O_{78}^{-3}$, etc., have been reported.

Mo^{II} is known in *molybdenum "dichloride"* $[Mo_6Cl_8]Cl_4$, prepared by chlorine and the metal. *Molybdenum(III) chloride* and *bromide* have been made. Heat causes $MoCl_3$ to disproportionate into the (II) and (IV) chlorides. The (III) halides hydrolyze in water to form possibly MoO. The bonding is largely covalent and the compounds nonionic. *Molybdenum(IV) compounds* are not stable in aqueous solution or to heat, disproportionating into Mo^{III} and Mo^{V}. MoO_2 is made by H_2 reduction of MoO_3. *Molybdenum(V) salts* are little known, but its complexes are stable in water. $MoCl_5$ is the only pentahalide. It is formed by direct chlorination of the metal. H_2 reduces it to $Mo + MoCl_3$. Unlike tungsten, Mo_2S_5 and Mo_2O_5 are known. Molybdenum(VI) is similar to chromium(VI) but has a far greater power to form complicated ions, since chromium does not condense much farther than $Cr_4O_{13}^{-2}$. The simple molybdates, MoO_4^{-2}, are known to condense into radicals containing up to 16 MoO_3 groups in the anion.

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* A *condensation* is a reaction in which two or more molecules or ions give a more complex substance with the elimination of water. A *polymerization* is the same except that water is not a by-product.

Brown MoS_3 is partially precipitated under cation group 2 precipitation conditions, leaving a blue color in the supernatant liquid which helps identify the element. This "molybdenum blue" is still of doubtful structure, apparently being a colloidal dispersion of a molybdenyl molybdate hydrate whose approximate formula is $MoO_2(MoO_3)_4 \cdot xH_2O$. The *sulfide* is soluble in alkaline sulfides giving reddish *polysulfides* like MoS_4^{2}.

With a mixture of H_2SO_4, excess SCN^-, and Sn^{II}, Mo^{VI} gives a reddish *thiocyanate complex* of variable composition, possibly $Mo(SCN)_5$, which is good qualitative evidence for the presence of the metal in solution. The thiocyanate ion stabilizes the (V) oxidation state. A reversal of the test later described for phosphate may also be used to detect Mo; a yellow *ammonium molybdophosphate*, $(NH_4)_3P(Mo_3O_{10})_4 \cdot 2HNO_3 \cdot 2H_2O$, is formed when MoO_4^{-3} reacts with PO_4^{-3} in hot HNO_3. A number of organic reagents are useful in molybdenum analysis; one of the most reliable of which is phenylhydrazine in acetic acid. Molybdates give a pink to red color. See problem 1, p. 357.

Uranium

This element is a silvery, radioactive metal having three allotropic forms. The properties of the allotropes vary considerably. The low-temperature form is fairly ductile but presents a unique problem in shaping in that heating causes its lattice to expand in two dimensions and contract in the third. At 660 C an allotropic change occurs to a complex, brittle lattice which in turn at 770 C gives way to a body-centered cubic form that is as soft as room-temperature lead. All the forms tarnish rapidly in air and become covered with a black oxide, UO_2.

The important minerals are pitchblende, U_3O_8, and carnotite, a complex oxide. Either of these is reducible with magnesium or carbon to give the metal. Acid leaching of ores leads to uranium salts by evaporation of the liquors. All uranium compounds are radioactive and poisonous. The metal is used almost entirely in the atomic energy program. The 235 isotope is fissioned directly by slow neutrons, while the 238, the much more abundant isotope, is converted via neutron capture and nuclear reorganization to neptunium and plutonium. (Pu^{239} is neutron fissionable.) U metal sells for about $18 a pound.

Uranium is chemically quite active. With H_2 at 225 C it forms a *hydride*, UH_3. Since H is a good neutron velocity moderator, the critical mass of the hydride is smaller than that of the free metal itself. The metal dissolves in acids; HCl gives H_2 and green U^{IV}; HNO_3 gives some H_2, NO_3^- reduction products, and yellow UO_2^{+2}.

In being oxidized, $U \rightarrow U^{+3}$, uranium is almost as good a reducing agent as metallic aluminum. *Oxidation states* of (IV) and (VI) are uranium's most important, but U^{III} (purple and green) and (V) (green) are also known under special conditions. The (V) salts disproportionate in water yielding the (IV) and (VI) states. The most common ion in acidic or neutral solution is the yellow, fluorescent *uranyl* ion, UO_2^{+2}, and in basic solution the *diuranate* ion, $U_2O_7^{-2}$, and *uranate* ion, UO_4^{-2}. U^{VI} forms three kinds of compounds; first, simple ones like UF_6, second, salts derived from UO_3: the uranates UO_4^{-2} and diuranates $U_2O_7^{-2}$ (which resemble chromium and lack the condensing ability of WO_4^{-2} and MoO_4^{-2}), and third, uranyl compounds containing the ion $O{=}U{=}O^{+2}$. It is covalent and characteristic of uranium and most of the elements following it in the periodic table. (Np, Pu, and Am have the same four oxidation states as well.) Among typical compounds in these series are $Na_2U_2O_7$, which is insoluble in water (as are many U^{VI} compounds) and $UO_2(NO_3)_2$, which is soluble in ether (as are most UO_2^{+2} salts). Both compounds are used in analytical separations from other cations. The *hydroxide*, $UO_2(OH)_2 \cdot xH_2O$, gives water soluble uranyl salts with acids, like $UO_2Ac_2 \cdot xH_2O$.

Uranyl compounds tend to form double and triple salts, as $NaMg(UO_2)_3Ac_9 \cdot 6H_2O$, which are sparingly water soluble and used as analytical precipitates. Divalent ions of Co, Cu, Fe, Ni, and Zn may be used in place of Mg. Uranyl ion hydrolyzes upon dilution to ions containing U and O of indefinite proportions. The volatility of *uranium hexafluoride*, UF_6, makes possible the separation of U-235 and U-238 by diffusion methods at the Oak Ridge plant.

Many organic reagents have been discovered that aid both qualitative and *quantitative analysis* for uranium. For example, tannic acid, 8-hydroxyquinoline, and α-nitroso-β-naphthol all give precipitates with U ions. With excess $(NH_4)_2CO_3$, U forms a soluble carbonate complex. Under the same conditions Fe and Al in cation group 3 form precipitates. The centrate containing the soluble uranium is then rendered basic with NH_4OH and insoluble $(NH_4)_2U_2O_7$ falls out. Alternatively, the solution is made acidic with HNO_3, and UO_2^{+2} is shown to be present by using $K_4[Fe(CN)_6]$ to precipitate brown *uranyl ferrocyanide*. Several peroxide–U systems have been studied a great deal, not only because they are the basis for colorimetric methods but also because U ions in aqueous solutions containing H_2, O_2, and H_2O_2 as products of fission radiation are common in atomic plants.

Titanium

Titanium is a silver-grey metal with low malleability and ductility except at higher than room temperatures. It has two allotropic forms, α, hexagonal below 885 C, and β, body-centered cubic above that temperature. The most important minerals are ilmenite, $FeTiO_3$, and rutile, TiO_2. The metal is produced in sponge form 99.5% pure by the Kroll process in which Mg is used to reduce $TiCl_4$ at high temperature and $MgCl_2$ is distilled off under reduced pressure. Ti technology is a continual source of speculation and invention, and several new methods are announced yearly for metal recovery. A recent one involves the reduction

$$\mathrm{TiC} + \mathrm{2ZnO} \xrightarrow{\Delta} CO + 2Zn + \mathrm{TiO}$$

followed by electrolysis in molten TiO–$CaCl_2$. Another method for commercial metal production centers about electrolysis of $K_2[TiF_6]$ in molten NaCl. Melting the sponge by induction or arc heating in an inert atmosphere has permitted preparation of ingots weighing over two tons.

A preparation of $TiCl_4$ from the cheaper ilminite ores has recently been announced and hinges upon the stability of a titanium Werner ion. The ore is dissolved in H_2SO_4 and iron salts eliminated by fractional crystallization. The $TiOSO_4$ solution is gassed with HCl at 0 C, then saturated with KCl, whereupon K_2TiCl_6 precipitates. This is filtered off, heated at about 400 C, and pure $TiCl_4$ is evolved. Impurities and KCl are left behind.

Among the important structural metals, only Al, Fe, and Mg are more abundant in the earth's crust than is Ti, but the recovery of Ti is hindered greatly by its high melting point (1727 C) and the fact that at high temperatures it readily combines with O_2, N_2, and many crucible materials. Despite these difficulties, its low density (4.5 compared with 7.86 g/cc for Fe), good corrosion resistance (particularly against HNO_3), high melting point, one of the highest known metallic strength-to-weight ratios, and ability to form many alloys of desirable properties, make Ti attractive in engineering uses, and it is rapidly becoming one of the most important "new" metals.

Alloys are made by sintering other metal powders with *titanium hydride*. Hydrogen is released at elevated temperatures to produce a reducing atmosphere in the furnace which is desirable, unless hydrogen embrittlement of metals takes place. Titanium powder is as dangerous to handle as magnesium powder, however, since a spark is capable of igniting a fire that is next to impossible to put out: $\mathrm{Ti} + O_2 = \mathrm{TiO_2}$.

Titanium does not absorb lubricants well and is difficult to use in low-friction applications. Alloys may be made with good structural properties, however, since Ti like Fe undergoes an allotropic transformation which allows great alteration of character by heat treatment. The better alloys are two phase at room temperature. Titanium is only difficultly surface hardened. The best method so far is a nitriding treatment, since the solubility of C in Ti is less than 0.1%. Combinations of TiC, Ti, and other refractory materials are sintered for high-temperature applications such as parts in jet aircraft after-burners. Combinations of metals and ceramics are given the general name of "cermets." Such materials are difficult to form and have low impact resistance but possess the advantages of hardness and high melting point. *Titanium dioxide* is trimorphic like SiO_2 and is a dense, brilliant white pigment widely used in paints. $TiCl_4$, another useful chemical, is employed in smoke screens and sky writing.

Titanium metal dissolves slowly in HCl or H_2SO_4 to yield H_2 and *titanous oxychlorides* or *sulfates* which have variable formulas due to hydrolysis. These compounds are usually represented as TiOCl or $(TiO)_2SO_4$, but no specific ions like TiO^+ or TiO^{+2} have been proved capable of individual existence. The metal dissolves in hot HNO_3 to give *titanic acid* as an oxidation product, the formula is again uncertain but is written $H_2TiO_3 \cdot xH_2O$. TiO_2 is the only Ti oxide stable in water, though both TiO and Ti_2O_3 are also known. *Titanium dioxide* dissolves only slightly in hot concentrated H_2SO_4, but when the solid residue from that treatment is mixed with water, solution takes place. The solid is a *titanic oxysulfate*. This and all other titanic salts hydrolyze readily so that no simple Ti^{IV} compound like $Ti(SO_4)_2$ is ever found in aqueous solution. Due to its very weak basicity, titanium forms few normal salts of oxygen-containing acids. $TiCl_4$ can be stabilized only in the anhydrous condition or in strong HCl; in the latter the substance present is $H_2[TiCl_6]$.

The oxidation states of Ti are (II), (III), and (IV). Little is known about Ti^{II} except that it is not formed on reduction of Ti^{IV} as is Ti^{III}, but must be prepared by heating a Ti^{III} compound to effect a disproportionation to Ti^{II} and Ti^{IV}. Ti^{IV} is reducible by reductants like zinc in acid solution, giving Ti^{III}, itself a good reducing agent as shown, for example, by its reaction with sulfite to produce sulfur. Ti^{III} resembles Cr^{III} to some extent; all compounds are colored, usually green or violet.

In acid solution, Ti^{IV} gives *peroxy compounds* like H_4TiO_5(?) with hydrogen peroxide. Their yellow to brown color is a good qualitative test and adaptable to colorimetry. This behavior resembles that of Zr^{IV} and Cr^{VI} with H_2O_2. Thiocyanate, acid and Ti^{IV} yields yellow *titanyl thiocyanates* nominally, (TiO)SCN(?). Both color tests are low in sensitivity if fluoride is present since stable, colorless TiF_6^{-2} forms preferentially. Fluoride added to either of the color tests bleaches the color in proportion to $[F^-]$. There are several organic reagents recommended for Ti^{IV} analysis. Titanium is analyzed in cation group 3; its *hydrated oxide* $Ti(OH)_4 \cdot xH_2O$ is not appreciably amphoteric (*meta titanates* like $K_2TiO_3 \cdot 4H_2O$ hydrolyze readily) so it separates with $Fe(OH)_3 \cdot xH_2O$.

The Fe^{III}-Ti^{IV} mixture is dissolved in H_2SO_4, diluted, and H_2O_2 added. The characteristic peroxy titanium color is observed even in the presence of ferric ion.

Quantitatively, Ti is determined after removal of interfering elements like Fe, by colorimetric analysis of the peroxy color, or by titration of Ti^{III} with standard MnO_4^-.

Zirconium

Zirconium is a silvery metal that is malleable and ductile at room temperature when pure and fully annealed. It has an allotropic transformation at 865 C, at which temperature hexagonal α-Zr changes to body-centered cubic β-Zr. Zr reacts with air at elevated temperatures and burns brightly to the dioxide. There are two important minerals, baddeleyite, ZrO_2, and zircon, $ZrSiO_4$. Both contain hafnium as an impurity and since this metal is very like Zr (the most similar pair of elements in the periodic table), it is carried through metallurgical processes and found in all commercial Zr. Zirconium is the eleventh most abundant element in the earth's crust, its quantity estimated to be more than the combined amounts of Cu, Ni, Pb, Hg, and Zn.

Two methods are used to obtain Zr metal. The older de Boer–Van Arkel process (1924) produces a high-grade product by the thermal decomposition of ZrI_4 in which the metal collects on electrically heated wires of pure Zr. The newer Kroll process (1947) yields slightly less pure metal but is cheaper to operate and capable of larger production. This process utilizes a Mg reduction of fused $ZrCl_4$ at high temperature, giving a sponge of Zr from which the salt residue is melted away in a vacuum furnace. The sponge is compacted and melted by resistance at about 1875 C in an inert atmosphere.

Getting rid of hafnium, found in all zirconium ores, is the main beneficiation problem. The most recently announced process utilizes a separation based upon solubility differences of some Werner complexes. The mixed Zr and Hf tetrachlorides are dissolved in water giving $ZrOCl_2$, $HfOCl_2$, and HCl. To this is added NH_4SCN and NH_4OH, yielding thiocyanato complexes of ZrO^{+2} and HfO^{+2}. The hafnium compound is soluble in an extracting solvent, methyl isobutyl ketone. The Zr complex remaining behind is decomposed with H_2SO_4 and zirconium hydroxide is precipitated using NH_4OH, and separated by filtration. It is fired at 800 C, giving ZrO_2 which is chlorinated to $ZrCl_4$, ready for Mg or Na reduction. Sodium is replacing magnesium as a reductant today. Zr sells now for about $4.50/lb.

Zirconium is used in a few alloys that are interesting because of the moderate density of Zr, the ease with which it alloys, and the high hardness, corrosion resistance, and melting point of the product. Some relatively high-temperature (200–400 C) Mg and Zn alloys contain zirconium. The metal, as such, is used extensively in atomic installations. In addition to possessing good structural features, Zr is transparent to thermal neutrons and neutron economy is important in nuclear reactors. Zr dissolves gases in large volume and is employed for this purpose in vacuum tubes. *Zirconium boride* is a refractory used at temperatures above 3000 C, the nitride with a melting point of 3200 C is stable and electrically conducting. Zirconia, ZrO_2, is made by heating dolomite and zircon sand. It is used as a furnace lining material.

The metal is not attacked by dilute acids, concentrated HCl, or any bases, but will dissolve slowly in hot concentrated HF, H_2SO_4, or H_3PO_4. The metal forms nonadherent ZrO_2 in moist air at elevated temperatures, but, at moderate temperatures and below, its resistance to attack is comparable to 18-8 stainless steel.

Zirconium has oxidation states of (II), (III), and (IV), but only the last is stable in aqueous solution; $ZrCl_3$ put in water, for example, liberates H_2 and forms a hydrolyzed Zr^{IV} mixture. The *halides* (except F) *of* Zr^{II} are known and are all very dark colored compounds. When heated they disproportionate into $Zr + Zr^{IV}$. Zr^{III} forms *halides* also of Cl, Br, and I, and these are the only well-defined zirconous compounds prepared. Zr^{IV} salts like those of Ti^{IV} are strongly hydrolyzed, and it is not possible to crystallize simple salts like $Zr(SO_4)_2$ from water. Hydrolysis gives basic salts but as in titanium chemistry, no single ions like ZrO^+ or ZrO^{+2} are observed and definite formulas are not given. For the sake of simplicity, however, one may say the ZrO^{+2}, *zirconyl ion*, will serve to describe the behavior of Zr^{IV} in water solutions.

Zirconates, ZrO_3^{-2}, are formed when the oxide ZrO_2 is fused with alkalis, much as titanates and silicates are made from TiO_2 and SiO_2. Zirconate salts have low solubility, as contrasted to zirconyl compounds. With oxalate, ZrO^{+2} gives white $ZrO(C_2O_4)$ which dissolves in excess reagent to form $ZrO(C_2O_4)_2^{-2}$. From hot solutions strongly acidified with HNO_3, any phosphate, including H_3PO_4, will precipitate zirconium as $ZrO(H_2PO_4)_2 \cdot H_2O$. This precipitation is almost specific for Zr in a general ion mixture. In cation group 3 where Zr is normally analyzed, its *hydroxide* is not particularly amphoteric and is insoluble in dilute NaOH, classing it with Fe^{III} and Ti^{IV}. It may be separated from these by adding HNO_3 and H_3PO_4. In this procedure $Fe(OH)_3$ and $Ti(OH)_4$ dissolve while Zr^{IV} forms the insoluble, gelatinous *phosphate*. Alternately Zr^{IV} may be separated from other group 3 cations by means of $(NH_4)_2S + (NH_4)_2C_4H_4O_6$, with which combination Zr^{IV} forms a soluble *tartrate complex*, whereas the other metals form insoluble sulfides and hydroxides. From the centrate, Zr^{IV} can be precipitated as the *zirconyl dihydrogenphosphate hydrate* which in *quantitative work* is filtered off and ignited to ZrP_2O_7.

The fluoride test with alizarin, as described under fluoride among the anion analyses, may be reversed to test for Zr; a solution of ZrO^{+2} and alizarin red-S in acid solution give a red color which is bleached yellow if F^- is added. The fluoride is capable of decomposing the Zr-dye lake by forming the more stable ZrF_6^{-2}. Zr compounds do not give colored bead tests, but when subjected to the blow pipe–dilute Co^{+2}–charcoal block technique explained previously under Al and Zn, a faint yellowish green, reminiscent of Rinmann's green, appears.

Vanadium

Vanadium is a steel grey, slightly magnetic, brittle metal having the highest hardness of any element except the diamond allotrope of carbon. The principal ore is patronite, the empirical formula for which is approximately VS_4. Vanadium is common in small amounts in many rocks and uranium minerals and is recoverable also from concentrates like slags and ash heaps. Minor ores include vanadinite, $Pb_4(PbCl)(VO_4)_3$, and roscoelite, $H_8K_2(Mg, Fe)(Al, V)_4(SiO_3)_2$. Vanadium is obtainable by the Goldschmidt process, but since no use is made of the pure metal, its ores are frequently mixed with those of iron, reduction of the mass made, and the mixture of Fe and V used as an additive in steel manufacture, which is its main use. The finished steel may contain up to 4.8% V and finds wide acceptance for cutting tools in alloys like vanite high speed, supervan dreadnought, etc. Vanadium has good solubility in many metals and is successfully alloyed with Al, Be, B, Nb, Cr, Co, Cu, Fe, Mo, Ni, Sn, Ti, W, and Zr.

The main *oxide* is V_2O_5, which is a contact catalyst in the high temperature oxidations of SO_2 to SO_3 and naphthalene to phthalic anhydride. V_2O_5 is a brown to black material while the next lower oxide, V_2O_4, is blue. The oxide VO_2 is also known, but VO is not.

The chemistry of vanadium resembles that of phosphorous and it is complicated.

The *oxidation states* of vanadium are (V), (IV), (III), and (II) in that order of importance, although numbers of compounds of each are known.

V_2O_5 can be made by heating *ammonium metavanadate*, NH_4VO_3. It is slightly soluble in H_2O, giving an acidic solution and hydrolyzes to produce *complex vanadates* bearing some resemblances to phosphates and some to chromates. The formula $(V_2O_5)_n \cdot xH_2O$ is used to describe the condensation products. With H_2O_2 and acid, *peroxyvanadates* like VO_4^- form; these solutions are yellow to red in color and are a color test for

V^V. Bases and vanadates yield condensation products as $V_2O_7^{-4}$, $V_4O_{13}^{-6}$, $V_5O_{16}^{-7}$, etc.

V^V is easily reduced to V^{IV}, an oxidation state which occurs in three common ways: *vanadium(IV) halides* as VCl_4, *vanadyl salts* as $VOSO_4$, and *vanadites* as $K_2V_4O_9$.

V^{III} is obtained on reduction of either V^V or V^{IV}. It resembles Fe^{+3}. It forms salts and can be present in solution as hydrated, green V^{+3} which then hydrolyzes to give oxygenated products, the ion VO^+ presumably being present in them.

V^{II} is not produced in the presence of air or water because of its reducing ability and not many compounds are known. A typical preparation is the heating of VI_3 to cause disproportionation to I_2 and VI_2 with reaction carried out in an evacuated tube. The peroxy vanadate color already described does not fade in the presence of H_3PO_4 or F^- as do colors of Ti and Fe compounds with the same reagents, and hence serves as a qualitative test for V as it appears in cation group 3. In basic solution, H_2S converts VO_4^{-3} to VS_4^{-3}, having a characteristic purple color from which some brown to black *oxy sulfides* of vanadium like $Na_4V_2O_2S_5$ precipitate upon acidification. Apparently the simple V_2S_5 has not been observed. The supernatent liquid from that treatment will appear blue due to VO^{+2} formed under the reducing action of H_2S in acid. These color changes qualitatively identify V in group 3.

It is *quantitatively* run by reduction in H_2SO_4 solution to V^{IV}, using SO_2, followed by expulsion of the gas by CO_2 and titration at 70 C to V^V with standard permanganate.

Beryllium

A silvery, brittle metal, Be is obtained from its only important mineral, beryl, $Be_3Al_2(SiO_3)_6$. Because beryl has about the same density as the gangue, no simple beneficiation methods are known, and the supply of beryllium ore for processing is dependent upon hand selection of pieces of worth-while size. Beryllium melts at 1350 C and its metallurgy is beset with difficulties. One method of obtaining the metal is via conversion of beryl to $BeCl_2$ or BeF_2, fusion with NaF, and electrolysis of the melt. These halides of Be, however, are very hygroscopic and the hydrolysis products like $Be(OH)Cl \cdot xH_2O$ do not give the original materials again upon heating. Beryllium metal has a sp. gr. of 1.86 and tends to form droplets which resist coalescence and float on the top of the bath where they oxidize and occlude impurities. Another method of obtaining the metal is the thermal reduction of BeF_2 with Mg, giving a large aggregate of Be together with a fusible slag that is melted away under vacuum. This is essentially the Kroll method again. The crude lump is vacuum melted and purified to metal selling now for about $55 per lb. Molten Be is very reactive and fusions are conducted under special atmospheres in BeO crucibles, which themselves are a major production problem. *Beryllium oxide* is a refractory material that is formable by pressure only in graphite molds at high temperatures. At present, ingots of Be are produced mostly by powder metallurgy and are not easy to work due to the brittle character of the metal.

A more recently reported extractive method is the Sheer–Korman process. Raw ore is mixed with one-third its weight of soft coal and shaped and baked into electrically conducting rods. An arc is struck between them, giving temperatures reported in excess of 8200 C. Elements from the ore issue from the arc as a high-speed flame and contact Cl_2 in the main part of the furnace, producing chlorides. These are fractionally condensed in cool zones to effect separations of various constituents. $BeCl_2$ is then electrolyzed in a molten bath to produce a nearly pure, nonbrittle metal which is machinable and estimated to cost about half that of metal produced by older processes.

Beryllium has two important uses, one in copper, nickel, and aluminum alloys and one in the atomic energy program. In the alloys, Be imparts considerable strength. A 3%, Be-copper alloy is age hardenable, six times stronger than pure copper, nonmagnetic and nonsparking, and used widely in the electrical and machine industries for tools, springs, diaphrams, heater controls, connectors, cams, gears, oil seals, gauge elements, etc. Beryllium is a better electric conductor than copper In the atomic program, Be and BeO are used as neutron reflectors, thus enabling a neutron-producing mass smaller than normal to be critical, because neutrons escaping the mass are reflected into it. This may be the principle by which relatively small atomic artillery shells function. Be metal, BeO, and the soluble compounds are very toxic.

The oxidation state of the element is (II), and it acts in solution as an intermediate between aluminum and magnesium. Both the metal and oxide are slowly soluble in acids.

Beryllium has a marked tendency to form four covalent bonds, and it has a stronger ability to hydrate than any other dipositive ion due to its small size. Covalency explains the phenomena of BeO being insoluble in water but soluble in Be^{II} salt solutions—the oxide coordinating with the ion giving groups like $(\mathrm{Be}\ \ \mathrm{O}\rightarrow\mathrm{Be})^{+2}$ to build up polymeric ions. Evaporation of these gives gels of no special stoichiometry. The hydrolysis of Be^{+2} in water is virtually complete; therefore, one cannot obtain beryllium salts of weak acids from solution.

BeS is not hydrolyzed in H_2O as is Al_2S_3, but, like $Al(OH)_3$, $Be(OH)_2$ is amphoteric and dissolves in bases to furnish oxygenated ions such as

$BeO(OH)^-$, and is formed in preference to the sulfide in alkaline sulfide solution.

$Be(OH)_2$ normally appears in cation group 3 and is separated from $Al(OH)_3$, utilizing the fact that $Be(OH)_2$ is soluble in hot 1.5 *M* $NaHCO_3$ whereas $Al(OH)_3$ is not. Another method is to precipitate Fe^{+3} and Al^{+3} from an acetate buffer at *p*H 5.5 with 8-hydroxyquinoline, then to precipitate Be^{II} in the centrate as $Be(OH)_2$ with NH_4OH. For *quantitative* determinations, the hydroxide is ignited to BeO, which is weighed.

Lithium

Lithium is the lightest metal. Its sp. gr. is 0.53, its m.p. is 186 C, and b.p. is 1336 C. It is harder than sodium or potassium but softer at room temperature than lead. The crystal structure, like that of other alkali metals, is body-centered cubic at room temperature, but, aided by pressure, at −196 C it undergoes an audible lattice change to a face-centered structure. Two mixed silicates are mineralogically important, lithium mica, $K_2Li_2Al_2Si_3O_9(F, OH)_2$, and spodumene, $LiAl(SiO_3)_2$. In addition, mixtures of salts containing some $Li_3(PO_4)$ are found in saline deposits. The free metal is obtained by electrolysis of its fused chloride.

Per se, lithium is used in a few light alloys as a hardening agent and with iron as a mixed catalyst for the ammonia synthesis, but beyond that the metal has little application. Lithium compounds on the other hand are finding wide use and frequently the demand runs ahead of supply. *Lithium deuteride*, LiD, is probably used in the hydrogen bomb, this crystalline solid allowing a relatively large mass of those light elements to be packed close to the reaction center to insure fusion. Temperatures then reached are guessed as high as 10^8 C. Whereas the critical mass of a fissionable element may be small, LiD is handled in inert atmospheres in any mass, leading to awesome speculation concerning the power of thermonuclear devices. *Lithium aluminum hydride*, $LiAlH_4$, is a powerful reducing agent, having a specificity of reaction toward certain reducible groups. Lithium greases are used in military vehicles because of their good performance under drastic conditions; Li_2CO_3 is used in glass and porcelain manufacture to produce a high index of refraction; LiCl is used in drying systems; LiF is used as a welding flux; *lithium stearate* is used in cosmetics and waxes; Li_2CrO_4 is alcohol-soluble and used as a rust inhibitor in radiators, *lithium aluminum silicate* is a filler in rubber, *lithium hydroxide monohydrate* is the electrolyte in one Edison type battery, *lithium chlorate* is used to impart a red color in pyrotechnics, *lithium cynide* is used in plating, *lithium perchlorate* is an oxidant in solid rocket propellants, etc.

The chemistry of lithium is something like that of Na^+ and K^+ but also bears resemblance to that of Mg^{+2} and Ca^{+2}. Its only valence state is (**I**). Lithium may be melted and poured in air without tarnishing whereas the other alkali metals cannot. Molten, however, it shows an

TABLE 20–1. SOME MOLAL OXIDATION POTENTIALS* FOR THE LESS FAMILIAR ELEMENTS

Half-Cell Reaction	$E°$
$W + 2H_2O = WO_2 + 4H^+ + 4e^-$	0.12
$W + 8OH^- = WO_4^{-2} + 4H_2O + 6e^-$	1.05 (E_B°)
$Mo + 8OH^- = MoO_4^{-2} + 4H_2O + 6e^-$	1.05 (E_B°)
$Mo + 4H_2O = H_2MoO_{4(aq)} + 6H^+ + 6e^-$	0.0
$(MoO_2)_2MoO_4 + 4H_2O = 3H_2MoO_4 + 2H^+ + 2e^-$	$\simeq -0.6$
$U = U^{+3} + 3e^-$	1.80
$U^{+4} + 2H_2O = UO_2^{+2} + 4H^+ + 2e^-$	-0.33
$Ti + 2H_2O = TiO_2$ (hydrated) $+ 4H^+ + 4e^-$	0.86
$Ti^{+3} + H_2O = TiO^{+2} + 2H^+ + e^-$	$\simeq -0.1$
$Zr + 2H_2O = ZrO_2 + 4H^+ + 4e^-$	1.43
$Zr = Zr^{+4} + 4e^-$	1.53
$VO^{+2} + 3H_2O = V(OH)_4^+ + 2H^+ + e^-$	-1.00
$V^{+3} + H_2O = VO^{+2} + 2H^+ + e^-$	-0.36
$V^{+2} = V^{+3} + e^-$	0.26
$V = V^{+2} + 2e^-$	$\simeq 1.18$
$Be = Be^{+2} + 2e^-$	1.85
$2Be + 6OH^- = Be_2O_3^{-2} + 3H_2O + 4e^-$	2.62 (E_B°)
$Li = Li^+ + e^-$	3.05

* Reprinted by permission from W. M. Latimer, *Oxidation Potentials*, 2nd ed., Prentice-Hall, New York (1952).

TABLE 20–2. SOME IONS AND RADICALS OF THE LESS FAMILIAR ELEMENTS

Name	Formula	Valence	Name	Formula	Valence
Orthotungstate	WO_4	−2	Titanous	Ti	3
Polytungstate*	W_7O_{24}	−6	Titanic	Ti	4
Metatungstate*	W_4O_{13}	−2	Titanyl	TiO	2
Tungstanyl(V)	WO_2	1	Titanate	TiO_3	−2
Per (oxy) tungstate	WO_8	−2			
Paratungstate	$W_{12}O_{41}$	−10	Beryllium(II)	Be	2
			Beryllate	$Be(OH)_4$	−2
Orthomolybdate	MoO_4	−2			
Polymolybdate*	Mo_3O_{11}	−4	Zirconium(II)	Zr	2
Paramolybdate	Mo_7O_{24}	−6	Zirconium(III)	Zr	3
Molybdophosphate	$P(Mo_3O_{10})_4$	−3	Zirconium(IV)	Zr	4
Molybenyl(VI)	MoO_2	2	Zirconyl	ZrO	2
			Zirconate	ZrO_3	−2
Orthovanadate	VO_4	−3			
Vanadyl	VO	2	Uranium(III)	U	3
Pervanadyl	VO	3	Uranium(IV)	U	4
Vanadol	VO_2	1	Uranium(V)	U	5
Polyvanadate*	V_2O_7	−4	Uranium(VI)	U	6
Pentavanadate	V_5O_{16}	−7	Uranyl	UO_2	2
Peroxyvanadate*	VO_4	−1	Diuranate	U_2O_7	−2
Vanadous	V	2	Uranate	UO_4	−2
Vanadic	V	3			
Metavanadate	VO_3	−1	Lithium	Li	1
Pyrovanadate	V_2O_7	−4			

* One of several known variations

avidity for nitrogen and forms a *nitride*, Li_3N, reminiscent of magnesium action. Li metal reacts only slowly (like Mg, unlike Na) with water, and gives only Li_2O (no Li_2O_2, lithium peroxide) with hot oxygen. By way of further contrast, Li^+ complexes more readily due to its small size and forms some *hydrates*, *alcoholates*, *ammoniates*, and neutral complexes with organic reagents; its *halide salts*, except fluoride, are more soluble and its *carbonate*, *phosphate*, and *hydroxide* are less soluble than those of other metals in group IA of the periodic table.

Lithium is analyzed in cation group 5 usually by two methods. The first is to boil the sample just to dryness with HCl, then extract LiCl with acetone, or alcohol, leaving the other chlorides behind. A flame test on the extract will be a brilliant red if lithium is present. The second method hinges on precipitation of Li^+ as Li_3PO_4 from an alcohol-water mixture followed by a flame test on the washed residue. The precipitating agent is $NH_4(H_2PO_4) + NH_4OH$. and while Mg may also precipitate as $Mg(NH_4)(PO_4)$ if not removed in group 4, its presence will not alter the conclusive Li flame test. In *quantitative analysis*, LiCl is separated by organic solvent extraction as above after removal of interferences, then heated to dryness with H_2SO_4 to produce Li_2SO_4 which is weighed. See also test 20–23 for a colorimetric method.

LABORATORY TESTS WITH THE LESS FAMILIAR ELEMENTS

If samples of the eight metals as well as specimens of other rarer metals like tantalum, hafnium, niobium (columbium), etc., are available, examine and characterize them briefly in the notebook. Examine a few of their salts also, noting color, formula, and other features of each.

Most of the following laboratory experiments use a few milligrams of dry salt, metal, or mineral for each test. The student should attempt to write the equations for all reactions described and should make a note of the characteristics of each reaction, including speed, colors, types of precipitates, etc.

Test 20–1. Tungsten Blue. Dissolve a crystal of H_2WO_4 H_2O in a few drops of dil. NH_4OH, then add 10 drops of concd. HCl and a few granules of Zn or a few drops of 25% $SnCl_2$ in concd. HCl, and stand the tube in a warm water bath. Note the development of color over the next 5–15 min. (The blue color does not disappear with excess $SnCl_4^{-2}$, whereas the analogous molybdenum blue does fade.) The concn. limit is about 50 ppm W.

Test 20–2. W in Steel. (*a*) Dissolve at least 10 mg of sample in aqua regia. Any residue is probably C, SiO_2 and/or WO_3. Remove the soln., treat the residue with a few drops of concd. NH_4OH, stir, add a ml of H_2O, and centrifuge. Remove the soln. (which contains tungstate), acidify with HCl, and run test 20–1, or acidify with concd. H_2SO_4 and run test 20–3 on the precipitate.

(*b*) Try this as a *metal surface spot test* if a larger steel sample contg. at least 1% W is available: file a spot clean, then etch it with a drop or two of aqua regia made from 6 *M* acids. After a few min., carefully remove the drop with a dropper and blot with a piece of filter paper. Add a drop of 6 *M* HCl to the spot and remove it after several min, as before. Put a piece of filter paper over the spot, add a drop of H_2O and a drop of 25% $SnCl_4^{-2}$ reagent. The color intensity is an approx. measure of W content.

Test 20–3. The Defacqz Method for W. Mix a small amount of a W-contg. solid, such as a mineral or a salt, with 5 times its wt of $KHSO_4$, and heat gradually to melt and fuse the mass. Keep it molten for 5–10 min. Cool. Add several drops of concd. H_2SO_4 and mix well. Add a crystal or two of hydroquinone $C_6H_4(OH)_2$. Tungstates give a violet color reaction but molybdates do not. The concn. limit is 20 ppm W.

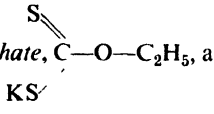
Test 20–4. Tungstic Acid from Wolframite Ore. Fuse 5 parts of powd. wolframite with 8.5 parts of anhyd. Na_2CO_3 and 1.5 parts of $NaNO_3$ in a suitable container like a Pt crucible. After the mass has cooled, extract it with hot water and filter. To the filtrate, add excess HCl to ppt. $H_2WO_4 \cdot H_2O$.

Try the bead test in special experiment 4 for W minerals, using microcosmic salt.

Test 20–5. Mo in Minerals Using SCN^-. Make a test tube from a 3-in. piece of 8-mm soft glass tubing by melting one end shut and turning a lip on the other end with the aid of a file. Make an intimate mixt. of 250 mg of Na_2CO_3, 250 mg of KNO_3, and 100 mg of powdered mineral. Pour into the tube and heat gradually, finally fusing at a red heat for about 5 min. While the tube is still hot, touch the bottom in 8 ml of H_2O contained in a 50 ml beaker to break the tube. Pick out the pieces of glass and discard them in the waste jar. Heat the rest of the mixt. and boil gently to evaporate 2–3 ml of soln. during the next 5 min, then pour it into two test tubes and cent. Combine the centrates in a small beaker, add a drop of phenolpthalein, then add 1 *M* HCl dropwise until the red color fades. Add 200 mg of $Na_2(C_4H_4O_6) \cdot 2H_2O$, which will form a tartrate complex with any tungsten present. Add 12 drops of concd. HCl and shake. Add 6 drops of KSCN and 10 drops of $SnCl_4^{-2}$ solution (made by dissolving 10 g of $SnCl_2 \cdot 2H_2O$ in 100 ml of 2 *M* HCl). After 1 min, add 6 drops of diisopropyl ether and shake. A blue organic layer indicates molybdenum. This method is adaptable to quant. colorimetry in field testing, in the range 0–32 ppm molybdenum. See reference 6, p. 356.

Test 20–6. Molybdenum Blue. Dissolve a few mg of ammonium molybdate in a few drops of concd. HCl and dil. to 2 ml with H_2O. Put 1 drop of this soln. in one test tube, 2 drops in a second, 5 drops in a third, and 10 drops in a fourth. To each of these add enough H_2O to give a total vol. of 2 ml, then to each add 3 drops of 0.2 *M* $(NH_4)_2HPO_4$. To each tube add 2 drops of 0.25 *M* $SnCl_4^{-2}$. The blue colloidal suspension has the approx. formula $Mo_8O_{23} \cdot xH_2O$ and is analogous to tungsten blue.

Test 20–7. Mo in Steel. Dissolve a small steel shaving in aqua regia, dil. to about 2 ml, and centrifuge; the residue is probably C, SiO_2, and/or WO_3. Discard the residue. Add excess 6 *M* NaOH to the soln. and centrifuge; the residue is primarily $Fe(OH)_3$ with molybdates retained in soln. Reacidify the soln. with 6 *M* HCl. Use portions of the soln, for the test below and also for previously described Mo tests.

Put a few drops of soln. on a spot plate, add a drop of 6 *M* H_3PO_4, a crystal of *potassium xanthate*,  $\overset{S\diagdown}{\underset{KS\diagup}{C}}{-}O{-}C_2H_5$, and a drop of 3 *M* HCl. A violet color, due probably to $MoO_2[SC(SH)OC_2H_5]_2$, indicates Mo. The concn. limit is 3 ppm.

Test 20–8. V in Steel. Dissolve a small shaving in a mixt. of 6 *M* H_2SO_4 and HNO_3, dil., and decolorize the Fe^{+3} with a few drops of concd. H_3PO_4. Add several drops of 5 or 10% H_2O_2. A yellow to brown color indicates Ti^{IV} or V^{V}. Add a few mg of solid NaF to decolorize the titanium peroxide. The residual color is due to vanadium. The test will detect 500 ppm V.

Test 20–9. Heteropoly Acid Color Test for VO_3^-. Put a speck of NH_4VO_3 on a spot plate, add 2 drops of H_2O, 1 drop of 6 *M* H_3PO_4, and 1 drop of 10% Na_2WO_4 soln. The formation of a yellow-orange color constitutes a test for V and is probably due to a series of vanadotungstic and vanadophosphoric heteropoly acids such as $H_2WO_3(VO_3)$, $HPO_2(VO_3)_2$, etc. Alternately this test may be used to detect WO_4^{-2} or PO_4^{-3}.

Test 20–10. Vanadium and Its Minerals. Fuse one part of powd. mineral with three parts of KNO_3 for 5 min., then extract the potassium vanadate with hot H_2O. Add $BaCl_2$ soln. to the clear extract as long as pptn. occurs. Collect the barium vanadate and decompose it with H_2SO_4. Centrifuge. Discard the residue of $BaSO_4$ and saturate the centrate with NH_4Cl. A ppt. of $(NH_4)_3VO_4$ slowly forms. Dissolve a little in H_2O, and try tests 20–8 and 20–11. (See reference 8, p. 356.)

Test 20–11. Strychnine Test for VO_3^-. A test which uses strychnine as a reagent for vanadate (or vice versa) is as follows: put a drop of ammonium vanadate on a spot plate and add a drop of concd. H_2SO_4 and a crystal of a strychnine salt. A violet to rose color is a positive test. The cause of the color is not definitely known. Determine, roughly, the concn. limit.

Caution! Strychnine is poisonous.

Test 20–12. Precipitation of $Be(OH)_2$. Caution! *Beryllium metal, particularly in the finely divided state, and beryllium salts are poisonous.* Dissolve a few mg of a beryllium salt, such as $BeSO_4 \cdot 4H_2O$, in a ml of H_2O and add a drop of 6 *M* NaOH. The white gelatinous ppt. is beryllium hydroxide. Add, with shaking, additional drops of NaOH to *just* dissolve the ppt., giving the beryllate ion, $Be(OH)_4^{-2}$, in soln. Save this soln. for test 20–13. (Alternately one could have shown that $Be(OH)_2$ is not sol. in excess NH_4OH since no ammonia complex forms, but that in boiling 5% $NaHCO_3$ soln., $Be(OH)_2$ is sol., in contrast to $Al(OH)_3$. This test effects a separation of the two metals in group 3 if Be^{II} is part of a general unknown.)

Test 20–13. Reprecipitation from $Be(OH)_4^{-2}$. Place the tube contg. the soln. from test 20–12 in a boiling water bath for 8–10 min. and note the gradual pptn. of β-$Be(OH)_2$. This is only about 1/25 as soluble as $Be(OH)_2$ originally prepd. The test also distinguishes Be^{II} from Al^{+3}, since the latter's hydroxide does not ppt. from $Al(OH)_4^-$ in the same test.

Test 20–14. Quinalizarin Method for Be in Minerals. If a beryllium mineral is available, powder a little and fuse it (hood) with about four times its weight of potassium bifluoride, KHF_2, using the technique described in test 20–5. Put 1 drop of clear aq extract on a spot plate, a drop of a known Be salt soln. in another depression on the plate, and a drop of water in a third depression. To each add a drop of quinalizarin (50 mg in 100 ml of 10% NH_4OH) and note the color changes which indicate a positive reaction. To each add a drop of bromine water. Only the blank will be bleached. The concn. limit is 3 ppm. See reference 5, p. 356.

Test 20-15. Identification of Ti Metal. (*a*) Examine a piece of Ti sheet. Note that its sharp edge can be used to mark glassware, since it is just hard enough to scratch and leave a metallic coating in the scratch.

(*b*) Dissolve a tiny piece of Ti in a ml of dil. H_2SO_4 kept hot in a bath for 15–30 min. Note the violet color of Ti^{III}. Put a few drops in another tube, add a drop of concd. H_3PO_4 and a drop or two of 3% H_2O_2. Ti^{IV} is the oxidation product and it forms the yellow to red pertitanic acid, H_2TiO_4 (?). Add a few mg of NaF and note the effect as the stable complex TiF_6^{-2} forms. Cr, Mo, and V interfere by giving peroxide colors but do not give the fluoride reaction. The concn. limit is 30 ppm.

(*c*) To another portion of soln. from (*b*), add a few drops HNO_3 and heat to oxidize Ti^{III}. Now make the soln. basic with 6 *M* NaOH and see if the hydroxide ppt. is amphoteric.

Test 20-16. Uranyl Ferrocyanide. In the range 8–40 ppm. of U, ferrocyanide will give a red color with uranyl ion in mildly acidic soln., and the color is suitable to colorimetry. (In higher concns., a reddish ppt. of uranyl ferrocyanide forms.)

Dissolve a few mg of a uranyl salt such as $UO_2Ac_2 \cdot 2H_2O$ in 1 ml of H_2O and divide the soln. between two tubes. To one add a few drops of $K_3[Fe(CN)_6]$ and to the other a few drops of $K_4[Fe(CN)_6]$. The color in the latter reagent is due to $(UO_2)_2[Fe(CN)_6]$, or if excess reagent is present, the precipitate formed is $(UO_2)K_2[Fe(CN)_6]$. (This reaction is sometimes used to indicate the end point in titrations with ferrocyanide.) Many metallic ions, particularily Fe^{+3} and Cu^{+2} interfere by giving dark colored ferrocyanides.

Test 20-17. Peroxide Precipitation of U^{VI}. To 10 drops of UO_2^{+2} soln. add 6 drops of 10% H_2O_2. A yellow ppt. of peruranic acid appears. The reaction probably is

$$UO_2^{+2} + H_2O_2 + 2H_2O = 2H^+ + UO_2(OOH)(OH) \cdot H_2O$$

Uranium may be quant. separated using this method, followed by freezing the mixture, then thawing and filtering off the peroxy acid hydrate at ice temp. The acid is sol. in alkalis from which one obtains sol., orange colored peroxide uranates, as $Na_2O_2 \cdot UO_4$.

For *uranium in minerals*, see special experiment 4, part 3(*b*).

Test 20-18. Formation of $ZrO(H_2PO_4)_2$. Dissolve a few mg of $ZrOCl_2 \cdot 8H_2O$ in 15 drops of H_2O. Add 5 drops of dil. HNO_3, heat to boiling, add 2 drops of concd. H_3PO_4, and observe the gelatinous ppt. of zirconyl dihydrogenphosphate. This material is only slightly sol. in dil. nitric acid and the method is capable of detecting small amounts of Zr in complex mixtures. Apparently there are no common interferences to this test except Ti^{IV}, which can be kept in soln. with 10% H_2O_2.

Test 20-19. Colorimetric Test for Zirconium. Dissolve a few mg of α-nitroso-β-naphthol in 1 ml of ethyl alcohol and to this add several drops of ZrO^{+2} solution. A reddish color or ppt. similar to that obtained with Co^{+2} and the same reagent results. Alternately the org. soln. may be spotted on filter paper or a spot plate and drops of zirconium soln. added to that. The concn. limit is about 10 ppm zirconium.

Test 20-20. $K_2[ZrF_6]$ from Zircon. (*a*) Fuse one part of powd. zircon mineral with three parts of KHF_2 in a Pt or Ni dish. When cool, grind the mass and extract with hot H_2O, contg. a few drops of HF. Decant into an inert container like a rubber beaker, or filter into it via a rubber funnel. Upon standing, potassium hexafluorozirconate crystallizes.

Test 20-21. Precipitation of Lithium as the Phosphate. To 1 ml of Li^+ soln., add 6 drops of $(NH_4)_2HPO_4$ and heat the tube in a water bath. When hot, add 3 drops of dil. NH_4OH and note the gradual accumulation of white, crystalline Li_3PO_4. In one quant. method for Li, this residue is filtered, dried, and weighed. Would any cations from group 5 (where Li^+ is normally analyzed) interfere with the procedure? If so, how could interference be obviated?

Test 20-22. Solubility of LiCl. Put a few crystals of LiCl in each of several tubes and determine its solub. in several org. solvents. Using the best solvent, try it on KCl and NaCl, and suggest a means of separating LiCl from other chlorides in group 5.

Test 20-23. The Potassium Ferric Periodate Method for Li^+. To a half ml of LiCl soln., add 1 ml of 1 *M* KOH and place the tube in a hot-water bath. In another tube put 2 ml of potassium ferric periodate reagent (see appendix A13 for prepn.) and heat this also in the bath. When hot, pour the latter into the lithium soln. and allow the mixt. to remain hot for 5 min. The formation of light yellow lithium potassium ferric paraperiodate, $LiKFe(IO_6)$, is evidence that Li^+ was in the soln. (This method is adaptable to the quant. anal. of lithium in an indirect way. The ppt. is segregated, washed with 1 *M* KOH, dissolved in 1 *M* HCl, and to the acidic soln. is added an excess of 2 *M* KSCN. The concn. of red $Fe(SCN)^{+2}$ is determined colorimetrically and since lithium is stoichiometrically related to ferric iron in the periodate ppt., one is able to relate color density of $Fe(SCN)^{+2}$ to $[Li^+]$ in the orig. soln. See reference 6, Chapter 12.)

Test 20-24. Lithium by the Triple Acetate Method. Add a ml of zinc uranyl acetate (Na^+ reagent, test 19-6) to a crystal of a sol. Li^+ salt, shake the mixt., and note the pptn. of yellow $LiZn(UO_2)_3Ac_9 \cdot 6H_2O$. This method is used in quant. gravimetry for lithium.

Analysis of an Unknown

An instructive exercise at this point is to give the student a sample of salt, oxide, pure metal, alloy steel, or other mixture of the less familiar elements for analysis. There is enough experimental method given for simple samples. The student should first do problem 2 below.

PROBLEMS

1. The diagrams* p. 357 can be largely constructed from the discussion on molybdenum. Prepare similar diagrams for the other seven elements described in the chapter.

2. Consider having a solution containing equal quantities of WO_4^{-2}, MoO_4^{-2}, VO_3^-, TiO^{+2}, ZrO^{+2}, $BeOH^+$, UO_2^{+2}, and Li^+. Prepare a flow sheet from information in the chapter and supplementary reading, as necessary, for the partial separation and identification of the ions.

3. Consider having a solution containing the ions of problem 2, plus all the other cations described for analysis in this text. Prepare a flow sheet showing separation of every ion, and confirmatory tests where desirable.

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* Adapted by permission from data furnished by Climax Molybdenum Co., 500 Fifth Ave., New York 36, N.Y.

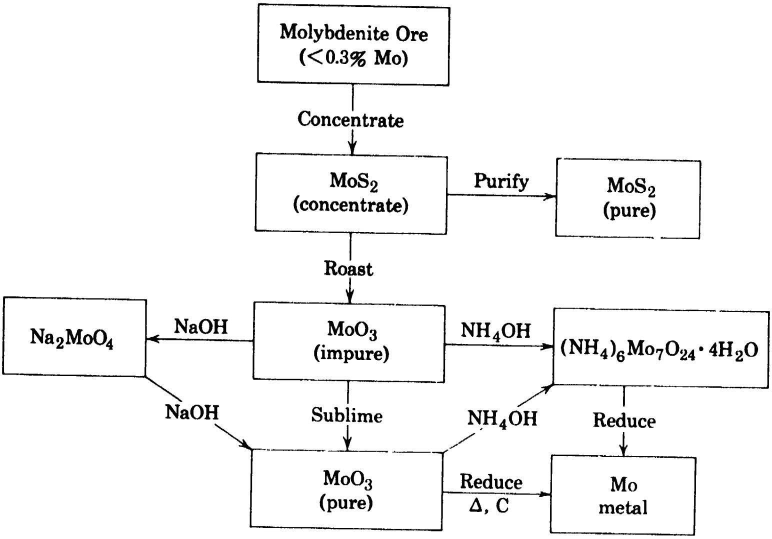

FIG. 20-2. Molybdenum process metallurgy.

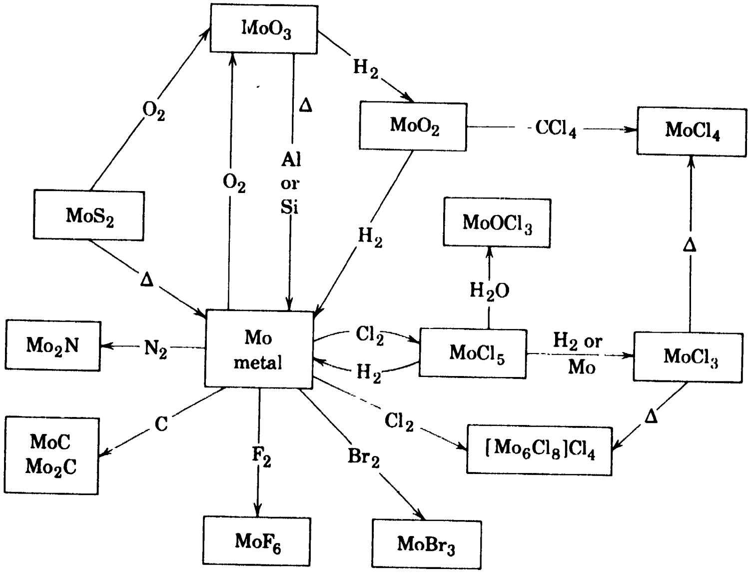

FIG. 20-3. Reactions of metallic molybdenum and some of its compounds.

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ANALYSIS OF A GENERAL CATION UNKNOWN

The student who has studied Chapters 14–20* should by this time have a good idea concerning the direction that analysis of a general cation unknown will take. *The flow sheet in Chapter* 14 *is a summary of this. Generally speaking, the sample is separated into groups in the order given and the individual groups analyzed according to their respective flow sheets.* Student samples are assumed to be free of serious interferences such as unknown complexing agents and/or elements not described for separation, though such complications are the rule in samples the industrial laboratory gets. *Three common interferences are organic materials, borates, and phosphates*, and the paragraphs following illustrate typical methods used in their presence.

The instructor will inform the class if the following precautions need be taken.

If the sample is already in solution, start with 1–3 ml, as directed by the instructor, and begin analysis with group 1, p. 243.

If the sample contains some solid material, the solid is probably a combination of group 1 chlorides and/or group 2 hydrolysis products of Bi, Sb, and Sn. The solid may be separated by centrifuging and treated as an individual sample. Directions for solid mixtures are given below.

Detection and Removal of Organic Compounds

Evaporate a small portion of unknown slowly in a crucible and bake

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* The "less familiar" elements of Chapter 20 will not be included in this discussion.

the residue. A *charring* may indicate the presence of *carbon-containing compounds*, though some *inorganic* compounds may become dark also, as for example cupric nitrate which is converted to black cupric oxide by heat. It is assumed that explosive mixtures, which might include chlorates and perchlorates, are *not* present.

Organic matter is removed from samples prior to inorganic analysis because it may color the solution, complex or precipitate ions, or use up carefully measured reagents that otherwise would be reacting with specific ions. Hot acid digestion is the usual method of decomposition. In the hood using a 20–30-ml crucible, heat a mixture of 2 ml of unknown with 5 drops of concentrated H_2SO_4 and 10 drops of concentrated HNO_3. Evaporate to a volume of about 5 drops, whereupon white fumes of SO_3 will be visible. Further HNO_3 addition and heating may be necessary if decomposition appears incomplete. This treatment not only rids the solution of organic compounds in general but specifically oxidizes and destroys the common tartrate and oxalate ions and the NH_4^+ ion, and will distill out all low-boiling acids such as HAc and HF which otherwise would form complexes with Fe^{+3}, etc.

Dilute the cooled mixture dropwise with 2 ml of H_2O, transfer it to a tube, and centrifuge. Any residue that was not present before will be the sulfates of Pb, Ba, and possibly Ca and Sr. After washing, this solid may be put into solution by boiling with 2 ml of 1.5 *M* Na_2CO_3; the carbonates are then solubilized in HAc and tested separately. The centrate from above is analyzed as a general unknown.

Detection and Removal of Borates

Borates precipitate certain group 3 and 4 ions and can confuse analysis because of that action. Borates are detected by tests 22–23, 22–25, and 22–26.

To the *centrate after group* 2 *removal*, add 10 drops of concentrated HCl and 10 drops of methyl alcohol. Boil the solution under the hood and resupply HCl and alcohol several times until the alcohol vapors burn light blue, as contrasted to the previous green due to methyl borate, $B(OCH_3)_3$. Let the excess alcohol burn off. The solution is then carried to the group 3 procedure, and since all the CH_3CSNH_2 has now hydrolyzed it will be necessary to add more $(NH_4)_2S$ than provided for in the group 3 description which assumes the solution for testing is directly from group 2 removal.

If borate is removed prior to group 2 analysis in the manner described above, Sb, As, and Sn are largely lost as their volatile chlorides, so the group 2 procedure is run first.

Detection and Removal of Phosphates

Orthophosphate precipitates tripositive ions in group 3 at high *p*H or complexes them as soluble, stable acid phosphates at low *p*H. The procedure is to test the group 3 solution for Fe, then to precipitate PO_4^{-3} as $FePO_4$ by adding Fe^{+3}. Other phosphates can also cause trouble* but are converted with hot HNO_3 to the orthophosphate. See test 22-16 for PO_4^{-3} detection.

Boil *the group* 2 *centrate* to drive out all the H_2S. Add 3 drops of concentrated HNO_3 and reboil. Test 1 drop of this solution for Fe^{+3} with SCN^-. Report Fe present in the unknown if the test is positive. To the main portion of solution add 6 drops of NH_4Ac, then 15 *M* NH_4OH until basic, 6 *M* HAc until just acidic, and then 2 drops more. If Cr^{+3}, Fe^{+3}, and/or Al^{+3} are present they will precipitate as phosphates; if not present no precipitate will form. Add 0.1 *M* Fe^{+3} dropwise until no further $FePO_4$ precipitates, centrifuge, and note that the supernatant liquid is the Fe^{+3} color, indicating iron in excess of that needed for complete PO_4^{-3} precipitation. Adjust the volume to about 4 ml and boil the solution. After several minutes centrifuge. The residue may contain hydroxides (due to hydrolysis) and phosphates of iron, chromium, and aluminum, while the centrate contains the other group 3 ions as well as those of groups 4 and 5.† $Fe(OH)_3$ is separated from the residue by solubilizing the latter with excess 6 *M* NaOH plus heating with a few drops of 3% H_2O_2 and centrifuging. The centrate from the $Fe(OH)_3$ removal may contain CrO_4^{-2} (yellow) and $Al(OH)_4^-$ (colorless). This mixture is readily handled by methods given in Chapter 17. The centrate from the original basic acetate separation is analyzed for other group 3 ions by starting at the beginning of the group 3 procedure.

Solid Samples

Several cases may arise if the sample "as received" is not already in solution.

*1. **The Solid is Water Soluble.*** If this is observed, no preparation for general cation analysis is necessary.

Dissolve about 75–100 mg of solid in 5 ml of water and using a 1–2 ml sample, go through the five cation group procedures. Other portions of solid and liquid sample are then used for special tests as seem advisable.

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* Metaphosphate, PO_3^-, precipitates Ba^{+2} and pyrophosphate, $P_2O_7^{-4}$, precipitates Mn^{+2}.

† This method is called the *basic acetate separation*. The residue may also contain V, W, Zr, and Ti as hydroxides, phosphates, or basic acetates, and will contain the rare earths as phosphates if those ions are present. If PO_4^{-3} is not present, the rare earths (including uranium) are retained in the centrate.

More concentrated sample solutions are not needed because the text directions and equipment provide for handling small amounts.

2. The Solid Appears Nonmetallic and is Not Water Soluble. Minerals, ores, and nonsoluble salts fall within this classification. A first observation to make is the sample's color for a hint to its identity. The accompanying table lists a few typical cases.

TABLE 21-1. COLORS* OF SOME COMMON TYPES OF LOW-SOLUBILITY COMPOUNDS

Color	Compound Type	Metals Possibly Present
White	Oxides	As, Sb, Sn, Al, Zn, Mg, Si, Ti, Zr, Be
White	Sulfides	Zn
White	Carbonates	Pb, Ba, Sr, Ca, Mg
White	Sulfates	Pb, Ba, Ca
White	Fluorides	Ca, Mg
Black	Oxides	Bi, Cu, Fe, Ni, Co, Mn, V, U
Black	Sulfides	Ag, Pb, Hg, Cu, Sb, Fe, Ni, Co, Mo, W, Pt
Brown	Oxides	Pb, Bi, Cd, Fe, Mn
Red	Oxides	Pb, Hg, Cu, Fe
Yellow	Sulfides	Cd, As, Sn
Blue-Green	Carbonates, hydroxides	Cu, Ni
Green	Oxides	Cr
Various	Other salts	Many insoluble salts. See solubility tables in handbooks and this text.

* Colors of natural minerals vary widely and are sometimes different from the compounds prepared in the lab; solubility of the former is apt to be lower as well. See mineralogy references following special experiment 4.

Use a few milligrams of sample to determine its solubility in the following solvents used both dilute and concentrated, hot and cold: HNO_3, HCl, and aqua regia (one part of HNO_3 to three parts of HCl). If HCl or aqua regia is used, a white precipitate may indicate the presence of group 1 ions. Some common substances which aqua regia will not dissolve are the sulfates of Pb and of the group 4 metals, CaF_2, the Ag halides, C, S, Al_2O_3, SiO_2, and most silicates. The acid solution will probably contain some ions from the sample that may be partly soluble and is analyzed as a general unknown after boiling down to decompose excess aqua regia.

The acid-insoluble residue is centrifuged, washed with water several times, and boiled with 2 ml of 1.5 *M* Na_2CO_3 to transpose it to the carbonates of metals that are then soluble in dilute HNO_3. This treatment will not solubilize the last five mentioned substances, however, and further, more drastic methods are needed. The silver halides are solubilized by heating with a mixture of 3 *M* H_2SO_4 and granular zinc, the metal reducing Ag^+ to Ag, which then can be dissolved in HNO_3 and tested as in group 1. The remaining insoluble materials can be fused in a nickel crucible with a Na_2CO_3–K_2CO_3 mixture or with any of these: Na_2O_2, $K_2S_2O_7$, or $KHSO_4$. The cooled melts are taken up in dilute HNO_3 and the solution treated as a general unknown. (Directions for fusions are given in books dealing with ore and mineral analyses.) Fusions can give high oxidation states like MnO_4^- and CrO_4^{-2}. MnO_4^- will oxidize HCl in group 1 precipitations to $H_2O + Cl_2$, and MnO_4^- or $Cr_2O_7^{-2}$ will oxidize H_2S to $H_2O + S$ under group 2 precipitation conditions. The color changes (review Chapter 17) will serve to indicate what is taking place and more of the precipitation reagents must be added to compensate for loss.

*3. **The Solid is Metallic.*** HNO_3 is the best solvent for most metallic samples, though Cr and Al are only partially soluble due to development of impervious oxide coatings. In addition. Sb and Sn form insoluble hydrated oxides. $HSb(OH)_6$ or $Sb_2O_5 \cdot H_2O$ and H_2SnO_3 or $SnO_2 \cdot H_2O$. Other than these cases, HNO_3 has the advantages of (*a*) yielding soluble nitrates with most metals and (*b*) oxidizing elements like P, As, S, and Hg (also Sb and Sn as above) to PO_4^{-3}, AsO_4^{-3}, SO_4^{-2}, and Hg^{+2}, which in the presence of hot HCl would be lost by the volatility of PH_3, AsH_3, H_2S, SbH_3, Hg, and $SnCl_4$.

A metallic sample not dissolving completely in HNO_3 after prolonged heating and further additions of acid. probably contains Sn and/or Sb among the common elements. This residue of hydrous oxide(s) can be solubilized by fusing in an iron dish with a mixture of $Na_2CO_3 + S$, giving SnS_3^{-2} and SbS_4^{-3}, which are extracted with hot H_2O. That solution is treated as a group 2B unknown while the centrate from the Sn–Sb separation is boiled down to expel most of the HNO_3, then diluted and handled as a general unknown. Group 2 will need extra time to precipitate because As^V present oxidizes H_2S until reduced to As^{III} (or NH_4I can be employed to effect the reduction). When the KOH separation is then made the centrate may be combined with the extract from the carbonate–sulfur fusion and analyzed as a 2B sample.* The analysis is continued through group 3 and the centrate, from its separation, should be colorless and will generally include only Mg^{+2} as a possibility.

If the alloy is not appreciably soluble in dilute HNO_3, aqua regia

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* The centrate for groups 3 through 5 should be tested for PO_4^{-3}, which may come from the oxidation of phosphides, and, if found. the group 3 procedure is altered to include the basic acetate separation already described. Student samples will rarely need this, though P is a common element found in small amounts in steels and bronzes.

should be tried and if that fails, one may try a mixture of concentrated HCl plus a few drops of bromine or saturated Br_2 water. (*Caution! Only the laboratory instructor or stockroom man should handle highly corrosive liquid* Br_2. *Any accidental contact with the skin must be counteracted by immediate application of sodium thiosulfate solution.*) In any case, excess solvent is evaporated under the hood, the residue of salts redissolved in water, and the analysis begun with group 1. A white-yellow residue may be AgBr, which is dissolved by the method described for AgCl on p. 362.

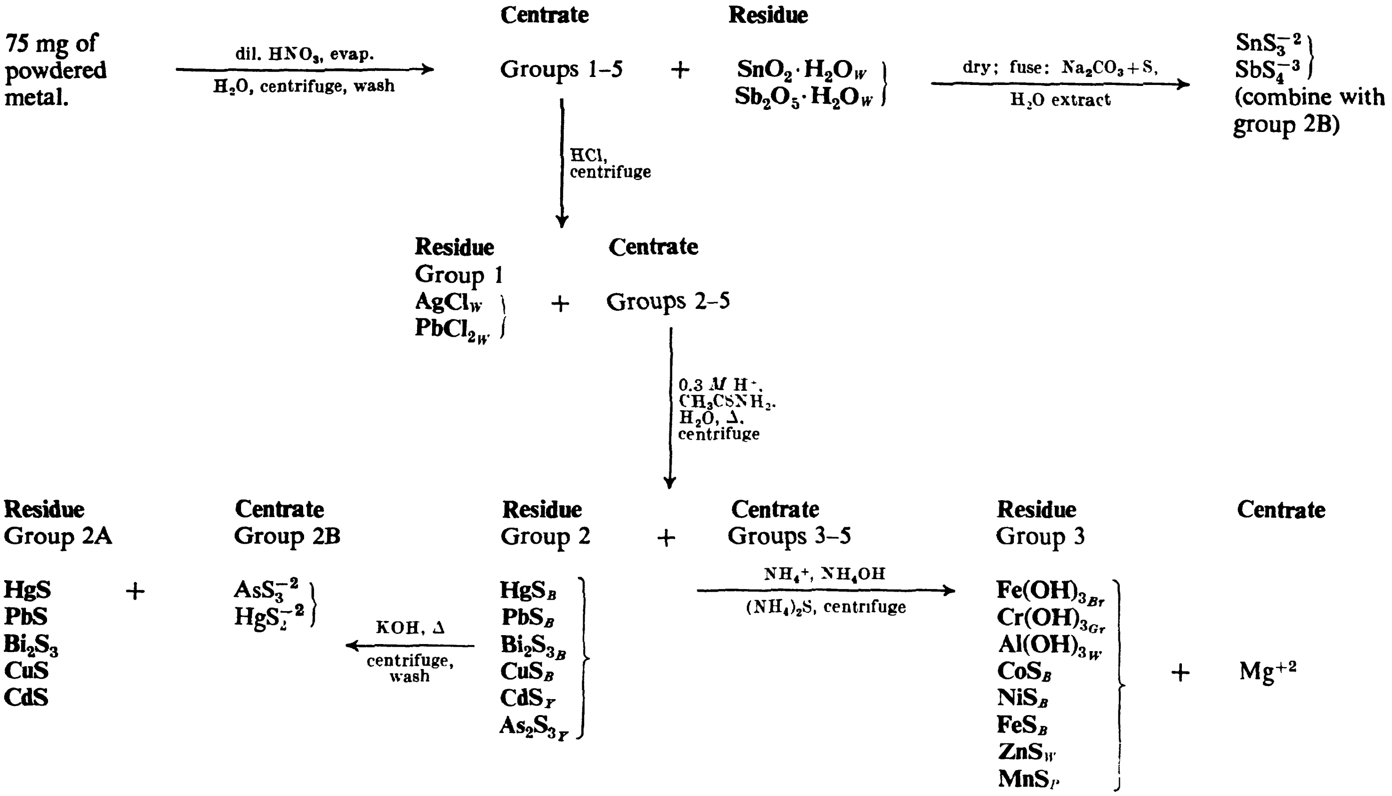
Samples for beginners are usually soluble in the common solvents and relatively free of complications such as the presence of unfamiliar elements. If the samples are commercial alloys, the student should make use of library references in the metallurgical field to get clues on the composition, physical appearance, and other characteristics of metals whose identity is sought. Such samples present the added problem of containing a few metals in major proportions and others in small amounts. Only careful work will discover the latter.

Dry Ignitions

Heating a small portion of solid sample on a wire gauze or in a test tube made from small-diameter glass tubing, sometimes gives the analyst valuable information on the composition of the material with a minimum amount of effort. Any clues he gets here will suggest spot tests for specific ions or elements.

1. The sample is metallic and burns brightly: **Mg and its alloys.**
2. The sample is metallic and melts at a relatively low temperature perhaps even in hot H_2O: **Bi, Pb, Sn, Sb, Cd, and their alloys.**
3. The sample is nonmetallic. A gas is released and color may change.
   (*a*) H_2O: **hydrates, NH_4^+ salts, bicarbonates, hydroxides.** If the steam is basic to litmus, **NH_4^+ salts** are indicated; if the reaction is acidic, **strong acid radicals** are indicated. Odor may help identification, as in the case of NH_3.
   (*b*) O_2, as tested by glowing splint: **nitrates.**
   (*c*) Nitrogen oxides: **nitrites and possibly nitrates.**
   (*d*) CO_2, as tested by lime water: **some carbonates, bicarbonates, organic matter.**
   (*e*) CO (**POISON!**), light blue flame when burned: **oxalates.**
   (*f*) I_2, purple gas: **some iodides.**
   (*g*) Cl_2, yellow gas: **some chlorides.**
   (*h*) Br_2. brown gas: **some bromides.**
   (*i*) H_2S, odor: **some sulfides.**
   (*j*) SO_2, odor: **sulfites, thiosulfates, some sulfates.**

FLOW SHEET—SIMPLE METALLIC SAMPLE



4. The sample is nonmetallic and changes color when heated and may change again when cooled.

   (*a*) Chars or burns: **organic matter.**

   (*b*) Simply turns black: **some Cu, Mn, Ni, Co salts.**

   (*c*) Yellowish when hot, fades when cool: **ZnO, SnO_2, some Zn salts.**

   (*d*) Yellow hot and cold, tends to fuse into the glass: **some Pb compounds.**

5. Sample may or may not appear metallic but gives a sublimate when heated.

   (*a*) Black to grey sublimate: **some iodides, and mercury and arsenic compounds.** The mercury coalesces in droplets, the arsenic has a garlic odor (POISON!).

   (*b*) White sublimate: **some Hg and NH_4^+ halides and arsenic and antimony oxides (POISON!).**

Industrial Analysis of Metallic Samples

Quantitative analysis of metal samples in industry is of prime importance since physical properties of alloys are altered by composition changes even of minor sorts; hence rapid, accurate, and sensitive methods are needed as quality controls. The *spectrograph*, which is most often used here, meets this need admirably. It is an instrument in which the sample is burned in a high temperature arc, the light from the combustion consisting of spectra of the metals in the sample. (See special experiment 5.) The spectra are broken up into their component lines by a diffraction grating, a section of metal surface on which is ruled some 10–35,000 lines to the inch, and the spectral lines photographed. Since each metallic element has its own characteristic lines, the photo is analyzed first qualitatively for the sample composition by the number and position of the lines. The density of important reference lines for each element is then determined with an instrument called a *densitometer*, which relates density of the photographed lines to the quantity of each element present. The automatic recording spectrograph (~ $40,000) when set up, for instance, to routinely analyze brass samples, is capable of analyzing a 10–15 element sample every 5–10 minutes and rendering a printed report. A recently developed *X-ray fluorescence spectrometer* does the same job without destroying the sample. Using it one can even monitor a flowing stream of substances in solution. The stream is irradiated by high intensity X-rays, causing a fluorescence from excitation of atoms. The wave length of the radiation is a qualitative indication of an element's presence, the radiation intensity at a particular wave length is the quantitative measure of the element. Potassium and all heavier atoms can be measured by this means.

Qualitative analysis of metal samples in industry is often still done by simple laboratory methods although test instrumentation increases every year. Inorganic alloying elements or impurities like S, P, C, N, and B are largely determined by old, familiar wet chemical methods. Most testing is done for the purposes of meeting specifications, identifying mixed up stock, and sorting scrap for salvage.

Methods for metal identification in industry are noted for their simplicity and speed, because only a limited number of possibilities are encountered in a given plant, and a single test may be sufficient in some cases. For example, the theoretician if asked to differentiate between type 310 stainless (20% Ni, 25% Cr, a little Mn and C, balance Fe), and type 446 stainless (28% Cr, a little C, balance Fe) might spend several hours cutting off samples, dissolving them in acid, neutralizing, eliminating iron and chromium, and testing for nickel and manganese. The practical man might have a magnet in his pocket and know that 446 is *magnetic* and 310 is not. In another instance the machinist might in a few seconds identify a bar of iron by the type of sparks it gives on grinding with an emery wheel (the *spark test*), while the chemist fresh from the classroom is still trying to remember where he stored his qualitative analysis book so he can look up a few clues on how to begin. Partial identification of metals by nondestructive means are common. A recent advance in qualitative testing for nonferrous metals is the *Sigmatest* (*Magnatest*) in which an electronic conductivity meter is used to induce a high frequency eddy current in the sample for pickup on a small probe in contact with the

TABLE 21–2.* SCREENING OF METALLIC SAMPLES ON THE BASIS OF SPECIFIC GRAVITY

Metal Designation	Specific Gravity	Metals and Their Alloys
Light	1.5–3.0	Be, Al, Mg. (Dowmetal, Alcoa, etc.)
Average	4.5–9.2	Co, Cu, Fe, Ni, Sn, Zn, Sb, Cd, Nb, Mn, Ti, V, Zr. (steels, brasses, bronzes, hastelloys, etc.)
Heavy	9.8–11.3	Pb, Ag, Bi, Mo. (solder, type metal, etc.)
Very heavy	12.0–22.5	Au, Ir, Hg, Os, Pd, Pt, Re, Rh, Ru, Ta, W, U. (jewelry, catalysts, etc.)

* Partially adapted from "Rapid Identification (Spot Testing) of Some Metals and Alloys," published by The International Nickel Co., Inc., New York 5, N.Y., and printed here by their permission. See also Appendix A23.

metal. Conductivity measured in this way is a function primarily of alloy composition. Industrial qualitative testing of metals is also done by the *electrographic method* (special experiment 13) and by some spot testing chemical procedures following observations on physical features of the sample which suggest or rule out various methods. The latter are perhaps of most interest to chemists.

Specific gravity is an obvious simple screening test for metals. The following table is self-explanatory in this regard.

Having classified a sample roughly by density and knowing further that only a limited number of commercial alloys would be used, one can devise quick tests for his own problems.

A Light Alloy Problem

Suppose one has a light metal sample and knows that only aluminums 2S, 3S, and 75S, and Dowmetals M and C are ordered in the factory. From a study of the compositions guaranteed by the manufacturers, one is able with a little ingenuity to arrive at a system for handling the matter, as shown in Table 21–3. One may draw upon facts like the following for differentiation of alloys in the table:

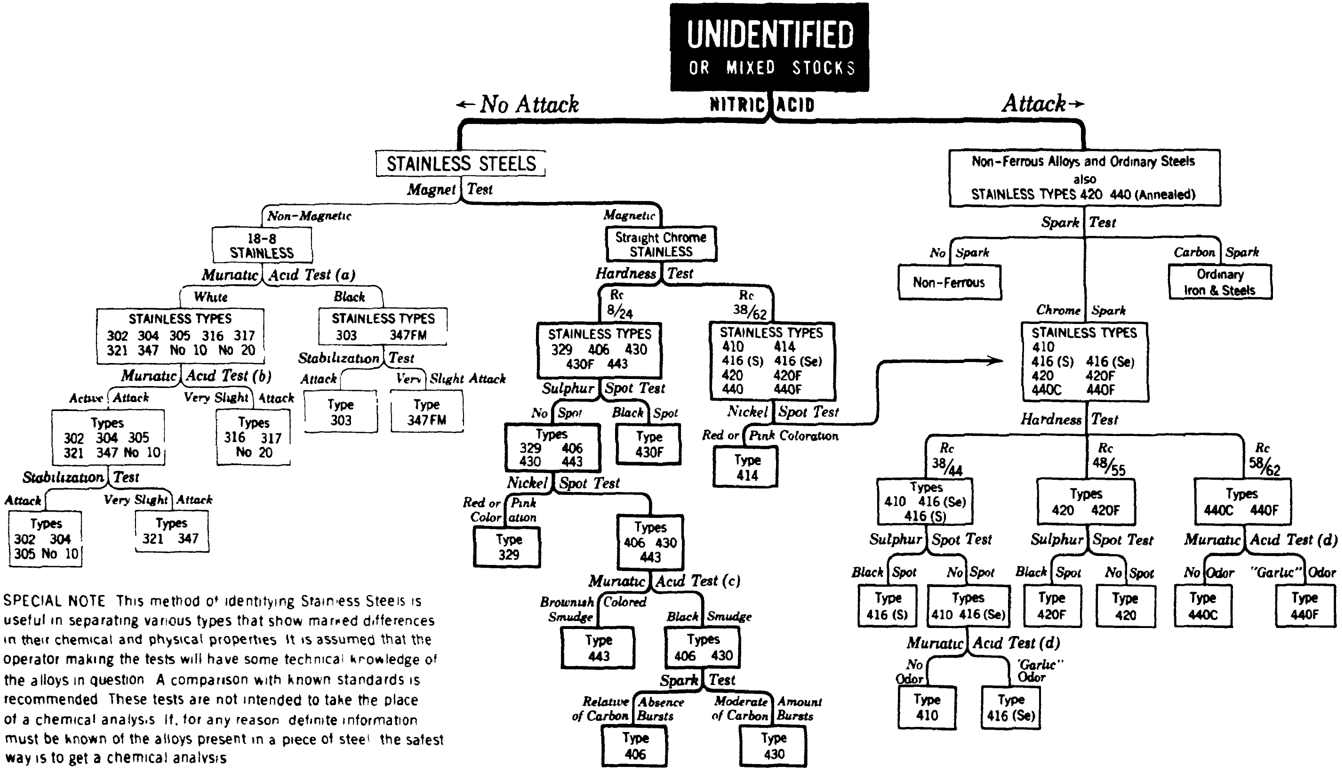
TABLE 21–3.* NOMINAL COMPOSITION OF SOME LIGHT ALLOYS

Alloy	Per Cent Composition								
	Al	Mg	Zn	Cu	Fe	Cr	Mn	Si	
Al-2S	99.5+								
Al-3S	97.6			0.1	0.5		1.3	0.5	
Al-75S	89.8	2.5	5.6	1.6		0.3	0.2		
Dowmetal M		98.8					1.2		
Dowmetal C	9.0	89.0	2.0						

* See note to Table 21–2.

(*a*) The Al-based alloys are known to have an oxide coating which the Mg alloys do not have, hence a dilute Ag^+ solution is rapidly reduced to black metallic Ag only on the Mg surfaces.

TYPE NO	CARBON	CHROMIUM	NICKEL	OTHER ELEMENTS	CARPENTER BRAND NAME
302	Over 0 08/0 20	17 00/19 00	8 00/10 00		Carpenter Stainless No 4
303	0 15 Max	17 00/19 00	8 00/10 00	P,S, Se Min 0 07, Mo Max 0 60	Carpenter Stainless No 8
304	0 08 Max	18 00/20 00	8 00/11 00		Carpenter Stainless No 4-A
305	0 12 Max	17 00/19 00	10 00/13 00		Carpenter Stainless No 305
316	0 10 Max	16 00/18 00	10 00/14 00	Mo 2 00/3 00	Carpenter Stainless No 316
317	0 10 Max	18 00/20 00	11 00/14 00	Mo 3 00/4 00	Carpenter Stainless No 317
321	0 08 Max	17 00/19 00	8 00/11 00	Ti 5 x C Min	Carpenter Stainless No 321
329	0 20 Max	23 00/28 00	2 50/5 00	Mo 1 00/2 00	Carpenter Stainless No 7-Mo
347	0 08 Max	17 00/19 00	9 00/12 00	Nb 10 x C Min	Carpenter Stainless No 347
	0 08 Max	15 50/16 50	17 50/18 50		Carpenter Stainless No 10
	0 07 Max	20 00	29 00	Mo 2 00 Min, Cu 3 00 Min	Carpenter Stainless No 20
406	0 15 Max	12 00/14 00		Al 3 50/4 50	Carpenter Stainless No 1-JR
410	0 15 Max	11 50/13 50			Carpenter Stainless No 1
414	0 15 Max	11 50/13 50	1 25/2 50		Carpenter Stainless No N-1
416	0 15 Max	12 00/14 00		P,S, Se Min 0 07: Mo Max 0 60	Carpenter Stainless No 5
420	Over 0 15	12 00/14 00			Carpenter Stainless No 2
420F	Over 0 15	12 00/14 00		S, Se 0 07 Min; Mo Max 0 60	Carpenter Stainless No 2-FM
430	0 12 Max	14 00/18 00			Carpenter Stainless No 6
430F	0 12 Max	14 00/18 00		P,S, Se 0 07 Min; Mo Max 0 60	Carpenter Stainless No 6-FM
440A	0 60/0 75	16 00/18 00		Mo 0 75 Max	Carpenter Stainless No 440A
440B	0 75/0 95	16 00/18 00		Mo 0 75 Max	Carpenter Stainless No 440B
440C	0 95/1 20	16 00/18 00		Mo 0 75 Max	Carpenter Stainless No 440C
440F	0 95/1 20	16 00/18 00		S, Se 0 07 Min, Mo Max 0 75	Carpenter Stainless No 440FM
443	0 20 Max	18 00/23 00		Cu 0 90/1 25	Carpenter Stainless No 3



SPECIAL NOTE This method of identifying Stainless Steels is useful in separating various types that show marked differences in their chemical and physical properties It is assumed that the operator making the tests will have some technical knowledge of the alloys in question A comparison with known standards is recommended These tests are not intended to take the place of a chemical analysis If, for any reason definite information must be known of the alloys present in a piece of steel the safest way is to get a chemical analysis

FIG. 21-1. Flow sheet for the identification of stainless steels. (Courtesy Carpenter Steel Co.)

(*b*) Mn may be found by putting a drop of NaOH on the specimen to dissolve the oxide coating, followed by excess concentrated HNO_3, H_3PO_4, and $NaBiO_3$ to produce the purple MnO_4^- color.

(*c*) A dilute $CdSO_4$-NaCl-HCl solution (5 g $CdSO_4 \cdot 3/8H_2O$, 3 g NaCl, 5 ml 14 *M* HCl, dilute to 100 ml) gives a dark spot of cadmium metal if zinc is present.

(*d*) Properly prepared, the aluminon test 17-6 for Al will differentiate the Dowmetals if (*c*) fails.

A Stainless Steel Problem

There are many stainless steels, all containing Fe, Cr, Ni, C, and minor elements. To distinguish among them might appear unfeasible without spectrographic analysis, but the flow sheet given in Fig. 21-1 and identification tests* show how the job is accomplished with a minimum of effort using ordinary laboratory tests.

IDENTIFICATION TESTS FOR THE STAINLESS STEEL FLOW SHEET

Preparation of Samples. All specimens must be free from scale . . . which may be removed by pickling or grinding. In making a Spot Test, always grind a fresh area before applying the solution.

Nitric Acid Test. This testing solution is made by mixing one part of concentrated *nitric acid* and one part of water. A drop of the solution is placed on a freshly ground spot on the specimen. Attack is denoted by a boiling action or gas evolution from the drop.

Magnet Test. Austenitic stainless steels (the 18-8 types) are nonmagnetic in the annealed condition, but become slightly magnetic when cold-worked. This slight magnetism can easily be distinguished from the stronger magnetism of the straight chrome types.

Spark Test. A spark test is made to separate stainless types 420 and 440 from nonferrous alloys and ordinary iron and steel as nitric acid, under certain conditions, may attack annealed specimens of some stainless types. These stainless steels are identified by the characteristic short "chrome" spark.

Hardness Test. Specimens are heated to 1850 F. and oil quenched. Various carbon percentage ranges will be noted by different hardnesses as quenched. The non-hardening types will show low hardness as oil quenched from 1850 F.

Muriatic Acid Tests. Specimens are placed in a solution of *Muriatic*

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* Both reprinted by permission of The Carpenter Steel Co., Reading, Pa. Rc refers to the Rockwell C scale of hardness. If these values are furnished, stainless samples make interesting unknowns. Standard samples should be available for student comparisons.

*Acid** (one part water, one part Muriatic Acid) at a temperature of 180–190 F. A fresh solution should be used for each of the following tests:

(*a*) After a five minute immersion, type 303 will be coated with a heavy black smudge.

(*b*) Within two minutes after immersion, Type 316 can be identified by the very slight acid attack as compared with the active attack and evolution of gas on types 302, 321, and 347.

(*c*) Immerse specimens for at least fifteen minutes. Type 443 can be identified by a brownish-colored smudge.

(*d*) Immerse specimens in a separate container for five minutes, then remove them from the solution. A pungent garlic-like odor (***Caution***) will be detected on types 416 (Se) and 440F. This characteristic odor of hydrogen selenide gas will not be present in pickling types 410 and 440.

Sulphur Spot Test. Three drops of *sulphuric acid* solution (one part sulphuric acid, three parts water) are placed on a newly ground spot on the specimen and allowed to react for one minute. One drop of a 5% solution of *lead acetate* in water is then added to the acid drop and allowed to react for 15 seconds. The spot is then washed with water and examined. A positive test for sulphur (stainless types 416 (S), 420F, and 430F) is the presence of a black sulphide deposit.

Nickel Spot Test. Three solutions are required for this test:

Solution no. 1*:* Mix 125 cc of water, 100 cc concentrated nitric acid, and 25 cc of 85% *phosphoric acid.*

Solution no. 2*:* One part water and one part muriatic acid.

Solution no. 3*:* Dissolve one g. of *dimethylglyoxime* in 60 cc of *glacial acetic acid.* To this solution add another solution, prepared by dissolving 10 g of *ammonium acetate* in 30 cc of *ammonium hydroxide.*

Procedure: Place one drop of solution no. 1 on a newly ground spot on the specimen. Allow it to react for 30 seconds and then add one drop of solution no. 2. This mixture is allowed to react for an additional 30 seconds and is then absorbed with white blotting or filter paper. One drop of solution no. 3 is then placed on the moist spot of the paper. The formation of a red or pink coloration in the spot denotes the presence of nickel.

Stabilization Test. Test specimens are heated to 1250 F for two hours and then cooled to room temperature in air. The specimens are then placed in a cold solution of three parts nitric acid, one part *hydrofluoric acid,* and six parts water and left for one hour. Remove specimens from solution and wash with water. Stainless types 321 and 347 will show a very slight attack from the acid. Stainless types 302 and 304 will have rough, granular surfaces.

The Practicing Quality Analyst

Many procedures of the types shown above have and are being routinely composed by analysts working in industrial laboratories. The information

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* Technical grade concd. HCl.

they want is, as a rule, not found in texts and they are continually forced to plumb their training in fundamentals, their imagination, experience, and inventiveness to produce answers to problems where no set approaches are known. It is evident that the more one knows of fields allied to qualitative testing, such as metallurgy, physics, and mathematics, the more valuable he is as an analyst. Almost anybody can follow cookbook directions or substitute numbers into formulas. But when no directions or formulas are given, only those people capable of doing original thinking and who are willing to put forth some study and effort go on from there. There is great satisfaction in being creative and chemistry offers opportunities for creativity in every direction.

PROBLEMS

1. Draw a flow sheet for the separation of the light metal alloys in Table 21-3 using the chemical methods described there.

2. How could one distinguish between the members of the following pairs of materials by simple chemical and/or physical tests? Give two methods where possible.

(*a*) Plain C steel and stainless steel.
(*b*) Brass and Cu.
(*c*) Sea water and NaCl solution of the same density.
(*d*) U and Fe.
(*e*) Al and Be.
(*f*) A 10-10-10 fertilizer and a 10-0-10 fertilizer.
(*g*) Tungsten carbide and iron carbide.
(*h*) Hadfield steel and high C steel.
(*i*) W and Ti.
(*j*) Hastelloy C (Ni, Fe, Mo) and Chromel C (Ni, Fe, Cr).

3. An alloy has a specific gravity of 9.5 and melts at 200 C. What elements might be present?

4. You are asked to determine whether a piece of wire is pure tantalum or pure rhodium. From the literature, find one physical and one chemical test for doing the job in a hurry.

5. One has three samples of pure metals: Pb, Mo, Bi. Of these, only one is attacked by HAc and of the two remaining, HNO_3 attacks only one. Explain.

6. What methods could one use to distinguish between a brass (Cu-Sn-Zn) and a bronze (Cu-Sn) which have about the same color and density?

7. (*Library*) Look up the spark method for testing steels and give a brief explanation and a few examples of observations on specific steels.

8. Hot H_2SO_4 is used to destroy organic matter in a sample and results in precipitating a white solid that may be $SrSO_4$, $PbSO_4$, and/or $BaSO_4$. This is

segregated. How does one proceed to put it back in solution and test for the metals? Prepare a flow sheet for this.

9. Why are Ba, Sr, Ca, Na, K, NH_4, Hg, and As seldom (and some of these, never) found in engineering alloys?

10. (*Library*) Look up a few of the main facts concerning Ta and compare it to Ti. Repeat for Nb and compare to V.

11. Refer to Appendix table A23. Suppose one had pieces of Hastelloy B, Hastelloy C, Hastelloy D, and Invar which needed sorting. Draw a flow sheet and implement it with directions for doing the job with minimum equipment.

12. (*a*) One has an irregular piece of alloy to identify. Explain at least two ways in which its density can be determined.

(*b*) Are there any metallic elements other than Cu and Au that are not silvery appearing?

13. Explain the chemistry behind the steps in the Carpenter methods for stainless steel analysis.

14. Jackson Slipshod says that hot acid digestion takes too long to decompose organic interferences and recommends heating the sample to 800 C and holding it there until the organic matter is gone. Is there anything wrong with this? Explain.

15. A stainless steel is not attacked by HNO_3, is magnetic, has a hardness, Rc, of 8/24, and gives a black spot with dilute H_2SO_4 followed by $PbAc_2$. Which alloy is it? Which elements has one tested? How could the others be identified? Prepare a complete flow sheet for testing all elements in the sample.

22

THE ANION GROUPS

The qualitative testing of negative ions is on the whole a less systematic job than the analysis of positive ions. The reason is that most anions are sufficiently different from each other so spot tests may be made directly upon complex mixtures without the necessity of much preliminary group or individual separations. Three reagents are used, however, to divide anions into four classes, and are employable in a first gross examination. A negative test with any of these is of utility in that further testing for the anion group(s) shown thereby to be absent is not necessary. Following this, small portions of sample are tested for individual ions in groups which are present. If cation analysis has preceded anion analysis on a sample, solubility data are also of assistance in ruling out some anions. Specific directions for handling the sample for anion analysis is given in the last section of this chapter.

Of the 30–40 common anions, 18 have been selected as being representative. They are divided into four groups:

Anion Group 1: Decomposed by Dilute H_2SO_4

$$\begin{array}{l} \text{A.} \\ \text{B.} \\ \text{C.} \\ \text{D.} \\ \text{E.} \end{array} \qquad \left.\begin{array}{r} NO_2^- \\ S^{-2} \\ SO_3^{-2} \\ S_2O_3^{-2} \\ CO_3^{-2} \end{array}\right\} + 2H^+ + SO_4^{-2} \begin{array}{l} \rightarrow H_2O + HNO_3 + \mathit{NO} \\ \rightarrow \mathit{H_2S} \\ \rightarrow \mathit{SO_2} + H_2O \\ \rightarrow \mathit{SO_2} + S + H_2O \\ \rightarrow \mathit{CO_2} + H_2O \end{array}$$

Tests are made for gaseous products by odor or by characteristic reaction when bubbled into reagent solutions. It is evident that these ions cannot exist in strong acid media. (Other anions also decomposed under these conditions include hypochlorite, ClO^-, and cyanate, CNO^-. These will not be considered.) See also paragraphs **W**, **X**, and **Z** concerning interferences among ions of the various groups.

Anion Group 2: Insoluble Ba^{+2} and/or Ca^{+2} Salts

$$\left.\begin{array}{lr} \mathrm{F.} & PO_4^{-3} \\ \mathrm{G.} & SO_4^{-2} \\ \mathrm{H.} & CrO_4^{-2} \\ \mathrm{I.} & BO_2^{-} \\ \mathrm{J.} & F^{-} \\ \mathrm{K.} & C_2O_4^{-2} \end{array}\right\} + Ba^{+2} + Ca^{+2} \begin{array}{l} \rightarrow Ba_3(PO_4)_{2_w} \\ \rightarrow BaSO_{4_w} \\ \rightarrow BaCrO_{4_Y} \\ \rightarrow Ba(BO_2)_{2_w} \\ \rightarrow CaF_{2_w} \\ \rightarrow CaC_2O_{4_w} \end{array}$$

When this combined residue is treated with hot, dilute HCl, only $BaSO_4$ remains undissolved. The solution and residue are tested further. Adding Ca^{+2} and Ba^{+2} solutions separately gives a rough indication of ions present, as the composition of the precipitate above shows.

Anion Group 3: Insoluble Ag^+ Salts

$$\left.\begin{array}{lr} \mathrm{L.} & Cl^{-} \\ \mathrm{M.} & Br^{-} \\ \mathrm{N.} & I^{-} \\ \mathrm{O.} & SCN^{-} \\ \mathrm{P.} & Fe(CN)_6^{-4} \end{array}\right\} + Ag^{+} \begin{array}{l} \rightarrow AgCl_w \\ \rightarrow AgBr_{w-Y} \\ \rightarrow AgI_Y \\ \rightarrow AgSCN_w \\ \rightarrow Ag_4Fe(CN)_{6_{w-Y}} \end{array}$$

The silver compounds are insoluble in dilute HNO_3. The residue or original solution is tested further.

Anion Group 4: Not Indicated by Other Group Reagents

$$\left.\begin{array}{ll} \mathrm{Q.} & NO_3^{-} \\ \mathrm{R.} & Ac^{-} \end{array}\right\}$$

One always must test for these, since no group reagent is available to rule them out by negative test.

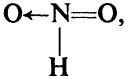
THE GROUP 1 ANIONS

A. Nitrite Ion, NO_2^-

Neither nitrous acid solutions nor most nitrites are stable. From the oxidation potentials below, one can deduce, for example, that nitrite is capable of reducing bromine and of oxidizing iodide:

$$HNO_2 + H_2O = NO_3^- + 3H^+ + 2e^- \qquad E^\circ = -0.94$$
$$NO + H_2O = HNO_2 + H^+ + e^- \qquad E^\circ = -1.00$$

Because of the many oxidation states of nitrogen, reactions of nitrites can be complex, and other products than the above often appear.

Nitrous acid may exist as either H—O—N=O or  $O \leftarrow \underset{\substack{| \\ H}}{N} = O$, and two groups of isomeric compounds are related to these structures, as discussed in Chapter 4. Resonance in the ion may lead to attachment through an oxygen (unstable nitrites) or through the nitrogen (more stable nitro derivatives).

Nitrogen has *oxidation states* (— **III**) as *ammonia* NH_3, (— II) as *hydrazine* $H_2N—NH_2$, (— I) as *hydroxylamine* H_2NOH, (I) as *nitrous oxide* N_2O, (II) as *nitric oxide* NO, (**III**) as *nitrogen trioxide* N_2O_3 (the anhydride of *nitrous acid* HNO_2), (IV) as *nitrogen dioxide* NO_2, and (V) as *nitrogen pentoxide* N_2O_5 (the anhydride of *nitric acid*).

Except for some complex compounds, all nitrites are water soluble. ($AgNO_2$ solubility = 3.4 g/liter; see also test 22–4.)

Nitrous acid may be prepared from NO_2 or N_2O_3 and H_2O or from a nitrite and strong acid. Many tests for nitrite are known. The most sensitive is the diazo reaction, given as example 11, Chapter 12, p. 195. Three others are (*a*) oxidation to NO_3^- with strong oxidants:

$$5HNO_2 + 2MnO_4^- + H^+ = 2Mn^{+2} + 3H_2O + 5NO_3^-$$

(*b*) with Fe^{+2} in dilute acid to give a brown color due to nitrosyl iron(II) ion

$$3HNO_2 + Fe^{+2} = H_2O + H^+ + NO_3^- + Fe(NO)^{+2}$$

and (*c*) reduction to nitrogen by heating with an ammonium salt, or with acidified solutions of urea, thiourea, or sulfamic acid:

$$NO_2^- + NH_4^+ = (NH_4NO_2) = \mathit{N}_2 + H_2O$$
$$2HNO_2 + (NH_2)_2CO = 2\mathit{N}_2 + \mathit{CO}_2 + 3H_2O$$
$$HNO_2 + (NH_2)_2CS = \mathit{N}_2 + HSCN + 2H_2O$$
$$HNO_2 + NH_2SO_2OH = \mathit{N}_2 + 2H^+ + SO_4^{-2} + H_2O$$

The last reaction is best for quantitative destruction of nitrite.

One *quantitative analytical method* is reduction with base and active metal to NH_3 and titration of the ammonia. See test 22–47. Others are illustrated in tests 22–5 and 22–6.

B. Sulfide Ion, S^{-2}

Sulfide sulfur has the lowest valence that element exhibits, therefore it can act only as a weak reducing agent:

$$S^{-2} = S + 2e^- \qquad E^\circ = 0.51$$

Many oxidizing agents are capable of causing sulfide decomposition in this way. H_2S is somewhat soluble in water ($\sim$ 0.1 M at 20 C and 1 atm); its aqueous solution is called *hydrosulfuric* or *hydrosulfic acid.* By odor alone one can detect this poisonous gas at a concentration of about 0.8 ppm in the air. Being a very weak diprotic acid, soluble sulfides are about as basic as comparable concentrations of strong bases, since hydrolysis to *bisulfide* is virtually complete. Little odor of H_2S is detected over Na_2S. See Chapters 7 and 10 for mathematical treatment of H_2S equilibria.

TABLE 22-1. EQUILIBRIUM CONSTANTS FOR SOME SULFIDE REACTIONS

Reactions (in order of decreasing $[S^{-2}]$)	K
$MnS = Mn^{+2} + S^{-2}$	8×10^{-14}
$FeS_{(\alpha)} = Fe^{+2} + S^{-2}$	4×10^{-17}
$ZnS = Zn^{+2} + S^{-2}$	1×10^{-20}
$NiS_{(\alpha)} = Ni^{+2} + S^{-2}$	1×10^{-22}
$CoS_{(\alpha)} = Co^{+2} + S^{-2}$	5×10^{-22}
$PbS = Pb^{+2} + S^{-2}$	4×10^{-26}
$SnS = Sn^{+2} + S^{-2}$	1×10^{-26}
$CdS = Cd^{+2} + S^{-2}$	6×10^{-27}
$Bi_2S_3 = 2Bi^{+3} + 3S^{-2}$	1×10^{-70}
$Cu_2S = 2Cu^{+} + S^{-2}$	1.2×10^{-49}
$Ag_2S = 2Ag^{+} + S^{-2}$	1×10^{-50}
$CuS = Cu^{+2} + S^{-2}$	4×10^{-36}
$Fe_2S_3 = 2Fe^{+3} + 3S^{-2}$	1×10^{-88}
$Hg_2S = Hg_2^{+2} + S^{-2}$	1×10^{-45}
$HgS = Hg^{+2} + S^{-2}$	1×10^{-50}

H_2S is usually made by reacting acids with metallic sulfides, or heating sulfur with hydrocarbons. Some sulfides like Al_2S_3, Cr_2S_3, MgS, CaS, and BaS react with water to give H_2S and insoluble metal hydrosulfides and hydroxides. Sulfur will dissolve in basic solutions to give various sulfides, depending upon the amount of sulfur added. Ions as S^{-2}, S_2^{-2}, S_3^{-2}, S_4^{-2}, S_5^{-2}, etc., are present. When acidified, these solutions yield H_2S, S, and unfamiliar *hydrides of sulfur* as H_2S_2 and H_2S_3. Cation group 3, 4, and 5 sulfides, except those of Co and Ni, dissolve readily in dilute HCl, those of Co, Ni, and group 2, except Hg^{+2}, require heating with stronger HCl, and aqua regia is needed to decompose HgS. The HCl reactions give H_2S, those with the oxidizing acid HNO_3 yield S; see list of reactions, Chapters 16 and 17.

Sulfides are handled *quantitatively* by (*a*) oxidation to sulfate and precipitation and weighing as barium sulfate or (*b*) absorption of H_2S in $ZnAc_2$ solution, followed by addition of a measured excess of I_2 and H^+ (to dissolve the ZnS formed and give $S + I^-$), and titration of unreacted I_2 with standard thiosulfate.

C. Sulfite Ion, SO_3^{-2}

Sulfurous acid is a diprotic acid made when SO_2 is dissolved in H_2O. It is one of the weak acids, though dissociating more readily than most; $K_1 = 1.25 \times 10^{-2}$. The sulfur *oxidation state* is (IV); intermediate among (—II) in H_2S; (0) in S; and (VI) in SO_4^{-2}, so sulfites may undergo reduction or oxidation. The partials show sulfurous acid to be a better oxidizing than reducing agent:

$$3H_2O + S = H_2SO_3 + 4H^+ + 4e^- \qquad E^\circ = -0.45$$

$$H_2O + H_2SO_3 = SO_4^{-2} + 4H^+ + 2e^- \qquad E^\circ = -0.20$$

Sulfur dioxide gas is given off when alkaline sulfites are acidified and it may be identified by its pungent odor. H_2SO_3 forms *three kinds of salts*: *normal*, MSO_3, *acid*, $M(HSO_3)_2$, and *meta*, MS_2O_5. Most sulfites and bisulfites except those of the alkali metals and NH_4^+ are only slightly water soluble.

TABLE 22-2. EQUILIBRIUM CONSTANTS FOR SOME SULFITE REACTIONS

Reactions (in order of decreasing $[SO_3^{-2}]$)	K (approximate)
$MgSO_3 \cdot 6H_2O = Mg^{+2} + SO_3^{-2} + 6H_2O$	3.8×10^{-3}
$ZnSO_3 \cdot 2H_2O = Zn^{+2} + SO_3^{-2} + 2H_2O$	7.8×10^{-5}
$BaSO_3 = Ba^{+2} + SO_3^{-2}$	8.3×10^{-7}
$SrSO_3 = Sr^{+2} + SO_3^{-2}$	3.9×10^{-8}
$Hg_2SO_3 = Hg_2^{+2} + SO_3^{-2}$	$\sim 9 \times 10^{-28}$

Qualitative testing for sulfite depends upon valence state changes, and release of SO_2 gas. Sulfites can be (*a*) reduced

$$3Zn + 6H^+ + H_2SO_3 = H_2S + 3H_2O + 3Zn^{+2}$$

and the H_2S tested as previously described; (*b*) oxidized by strong oxidants

$$2MnO_4^- + 5H_2SO_3 = 4H^+ + 5SO_4^{-2} + 3H_2O + 2Mn^{+2}$$

(*c*) precipitated and the solid changed in some characteristic manner

$$PbAc_2 + SO_3^{-2} = \mathbf{PbSO}_{\mathbf{3}_w} + 2Ac^-$$
$$\mathbf{2PbSO_3} + O_2 \text{ (air)} = \mathbf{PbSO}_{\mathbf{4}_w}$$

or (*d*) decomposed by heating with HCl or H_2SO_4 to give SO_2, whose odor is unmistakable:

$$2H^+ + SO_3^{-2} = (H_2SO_3) \overset{\Delta}{=} H_2O + \mathit{SO_2}$$

In *quantitative analysis*, sulfites are titrated in acetic acid solution with standard I_3^- solution, using starch indicator or, alternately, SO_3^{-2} is oxidized to SO_4^{-2}, precipitated, and weighed as $BaSO_4$.

D. Thiosulfate Ion, $S_2O_3^{-2}$

Pure *thiosulfuric acid* is not isolated, but its salts are known and their stability likewise is not great. Acidification of thiosulfates results in

$$2H^+ + S_2O_3^{-2} = (H_2S_2O_3) = S + H_2O + \mathit{SO_2}$$

although in the presence of excess strong acid, $H_2S_2O_3$ appears to be stabilized and the reaction stops there for some hours. Most thiosulfates are water soluble and many dissolve in excess $S_2O_3^{-2}$ to give Werner complexes.

The eventual precipitate of yellow–white, fine sulfur is one means of differentiating between $S_2O_3^{-2}$ and SO_3^{-2}. Thiosulfate is a reducing agent which gives *tetrathionate* or sulfite with mild oxidizing substances like I_2, and S or SO_4^{-2} with stronger ones like MnO_4^-. These reactions are *p*H dependent:

$$\begin{aligned} 2S_2O_3^{-2} &= S_4O_6^{-2} + 2e^- && E^\circ = -0.17 \\ S_2O_3^{-2} + 6OH^- &= 2SO_3^{-2} + 3H_2O + 4e^- && E^\circ_B = 0.58 \\ S_2O_3^{-2} + 3H_2O &= 2H_2SO_3 + 2H^+ + 4e^- && E^\circ = -0.40 \end{aligned}$$

$Na_2S_2O_3$ is made by heating sulfur with sodium sulfite, and the pentahydrate is the familiar "hypo" used in photography. There are many acids containing S, H, and O besides the four listed above. Some of these are *sulfoxylic*, H_2SO_2; *hyposulfurous*, $H_2S_2O_4$; *pyrosulfuric*, $H_2S_2O_7$; *peroxymonosulfuric*, H_2SO_5; *peroxydisulfuric*, $H_2S_2O_8$; *dithionic*, $H_2S_2O_6$; *trithionic*, $H_2S_3O_6$.

Qualitative evidence of $S_2O_3^{-2}$ presence hinges on (*a*) destruction by acid to give SO_2 + S as already mentioned (*b*) bleaching of I_3^- color as shown below (*c*) precipitation of white silver or lead thiosulfate, which on heating is converted to black silver or lead sulfide:

$$2Ag^+ + S_2O_3^{-2} + H_2O = \mathbf{Ag_2S_2O}_{\mathbf{3}_w} + H_2O \overset{\Delta}{=} \mathbf{Ag_2S}_B + 2H^+ + SO_4^{-2}$$

or (*d*) reaction in strong base solutions of cyanide to produce thiocyanate, which gives its characteristic red color with iron when $Fe^{+3} + H^+$ (**HOOD!**) are added.

$$S_2O_3^{-2} + CN^- = SCN^- + SO_3^-$$

Table 22–3. Equilibrium Constants for Some Thiosulfate Reactions

Reactions (in order of decreasing $[S_2O_3^{-2}]$)	*K* (approximate)
$SrS_2O_3 \cdot 5H_2O = Sr^{+2} + S_2O_3^{-2} + 5H_2O$	8×10^{-1}
$BaS_2O_3 = Ba^{+2} + S_2O_3^{-2}$	9.5×10^{-5}
$PbS_2O_3 = Pb^{+2} + S_2O_3^{-2}$	9×10^{-7}
$Hg_2S_2O_3 = Hg_2^{+2} + S_2O_3^{-2}$	1.8×10^{-35}

Thiosulfate solutions at approximately *p*H 7 are titrated *quantitatively* using standard I_3^- solution and starch indicator. The reaction is:

$$2S_2O_3^{-2} + I_3^- = 3I^- + S_4O_6^{-2}$$

In strong acid solution, $S_2O_3^{-2}$ is destroyed as noted above, and in strong basic solution, oxidation to sulfate can take place but the reaction is not stoichiometric:

$$10OH^- + S_2O_3^{-2} + 4I_3^- = 12I^- + 2SO_4^{-2} + 5H_2O$$

E. Carbonate Ion, CO_3^{-2}

When carbonates are acidified the reactions are

$$CO_3^{-2} + 2H^+ = HCO_3^- + H^+ = (H_2CO_3) = H_2O + \mathit{CO}_2$$

Carbonic acid is an unstable, weak diprotic acid similar to sulfurous acid. The solubility of CO_2 in H_2O is 1.50 g/liter at 20 C and 1 atm, so the solution is 0.034 *M*. Most carbonates are water-insoluble but will decompose in acids stronger than H_2CO_3, as shown above. With the exception of the alkali metal carbonates, most others are decomposed by heat to the corresponding oxides.

$$CaCO_3 \overset{\Delta}{=} CaO + \mathit{CO}_2$$

Suspended in water, $CaCO_3$ may dissolve if CO_2 is available,

$$CaCO_3 + \mathit{CO}_2 + H_2O = Ca^{+2} + 2HCO_3^-$$

a reaction of importance in water works engineering. Slightly soluble *calcium carbonate* may thus be caused to change to the more soluble *bicarbonate* by cooling the solution to dissolve more CO_2 and vice versa. Alkali metal bicarbonates are less soluble than the corresponding carbonates. See the discussion on H_2CO_3 in Chapter 7.

Carbonates and bicarbonates are identified by acid decomposition and absorption of CO_2 in lime water ($Ca(OH)_2$) or barytes water ($Ba(OH)_2$) to give a white alkaline earth carbonate precipitate:

$$CO_2 + Ca^{+2} + 2OH^- = \mathbf{CaCO}_{3_W} + H_2O$$

To test for bicarbonate in the presence of carbonate, excess $CaCl_2$ solution is added to precipitate carbonate, as above. The centrate from that is then treated with ammonia and half the (soluble) calcium bicarbonate is converted to insoluble carbonate:

$$Ca^{+2} + 2HCO_3^- + NH_3 = \mathbf{CaCO_3} + NH_4^+ + HCO_3^-$$

Mercuric chloride is also used to distinguish a bicarbonate solution from a carbonate; with the former it gives no reaction, with the latter it forms a brown basic carbonate.

TABLE 22–4. EQUILIBRIUM CONSTANTS FOR SOME CARBONATE REACTIONS

Reactions (in order of decreasing $[CO_3^{-2}]$)	K
$\mathbf{MgCO_3 \cdot 3H_2O} = Mg^{+2} + CO_3^{-2} + 3H_2O$	1×10^{-5}
$\mathbf{Ag_2CO_3} = 2Ag^+ + CO_3^{-2}$	8.2×10^{-12}
$\mathbf{NiCO_3} = Ni^{+2} + CO_3^{-2}$	1.36×10^{-7}
$\mathbf{CaCO_3} = Ca^{+2} + CO_3^{-2}$ (aragonite)	6.9×10^{-9}
$\mathbf{BaCO_3} = Ba^{+2} + CO_3^{-2}$	1.6×10^{-9}
$\mathbf{SrCO_3} = Sr^{+2} + CO_3^{-2}$	7×10^{-10}
$\mathbf{CuCO_3} = Cu^{+2} + CO_3^{-2}$	2.5×10^{-10}
$\mathbf{ZnCO_3} = Zn^{+2} + CO_3^{-2}$	2×10^{-10}
$\mathbf{MnCO_3} = Mn^{+2} + CO_3^{-2}$	8.8×10^{-11}
$\mathbf{FeCO_3} = Fe^{+2} + CO_3^{-2}$	2.11×10^{-11}
$\mathbf{CdCO_3} = Cd^{+2} + CO_3^{-2}$	5.2×10^{-12}
$\mathbf{CoCO_3} = Co^{+2} + CO_3^{-2}$	8×10^{-13}
$\mathbf{PbCO_3} = Pb^{+2} + CO_3^{-2}$	1.5×10^{-13}

Alkali metal carbonates are determined *quantitatively* by titration with standard acid, a first end point noted which corresponds to HCO_3^- formation, $pH \cong 8.3$, and a second end point corresponding to H_2CO_3, $pH \cong 3.8$. Alkaline earth carbonates are decomposed by heating to the oxide and CO_2, loss in weight being used to compute carbonate content.

Laboratory Study of the Group 1 Anions. Solutions of the anions contain 10 mg of ion per milliliter and their preparation is listed in Appendix A12. The student should pay attention to the features of analytical reactions which constitute positive tests for particular anions and also learn something of the interferences and sensitivity of the tests. The same reactions will be used later to test unknowns.

The instructor will comment on the notebook writeup for this work More important reactions are marked ★.

Test 22–1. Decomposition of NO_2^-. (*a*) To 4 drops of test soln., add 4 drops of H_2O and a drop of dil. H_2SO_4. Note that bubbles of nitric oxide appear. What is the brown gas that forms above the soln?

(*b*) To 2 drops of NO_2^-, add 8 drops of H_2O, 2 drops of 0.1 *M* sulfamic acid, a drop of 3 *M* H_2SO_4, and boil briefly. Cool. Neutralize with NH_4OH.

Test for NO_2^- via test 22–5 or another nitrite reaction. Explain.

Test 22–2. Thiourea Test for NO_2^-. To 3 drops of nitrite test soln., add 3 drops of H_2O, a few crystals of thiourea, and a drop of dil. HCl. Mix well. After bubbles of nitrogen have ceased to appear, add a drop of Fe^{+3} soln. To what is the red color due? Dilute the nitrite test soln. and rerun the test. Does the method have good sensitivity? How would one conduct this test if SCN^- were originally present also in the sample?

Test 22–3. Brown Ring Test for NO_2^-. Add a drop of *freshly* prepd. $FeSO_4$ soln. to 2 drops of nitrite soln. and dil. with 6 drops of H_2O. Keeping the tube inclined, carefully let 3–4 drops of dil. HAc or dil. H_2SO_4 run down the incline and form a layer at the tube's bottom. Explain the formation of the dark ring at the interface. (Nitrates give a similar reaction if concd. H_2SO_4 is used. Chromates, iodides, bromides, and ferrocyanides give colored products with iron and are removed by pptn. first with Ag_2SO_4.)

Test 22–4. $K_2Na[Co(NO_2)_6]$ from Nitrite. Mix 4 drops of nitrite test soln. with 3 drops of H_2O, 4 drops of 2 *M* KCl, 4 drops of 0.5 *M* Co^{+2}, and 2 drops of glacial HAc. Warm in a bath. The same yellow Werner compd. that appeared in the tests for Co^{+2} and K^+ slowly ppts. Attachment to cobalt is via the N atoms, as $-NO_2$ groups. Give the equation.

★Test 22–5. Diazo Test for Nitrite. Small amounts of nitrite may be detected by the *diazo or Griess reaction.* (See example 11, Chapter 12.) The interested student may wish to verify the sensitivity of the test.

Dilute the nitrite test soln. 5-fold. Put 2 drops on a spot plate with 2 drops of sulfanilic acid and 2 drops of α-naphthylamine solns. A red color appears due to azo dye formation. Color density and formation time vary with the nitrite concn. Run a blank and compare.

Test 22–6. Oxidation: NO_2^- to NO_3^-. To 4 drops of nitrite soln., add 4 drops of H_2O and 1 drop of dil. H_2SO_4. Dilute the $KMnO_4$ soln. on the shelf by three or four times and add this dropwise to the acidified nitrite, noting the bleaching of permanganate color, which indicates reduction of MnO_4^-. This soln. could now be tested for *nitrate* (outlined under that ion) as proof that a *nitrite* was in the original sample. Write the equation and show via redox potential data that this reaction is expected. Could acidified chlorine water have been used as an oxidant?

Test 22-7. Testing for S^{-2} and H_2S. Put 3 drops of sulfide test soln. in a tube, add 6 drops of H_2O, and a drop of Pb^{+2} test soln. Black PbS is sufficient evidence with even the general anion unknown to report sulfide.

By acidifying samples contg. considerable sulfide, H_2S (POISON!) is detected by odor alone, even in the event other gases are also released.

Several sulfides were mentioned in the descriptive section that normally react slowly with hot dil. HCl but are caused to yield H_2S if Zn metal were present. Prepare one and try the test. Write the equation.

Test 22-8. Oxidation: S^{-2} to SO_4^{-2}. With many oxidizing agents, S^{-2} is oxidized to free sulfur but with some more drastic combinations like HCl + HNO_3, HNO_3 + Br_2, or HNO_3 + $KClO_3$, sulfide is largely converted to sulfate, a change in oxidation state of eight units.

To a mixt. of 2 drops of concd. HCl and 3 of HNO_3, add 2 drops of sulfide test soln. and heat carefully to slowly evap. the liquid. Cool. Add 30 drops of H_2O and 10 drops of $BaAc_2$ soln. and mix. What is the slow-settling, fine, white ppt.? Give equations.

See special experiment 4, part 5 for another test of sulfur-contg. radicals.

Test 22-9. Production of SO_2 and SO_4^{-2} from SO_3^{-2}. Put 5 drops of sulfite test soln. in the gas generating apparatus, Fig. 14–7, add 4 drops of H_2O and 4 drops of 2 *M* HCl, warm the tube, and receive the distillate of gas in 1 ml of clear $Ba(OH)_2$ soln. A white ppt. of $BaSO_3$, contaminated with a little $BaCO_3$ from CO_2 in the air, forms.

To demonstrate that the ppt. is mainly $BaSO_3$ and not $BaCO_3$, add enough HCl to just dissolve it, then add 6–8 drops of satd. Br_2 water, and heat under the hood to expel bromine vapors. A white ppt. $BaSO_4$ (insol. in HCl) forms, showing SO_3^{-2} was oxidized by Br_2. Write equations.

Test 22-10. SO_3^{-2} in the Presence of $S_2O_3^{-2}$. (*a*) Acids decompose thiosulfates to yield $H_2O + S + SO_2$ so the presence of sulfur dioxide gas does not always mean that a sample under test contains sulfite. Sulfite may, however, be pptd. as the calcium salt since CaS_2O_3 is sol., and this residue is then tested for SO_2 release.

Mix 3 drops of each of the two test solns. with 4 drops of H_2O. To this add 5 drops of $CaAc_2$ soln., mix well, and cent. Wash the residue twice using a few drops of H_2O each time and discard the washings. To the solid in the gas generating setup, add 3 drops of H_2O and 6 of dil. HCl, quickly connect the delivery tube, warm, and collect the gas evolved in $Ba(OH)_2$. Again demonstrate as in test 22-9 that SO_4^{-2} is in evidence.

(*b*) Thiosulfates do not give the following test either, but sulfides and sulfites will bleach certain triphenylmethane dyes. Put 2 drops of malachite green on a spot plate and add dropwise a dil. neutral soln. of sulfite (the dye color changes with pH also, see chart of indicators, appendix). The reaction is given as example 10, Chapter 12. How could one remove sulfide in a mixture before this test?

(*c*) Another method has been suggested by Lundin (see references p. 416). If a sample is suspected of contg. other ions such as $S_2O_3^{-2}$, S^{-2}, and CO_3^{-2}, addn. of Sr^{+2} will precipitate only CO_3^{-2} and SO_3^{-2}. This residue is isolated by centrifugation, then warmed with HCl, and the vapors tested with moist starch-iodate paper; SO_2, but not CO_2, reduces IO_3^- to I_2, turning the paper blue.

Test 22–11. Strong Oxidants and SO_3^{-2}. Dilute 6 drops of SO_3^{-2} soln. to 1 ml and in another tube prep. a half ml of a mixt. of either MnO_4^- or CrO_4^{-2} solns. with an equal vol. of 2 M H_2SO_4. Add the oxidizing mixt. dropwise to the sulfite and account for the color change by writing the proper half reactions and $E°$ values from appendix A18.

★***Test 22–12. Decomposition of $S_2O_3^{-2}$.*** In the gas generator, acidify a few drops of thiosulfate test soln. with dil. HCl and pass the gas into a clear soln. of barium hydroxide. What is the white ppt. in the receiver and opalescent suspension in the generator? Write the reactions. Does S^{-2} or SO_3^{-2} interfere?

Test 22–13. $Ag_2S_2O_3$ and its Decomposition. Mix 2 drops of thiosulfate soln. with 3 drops of Ag^+ test soln. on a spot plate, then observe the color changes. Explain with equations. (Excess $S_2O_3^{-2}$ will give the soluble complex, $Ag(S_2O_3)^{-3}$, but this is decomposable as above if boiled.)

Test 22–14. $S_2O_3^{-2}$ in the Presence of SO_3^{-2} and S^{-2}. Mix 4 drops of each of these test solns., then add 6 drops of H_2O. Dropwise put in Zn^{+2} test soln. until pptn. is complete. Centrifuge and discard the white residue of ZnS. To the centrate, add Ca^{+2} test soln. until a new pptn. is complete, and discard the residue of calcium sulfite. (Ca and Sr sulfites are insoluble but their thiosulfates are fairly soluble.) To the centrate add 4 drops of dil. HCl and warm a little. The odor of SO_2 (CAUTION!) and ppt. of S proves $S_2O_3^{-2}$. Alternately, $BaCl_2$ soln. can be used to ppt. $S_2O_3^{-2}$ and leave SO_3^{-2} in soln. after sulfide removal.

★***Test 22–15. CO_3^{-2} in the Presence of SO_3^{-2} and $S_2O_3^{-2}$.*** In the gas generation apparatus, mix 4 drops of each of these 3 test solns., then add dil. $KMnO_4$ dropwise with stirring until a definite pink permanganate color is permanent above the ppt. of brown MnO_2. This treatment oxidizes the sulfur-contg. radicals to sulfate. Now add 3 drops of dil. HCl, quickly insert the delivery tube, and bubble the gas into $Ba(OH)_2$. The generator may be heated to increase the yield. A white residue in the barium soln. which is soluble in HCl but not repptd. by Br_2 treatment (see test 22–9) is proof that the sample contd. carbonate. Give equations.

Calcium hydroxide (lime water) may be used in place of barium hydroxide. The former is less sensitive, but the latter is more prone to interference by reaction with CO_2 in the air. A carbonate sample should give a very definite test, however, not just a trace of turbidity.

THE GROUP 2 ANIONS

F. (Ortho)phosphate Ion, PO_4^{-3}

Of the several acids formed when P_4O_{10} is dissolved in H_2O, H_3PO_4 is the most important. A purer product is obtained by the action of nitric acid on white phosphorous or by reaction of sulfuric acid on a phosphate salt. Upon heating, *phosphoric acid* dehydrates to yield *pyrophosphoric*, $H_4P_2O_7$, and *n-metaphosphoric*, $(HPO_3)_n$, acids in which n is 2, 3, 4, 6, and possibly 1. Solutions of pyro and metaphosphates are converted to orthophosphates on standing. Orthophosphate is the most important P^V radical. Titration of H_3PO_4 with NaOH can be followed by plotting pH versus volume of titrant (pH curve) or by the use of selected indicators. Either shows sharp changes as the first and second H^+ are neutralized. The third is too weak as an acid for accurate titration however. At the methyl orange end point, the salt formed is NaH_2PO_4, *sodium dihydrogen orthophosphate*, or primary sodium phosphate, and at the phenolphthalein point, is Na_2HPO_4, *disodium hydrogen orthophosphate*, or secondary sodium phosphate. Na_3PO_4 is called tertiary or *normal sodium orthophosphate*. Its solutions are strongly basic due to hydrolysis. The phosphates of Na^+, K^+, and NH_4^+ are soluble; most others including those of Li have low solubility. Pure H_3PO_4 can be crystallized from solution by vacuum evaporation; its melting point is 42.3 C. It is a weak acid, $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$.

$$H_3PO_3 + H_2O = 2H^+ + H_3PO_4 + 2e^- \qquad E^\circ = 0.276$$

$$HPO_3^{-2} + 3OH^- = 2H_2O + PO_4^{-3} + 2e^- \qquad E_B^\circ = 1.12$$

Phosphorous and its compounds are derived from phosphate rocks:

$$Ca_3(PO_4)_2 + 3H_2SO_4 \overset{\Delta}{=} 2H_3PO_4 + 3CaSO_4$$

$$Ca_3(PO_4)_2 + 5C + 6SiO_2 \overset{\Delta}{=} 5CO_2 + 6CaSiO_3 + 4P$$

Phosphorous chemistry is complex. The *oxidation states* are (—III) as *phosphine*, PH_3, (—II) as *hydrogen diphosphide*, P_2H_4, (I) as *sodium hypophosphite*, Na_3PO_2, (III) as *phosphorous trioxide*, P_4O_6, (IV) as *phosphorous tetroxide*, P_2O_4, and (V) as *phosphorous pentoxide*, P_4O_{10}. (The tri- and pentoxides were named before the correct formulas were known and the names persist.) Phosphorous and a number of its compounds exhibit allotropy; P has three modifications and P_4O_{10} has four. The phosphorous acids are water soluble, but many of the salts are not. Phosphates are used as fertilizers, as emulsifiers in cheese and ice cream, in water treating chemicals to complex Ca^{+2} and Fe^{+3}, and in cleaning preparations. H_3PO_4 and lime are used in raw sugar syrup purification.

Organic phosphates have also become important: some are used in insecticides (parathion, schradam, systox), while some fluoro organic phosphates form a new series of unusually deadly "nerve" gases for warfare. *Tricresyl phosphate* (T.C.P.) is a gasoline additive. These phosphates are not water soluble but can be made to yield PO_4^{-3} tests after hydrolysis by hot alkalis.

TABLE 22–5. EQUILIBRIUM CONSTANTS FOR SOME PHOSPHATE REACTIONS

Reactions (in order of decreasing $[PO_4^{-3}]$)	K
$Mg(NH_4)PO_4 = Mg^{+2} + NH_4^+ + PO_4^{-3}$	2.5×10^{-13}
$Mn_3(PO_4)_2 = 3Mn^{+2} + 2PO_4^{-3}$	$\sim 10^{-22}$
$Sr_3(PO_4)_2 = 3Sr^{+2} + 2PO_4^{-3}$	1×10^{-31}
$Ca_3(PO_4)_2 = 3Ca^{+2} + 2PO_4^{-3}$	1.3×10^{-32}
$Ba_3(PO_4)_2 = 3Ba^{+2} + 2PO_4^{-3}$	6×10^{-39}
$Fe(PO_4) = Fe^{+3} + PO_4^{-3}$	1.5×10^{-18}
$Pb_3(PO_4)_2 = 3Pb^{+2} + 2PO_4^{-3}$	1×10^{-54}

Large quantities of phosphate are *quantitatively determined* by precipitation as $MgNH_4PO_4$, ignition to $Mg_2P_2O_7$, and weighing in that form. Small quantities of PO_4^{-3} are handled colorimetrically. See the molybdate-benzidine test.

G. Sulfate Ion, SO_4^{-2}

Since the *oxidation state* of S here is (VI), the highest it can attain, sulfate may function only as an oxidizing agent:

$$H_2O + H_2SO_3 = 4H^+ + SO_4^{-2} + 2e^- \qquad E^\circ = -0.20$$

With hot, concentrated *sulfuric acid*, reducing agents liberate sulfur dioxide:

$$2H_2SO_4 + Zn = Zn^{+2} + SO_4^{-2} + H_2O + SO_2$$

Pure H_2SO_4 is an oily liquid only about 2% dissociated. It forms a number of hydrates, as $H_2SO_4 \cdot H_2O$, etc., which are quite stable and account for the speed and efficiency with which the acid dehydrates materials. In dilute water solutions, the first ionization is considered 100% complete and the second is appreciable. SO_3 dissolved in H_2SO_4 is called *fuming sulfuric acid* or oleum, and when hot, the mixture is a powerful oxidizer. H_2SO_4 is made by absorbing SO_3 in H_2SO_4 giving $H_2S_2O_7$, which upon dilution gives more H_2SO_4. The SO_3 is prepared from oxidation of SO_2, which in turn is made by burning sulfur in air. H_2SO_4 costs only a few cents a pound and is industrially very important. It is used to prepare other chemicals like phosphate fertilizers, for pickling metals prior to surface treatment, for absorbing unsaturates and other impurities from alkanes in petroleum refining, in neutralizing basic solutions for the production of synthetic fibers, etc. Natural sulfates like gypsum, $CaSO_4 \cdot 2H_2O$, occur in many minerals and waters and are used as a source of sulfate and in making plaster and cement. With the exception of the sulfates in the following table, the other common ones are fairly soluble.

TABLE 22–6. EQUILIBRIUM CONSTANTS FOR SOME SULFATE REACTIONS

Reactions (in order of decreasing $[SO_4^{-2}]$)	K
$Ag_2SO_4 = 2Ag^+ + SO_4^{-2}$	1.24×10^{-5}
$CaSO_4 \cdot 2H_2O = Ca^{+2} + SO_4^{-2} + 2H_2O$	2.4×10^{-5}
$Hg_2SO_4 = Hg_2^{+2} + SO_4^{-2}$	$\sim 1 \times 10^{-6}$
$SrSO_4 = Sr^{+2} + SO_4^{-2}$	7.6×10^{-7}
$PbSO_4 = Pb^{+2} + SO_4^{-2}$	1.3×10^{-8}
$BaSO_4 = Ba^{+2} + SO_4^{-2}$	1.5×10^{-9}

A number of titrations have been proposed for the *quantitative analysis* of sulfate, using $BaCl_2$, alcohol-water solutions, and indicators like alizarin, but none of these rival the accuracy of the old gravimetric method in which $BaSO_4$ is precipitated, ignited at 800 C, and weighed. The same precipitate is used in qualitative testing to indicate sulfate; it is insoluble in HCl.

H. Chromate, CrO_4^{-2}, and Dichromate, $Cr_2O_7^{-2}$, Ions

Dichromate ion is formed in acid solution, and chromate ion in basic solution. Equilibrium is established between the two as

$$Cr_2O_7^{-2} + H_2O = 2CrO_4^{-2} + 2H^+$$

$$K = [CrO_4^{-2}]^2[H^+]^2/[Cr_2O_7^{-2}] = 2.4 \times 10^{-15}$$

From this it is seen that in an acidic solution, say *p*H 2, the ratio $[CrO_4^{-2}]^2/[Cr_2O_7^{-2}] = 2.4 \times 10^{-11}$ and at a *p*H of 12, the ratio is 2.4×10^9. Further condensation to progressively darker $Cr_4O_{10}^{-2}$ and $Cr_5O_{13}^{-2}$ is known but is of minor importance.

Since chromates and dichromates are good oxidants they cannot be present in solution with good reductants:

$$2Cr^{+3} + 7H_2O = Cr_2O_7^{-2} + 14H^+ + 6e^- \qquad E^\circ = -1.33$$

All chromates and dichromates are colored. Aqueous solutions of CrO_4^{-2} are yellow and of $Cr_2O_7^{-2}$ are orange. Most dichromates are water soluble. The insoluble chromates in Table 22–7 dissolve in strong acid. The chromates of Hg^{+2}, Fe^{+2}, Mn^{+2}, and Sr^{+2} are a little more water soluble.

TABLE 22–7. EQUILIBRIUM CONSTANTS FOR SOME CHROMATE REACTIONS

Reactions (in order of decreasing $[CrO_4^{-2}]$)	K
$CaCrO_4 = Ca^{+2} + CrO_4^{-2}$	7.1×10^{-4}
$SrCrO_4 = Sr^{+2} + CrO_4^{-2}$	3.6×10^{-5}
$Hg_2CrO_4 = Hg_2^{+2} + CrO_4^{-2}$	$\sim 2 \times 10^{-9}$
$Ag_2CrO_4 = 2Ag^+ + CrO_4^{-2}$	1.9×10^{-12}
$BaCrO_4 = Ba^{+2} + CrO_4^{-2}$	8.5×10^{-11}
$PbCrO_4 = Pb^{+2} + CrO_4^{-2}$	2.0×10^{-16}

Chromates are used in tanning, in yellow paints, and as corrosion preventatives in water treatment.

Chromates and dichromates are determined *quantitatively* by reaction with excess I^- to give a stoichiometric amount of I_3^-, which is titrated with $S_2O_3^{-2}$ using starch indicator. For small amounts of chromium in the (VI) state, diphenylcarbazide is an excellent colorimetric reagent.

See Chapter 17 for further Cr chemistry.

I. Borate Ions, BO_2^-, BO_3^{-3}, $B_4O_7^{-2}$

These ions contain boron at an *oxidation state* of (III) and depending on temperature, *p*H and concentration, one or another predominates in solution. Acidification of borates gives H_3BO_3, *orthoboric*, or boracic acid. Heating converts it at 100 C to HBO_2, *metaboric acid*, then to $H_2B_4O_7$, *tetra-* or *pyroboric acid*, at 140 C, and finally to B_2O_3, *boric oxide*, the common anhydride. Important reactions are,

$$B + 4OH^- = BO_2^- + 2H_2O \quad \text{(only in strong base)}$$

$$B_2O_3 + 2OH^- = 2BO_2^- + H_2O \quad \text{(only in strong base)}$$

$$H_3BO_3 + OH^- = 2H_2O + BO_2^- = HBO_2 + OH^- + H_2O$$

$$BO_3^{-3} + 2H_2O = 2OH^- + H_2BO_3^-$$

$$2H_3BO_3 + 2BO_2^- = B_4O_7^{-2} + 3H_2O = HBO_2 + 2BO_2^- + 2H_2O$$

$$Ba^{+2} + B_4O_7^{-2} + 5H_2O = 2H_3BO_3 + Ba(H_2BO_3)_2 (\text{or } Ba(BO_2)_2 \cdot 2H_2O)$$

H_3BO_3 is a waxy solid, slightly soluble in H_2O at room temperature, giving reactions of a very weak monoprotic acid. It is used as an antiseptic. Borax, *sodium tetraborate decahydrate*, $Na_2B_4O_7 \cdot 10H_2O$, is the most common boron derivative. It is used in the manufacture of cleaners, water softening chemicals, soaps, glass, embalming fluid, etc. Alkali metal borates are soluble but others are usually only slightly soluble in water, though soluble in strong acids since boric acid is very weak.

Recent work in boron chemistry has been along two dissimilar lines: "super" abrasives and fuels. In 1957 the preparation of "Borazon," *cubic boron nitride*, was announced by General Electric. The cubic form was not known previously, and the structure was proved by X-ray diffraction. It is harder than diamond and much superior in oxidation resistance. It will be used in cutting tools. Boron hydrides, *diborane* B_2H_6, *pentaborane* B_5H_9, and *decaborane* $B_{10}H_{14}$, are being used as rocket fuels. When burned with liquid O_2, 40% more thrust is developed than when kerosene is burned under the same conditions. These hydrides are hypergallic in air, are toxic, and cost up to several thousand dollars per pound at this time. Some *borate esters* are added to gasoline to improve antiknock quality for motor car use.

One qualitative test for borates is acidification and treatment with an alcohol to form a volatile borate ester. When this is vaporized and burned, it imparts a green color to the flame:

$$B_4O_7^{-2} + 5H_2O + H_2SO_4 = H_3BO_3 + SO_4^{-2}$$

$$H_3BO_3 + 3C_2H_5OH \overset{\Delta}{=} 3H_2O + B(OC_2H_5)_3$$

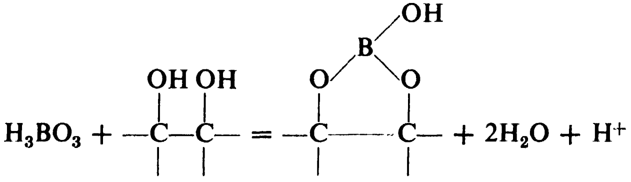
$$2B(OC_2H_5)_3 + 5O_2 \overset{\Delta}{=} 5H_2O + 4CO_2 + B_2O_3$$

Another test is with turmeric paper, which gives a brown color with borates + HCl, and after drying and rewetting with NaOH, the color turns dark green. Oxidizing agents interfere because they bleach the reagent. These are tests 22–23 and 22–25.

TABLE 22-8. EQUILIBRIUM CONSTANTS FOR SOME BORATE REACTIONS

Reactions (in order of decreasing $[BO_2^-]$)	K (approximate)
$LiBO_2 = Li^+ + BO_2^-$	4.5×10^{-1}
$Ca(BO_2)_2 \cdot 6H_2O = Ca^{+2} + 2BO_2^- + 6H_2O$	1.2×10^{-4}
$AgBO_2 = Ag^+ + BO_2^-$	3.6×10^{-3}
$Mn(BO_2)_2 \cdot 2H_2O = Mn^{+2} + 2BO_2^- + 2H_2O$	3.9×10^{-7}

Borax can be titrated with standard acid using methyl orange indicator. It acts like other salts of weak acids. Small amounts of borates are *quantitatively* found using colorimetric reagents. (See Chapter 12 on organic reagents for borates.) Borates in moderate amounts may also be determined by reaction with a poly alcohol like glycerol or mannitol and titration of H^+ liberated using standard base:



J. Fluoride Ion, F^-

HF is not a reducing acid as the other halogen acids may be, since no chemical oxidant is powerful enough to liberate F_2 from fluorides. In the vapor state it forms polymers like $(HF)_n$, where n has an average value of 6 at room temperature. With H_2O, it forms an azeotrope boiling at 120 C, which is about a 12 M solution. Both the vapor and solutions produce slow healing burns. HF will dissolve glass and silicate minerals, giving H_2SiF_6 and so is handled in lead lined equipment and dispensed in wax or plastic bottles. Fluoride ion forms strong complexes such as AlF_6^{-3}, BeF_4^{-2}, SnF_6^{-2}, FeF_6^{-3}, and ZrF_6^{-3}.

Hydrofluoric acid is used as an etchant and in the pickling of alloys like stainless steel after heat treating. *Sodium fluoride* is used in fluoridation of water, as F^- at a concentration of 0.8–1.6 ppm has been found to be beneficial for children's teeth; concentrations much greater result in mottled enamel, however. Teflon is a commercial polymer $\text{—}(CF_2\text{—}CF_2)_x\text{—}$ which is unusually inert and high melting. It is used as a gasket material, etc., in the most corrosive atmospheres.

OF_2, NF_3, and F_2 have been tried as rocket propellant oxidizers. Fluorine burning with kerosene, hydrazine, or liquid hydrogen gives higher energies than liquid ozone and the same fuels. Liquid F_2 is transported in nickle alloy containers kept cool with jackets of liquid nitrogen.

The H—F bond has probably the highest heat of formation of any measured; even solid fluorine and liquid hydrogen at -252.5 C explode when mixed. HF is the most associated substance known in aqueous solution. The equilibria are:

$$HF = H^+ + F^- \qquad K_1 = 6.71 \times 10^{-4}$$

$$HF + F^- = HF_2^- \qquad K_2 = 5.1$$

and because of this, HF is a weak acid, in sharp contrast to other halogen acids of the type HX. Oxygen fluorides are OF_2 and O_2F_2; the former, more common, is made by bubbling fluorine gas into 0.5 *M* NaOH.

Fluorine is one of the strongest oxidants known and is prepared only by electrolysis:

$$2F^- = F_2 + 2e^- \qquad E^\circ = -2.8$$

The fluorides of silver and the alkali metals are soluble, but most others are not, though they dissolve in strong acids.

TABLE 22–9. EQUILIBRIUM CONSTANTS FOR SOME FLUORIDE REACTIONS

Reactions (in order of decreasing $[F^-]$)	*K*
$BaF_2 = Ba^{+2} + 2F^-$	2.4×10^{-5}
$MgF_2 = Mg^{+2} + 2F^-$	$\sim 8 \times 10^{-8}$
$PbF_2 = Pb^{+2} + 2F^-$	$\sim 4 \times 10^{-8}$
$SrF_2 = Sr^{+2} + 2F^-$	7.9×10^{-10}
$CaF_2 = Ca^{+2} + 2F^-$	1.7×10^{-10}

Larger quantities of fluoride can be segregated for testing by distillation from sulfuric acid in glass, as H_2SiF_6, and titrated *quantitatively* with thorium nitrate using zirconyl-alizarin indicator. Small amounts are done colorimetrically using the same reagent. (See special experiment 3.) Al^{+3} is an interference, since it is capable of complexing F^- and preventing its reaction. PO_4^{-3} and $C_2O_4^{-2}$ also interfere by bleaching the reagent to a yellow color just as F^- does. All these hindrances are obviated by distilling, as mentioned above, and testing the distillate for F^-.

K. Oxalate Ion, $C_2O_4^{-2}$

Oxalic acid is readily crystallized from aqueous solution as the dihydrate, $H_2C_2O_4 \cdot 2H_2O$. Strong heating decomposes it to CO, CO_2, and H_2O. It is one of the stronger weak acids, $K_1 = 3.8 \times 10^{-2}$, $K_2 = 5.0 \times 10^{-5}$. Oxalates in general are not too water soluble but will dissolve in strong acids because $H_2C_2O_4$ is displaced. Some oxalates dissolve in an excess of $C_2O_4^{-2}$ because of complex formation.

Qualitative testing of oxalate is best done by showing that Ca^{+2} precipitates white *calcium oxalate* which is soluble in dilute sulfuric acid (a little $CaSO_4$ may precipitate) and the oxalic acid produced decolorizes potassium permanganate solution:

$$CaC_2O_4 + 2H^+ + SO_4^{-2} = Ca^{+2} + SO_4^{-2} + H_2C_2O_4$$

$$5H_2C_2O_4 + 2MnO_4^- + 6H^+ = 8H_2O + 10CO_2 + 2Mn^{+2}$$

TABLE 22–10. EQUILIBRIUM CONSTANTS FOR SOME OXALATE REACTIONS

Reactions (in order of decreasing $[C_2O_4^{-2}]$)	K
$MgC_2O_4 = Mg^{+2} + C_2O_4^{-2}$	8.6×10^{-5}
$SrC_2O_4 \cdot H_2O = Sr^{+2} + C_2O_4^{-2} + H_2O$	5.61×10^{-8}
$BaC_2O_4 \cdot 2H_2O = Ba^{+2} + C_2O_4^{-2} + 2H_2O$	1.5×10^{-8}
$CdC_2O_4 = Cd^{+2} + C_2O_4^{-2}$	1.5×10^{-8}
$CaC_2O_4 \cdot H_2O = Ca^{+2} + C_2O_4^{-2} + H_2O$	1.3×10^{-9}
$PbC_2O_4 = Pb^{+2} + C_2O_4^{-2}$	8.3×10^{-12}

Sodium oxalate is synthesized commercially by heating CO and NaOH in an autoclave; sodium formate is an intermediate. Oxalates are used in tanning, in certain cleaning preparations, and in dye manufacture.

Quantitatively, oxalates are precipitated as CaC_2O_4 and ignited to and weighed as CaO, or the calcium oxalate is dissolved in H_2SO_4 and the oxalic acid titrated, as shown above, with standard permanganate.

Laboratory Study of the Group 2 Anions

★***Test 22–16. Ammonium Molybdophosphate.*** To 4 drops of PO_4^{-3} test soln. add 4 drops of H_2O and 4 of concd. HNO_3. Shake. Then add 8 drops of ammonium molybdate, $(NH_4)_6Mo_7O_{24}$, and heat the tube in a water bath for a few min. A slow-forming yellow ppt. is the ammonium salt of a heteropoly ion. (See Chapter 4.) This material has a variable composition dependent upon pptn. conditions, but the ratio of PO_4 to MoO_3 is 1/12 and the accepted formula is $(NH_4)_3[P(Mo_3O_{10})_4] \cdot 2HNO_3 \cdot 2H_2O$. The complex radical is sometimes given as $(PO_4 \cdot 12MoO_3)^{-3}$. The ammonium molybdate reagent contains some NH_4NO_3, furnishing the common nitrate ion to decrease the solub. of the ppt. A known should be run since the reagent deteriorates slowly upon standing. Arsenates, which are not considered here, also give the test but may be treated first with CH_3CSNH_2 and NH_4I in acid soln. to ppt. As_2S_3.

Test 22–17. Reactions of Ag^+, Ba^{+2}, Ca^{+2}, Mg^{+2}, and Fe^{+3} with PO_4^{-3}.

(*a*) Put 4 drops of PO_4^{-3} soln. in a test tube, add a drop of dil. NH_4OH and 3 drops of Ba^{+2} test soln. Repeat using Ca^{+2} and Mg^{+2} in place of Ba^{+2}. What are the ppts.? Omitting the ammonia, which would complex silver, show that yellow silver phosphate, Ag_3PO_4, is also pptd. Try the solub. of these residues in 6 *M* HCl. Write the equations.

(*b*) To 6 drops of Fe^{+3} soln. add a drop of 3 *M* H_3PO_4. Note the colors of the soln. and the ferric phosphate ppt. Now, with stirring, add more H_3PO_4 dropwise and describe the change. Soluble complex acids of the type $Fe(HPO_4)(H_2PO_4)$ and $Fe(H_2PO_4)_3$ are present. Try the SCN^- test for Fe^{+3} and explain.

How does PO_4^{-3} hinder the analysis of Fe^{+3} in a general unknown? How could the phosphate complexes be decomposed so that one could get a good iron test? Try a method you propose and report its result.

Test 22–18. Molybdophosphate-Benzidine Oxidation-Reduction. (*a*) A sensitive variation of test 22–16 is treatment of the molybdophosphate with benzidine. The organic reagent is oxidized to *benzidine blue* (example 8, Chapter 12), and the heteropoly ion is reduced to *molybdenum blue* (test 20–6), the result being a dark blue color even with quantities of phosphate too small to give a ppt. with ammonium molybdate. Arsenates and free molybdic acid do not give the test.

Put a drop of dil. phosphate soln. on a spot plate and add a drop of ammonium molybdate and a drop of benzidine. In the next depression on the plate, put 2 drops of dil. NH_4OH. With a micro stirring rod, transfer small quantities of ammonium hydroxide into the other soln. A dark blue coloration is a positive reaction.

(*b*) Modification is possible using spot technique on filter paper, or other reducing agents like $SnCl_2$ in HCl. Try a variation and report the results. The concn. limit using Sn^{II} on the molybdophosphate is about 0.1 ppm PO_4^{-3}.

★***Test 22–19. $BaSO_4$ and its Solubility.*** Add 6 drops of H_2O to 4 drops of SO_4^{-2} soln., then add 3 drops of Ba^{+2} test soln., and shake. Centrifuge and test the solub. of the residue in hot 6 *M* HCl. How does this distinguish sulfate among ppts. of the other group 2 barium and calcium salts? The method outlined in part 2(*b*) of special experiment 4 illustrates one method of confirming the ppt's identity.

Test 22–20. Phenolphthalein-Barium Carbonate Test for SO_4^{-2}. In a crucible, evap. 6 drops of an Na_2SO_4 soln. with 50 mg of solid $BaCO_3$ by heating on a water bath. Allow it to cool when evapd., then add a drop of H_2O and a drop of 1% phenolphthalein. A pink coloration shows that the *p*H has increased due to formation and subsequent hydrolysis of a sol. carbonate produced from a transposition reaction. Write the equations. The concn. limit is about 150 ppm SO_4^{-2}.

★***Test 22–21. $BaCrO_4$; Oxidation to CrO_5.*** To 4 drops of chromate soln., add 2 drops of 2 *M* NaAc, 6 drops of H_2O and, 5 drops of Ba^{+2} test soln. centrifuge and wash the residue, rejecting the washings. Show that the $BaCrO_4$ is sol. in a few drops of dil. HNO_3. To this orange soln., now contg. dichromate ion predominantly, add a ml of H_2O and 5 drops of *n*-butyl alcohol. Put in 5 drops of 3% H_2O_2 and shake cautiously. The appearance of a blue color in the alcohol layer is due to peroxychromic anhydride, CrO_5.

Test 22–22. $Cr_2O_7^{-2}$ as an Oxidizing Agent. To 6 drops of 0.25 *M* $SnCl_4^{-2}$ soln., add 2 drops of 6 *M* H_2SO_4 and 4 drops of H_2O. Now add $Cr_2O_7^{-2}$ or CrO_4^{-2} soln. dropwise and note the evidence of reaction. Write the equations and relate to their oxidation potentials. To what is the green color due?

★***Test 22–23. Ethyl Borate.*** Mix 5 drops of $B_4O_7^{-2}$ test soln. with 8 drops of ethyl alcohol in a crucible. Add 3 drops of con. H_2SO_4, stir, then warm gently. Ignite the ethyl borate vapors and note the green flame, characteristic of B_2O_3. **Do not inhale the fumes!** The color is best observed in a semidark room. Methyl alcohol is a slightly more sensitive reagent. What are the reactions? Why must Cu^{+2} and Ba^{+2} be removed, if present, prior to making this test?

Test 22–24. Precipitation and Solution of Barium Metaborate. Calcium and barium metaborates are sol. in excess reagent, strong acids, or ammonium solns. Demonstrate this as follows: put 1 ml of $B_4O_7^{-2}$ soln. in a tube, add Ba^{+2} until a heavy ppt. is present, then divide it among 3 tubes. To one add 5 drops of 6 *M* HCl, to another 10 drops of Ba^{+2} soln., and to the last add 75 mg of solid NH_4Cl. Stir each and note the results.

Test 22–25. Turmeric Test for Borates. On a spot plate make a mixt. of a few drops of borate soln. and a drop of 6 *M* HCl. Put 2 drops of this on a piece of turmeric paper and dry it by waving over a low flame. Note the color. Now add a drop of 0.25 *M* NaOH to the spot and place another NaOH drop on another part of the paper. Compare the test spot color with the latter "blank." What substances interfere if not removed first? The reaction will detect as little as 1 ppm boron.

Test 22–26. Organic Reagents for Borates. A number of excellent organic reagents are capable of detecting low concns. of boron (as borates) without interference by moderate quantities of other common ions except strong oxidizing agents. (See example 3, Chapter 12, and part 1 of special experiment 8.)

(*a*) Put a drop of H_2O in one depression of a spot plate, a drop of 1 : 10 borate soln. in another, and a drop of undil. borate soln. in a third. To each, in order given, add a drop of concd. HCl and 2 drops of concd. H_2SO_4. Wait a minute for any NO_3^- which might be present to be decomposed, since it bleaches the reagent. Now add a drop of carmine soln. (appendix A15) to each. Give the plate a circular swirling motion to mix each spot, then note the color changes.

(*b*) Repeat using quinalizarin soln. instead of carmine.

Both methods are used in quant. colorimetry for boron.

★***Test 22–27. Alizarin–Zirconyl Test for F^-.*** This test will detect 0.1 ppm F^- and is used quantitatively for fluoride in the range 0.1–3 ppm. Larger concns. give a uniform color. Although this range is small, it is the important one in water works chemistry. See example 5, Chapter 12, p. 194, and special experiment 3.

(*a*) Put 1 drop of F^- soln. in a tube and add 29 drops of H_2O; in a second tube put 2 drops of F^- and 28 drops of H_2O; in a third put 8 drops of F^- and 22 drops of H_2O; in a fourth, put 2 ml of tap water; and in a last, put 2 ml of distilled water. To each add 2 drops of alizarin-zirconyl reagent (appendix A15) and shake. After 15–30 min observe the colors by looking through the tubes vertically as they are held before a white background. Note the color gradations.

(*b*) Oxalate and phosphate were mentioned in the fluoride discussion as ions which give false tests with the fluoride reagent. Try one or both and compare with previous colors. Suggest a way to remove either or both and give your plan a trial. Describe the results.

Test 22–28. Precipitation of CaF_2. To 4 drops of F^- soln., add 4 drops of H_2O, then 4 drops of Ca^{+2}. Centrifuge. To a part of the *centrate* try test 22–27. Make a 1:5 diln. with some of the remaining centrate and repeat test 22–27. What has been demonstrated?

Test 22–29. Etching Glass. With large quantities of F^- in a sample, this cumbersome method is sometimes used but it has been largely replaced by test 22–27 or other color tests of that principle.

Mix 500 mg of a solid fluoride with 2 ml of 6 *M* H_2SO_4 in a small lead dish in the hood. Cover it with a waxed glass plate, through which coating has been scratched some identifying marks. Warm the dish intermittently. After 2 hours remove the wax by warming and wiping, then examine the clean glass surface for evidence of HF attack.

★***Test 22–30. Precipitation of CaC_2O_4; Oxidation with MnO_4^-.*** To 6 drops of oxalate soln., add 4 drops of 6 *M* HAc, then calcium test soln. until pptn. is complete. Centrifuge, save the residue. To this add 6 drops of H_2O and 2 drops of 6 *M* H_2SO_4 and stir to dissolve the CaC_2O_4. Warm the tube, then add 0.01 *M* $KMnO_4$ dropwise and observe the decolorization denoting oxidation of oxalate. What gas is given off?

Test 22–31. Thermal Decomposition of $H_2C_2O_4$. In a gas generating tube, *in the hood*, heat a mixt. of 4 drops of oxalate soln. and 4 drops of concd. H_2SO_4, and bubble the distillate into $Ca(OH)_2$ or $Ba(OH)_2$. What gases are given off? Which one reacts to produce the white precipitate? How could one analyze for the other?

Test 22–32. Resorcinol Test for $C_2O_4^{-2}$. The reaction for this test is described as example 14, Chapter 12. To 4 drops of oxalate soln. in a small beaker, add a drop of 6 *M* H_2SO_4 and 4 drops of H_2O, then cautiously sprinkle in a little magnesium powder. When the metal has dissolved, pour the soln. into a test tube, add 2 drops of resorcinol reagent, mix, then carefully allow 6–7 drops of concd. H_2SO_4 to run down the side and form a layer at the bottom. A blue to red layer indicates glycolic acid, which in turn means a positive test for oxalate. The concn. limit is about 20 ppm $C_2O_4^{-2}$. Other common organic acids such as acetic and citric do not give the test.

THE GROUP 3 ANIONS

L. Chloride Ion, Cl^-

This ion is a very weak reductant:

$$2Cl^- = Cl_2 + 2e^- \qquad E^\circ = -\,1.36$$

Oxidation to give chlorine gas occurs only with such potent oxidizers as F_2, MnO_4^-, BiO_3^-, and $S_2O_8^{-2}$. HCl is a pungent gas made by direct combination of the elements or by heating NaCl with concentrated sulfuric acid:

$$H_2 + Cl_2 = 2HCl$$

$$NaCl + H_2SO_4 \overset{\Delta}{=} NaHSO_4 + HCl$$

HCl gas is not very soluble in nonionizing solvents but is quite soluble in water and yields *hydrochloric acid,* which in technical grade is known as muriatic acid. Infrared absorption study of the aqueous solutions gives no bands characteristic of HCl, showing that complete hydration has taken place. *Oxides of chlorine* are Cl_2O, ClO(?), ClO_2, and Cl_2O_7 in which the *oxidation states* of Cl are respectively (I), (II), (IV), and (VII). The most familiar valence, however, is (—I) as typified by chloride ion, Cl^-. It is detected, after oxidation or previous precipitation of interfering ions (such as Br^-, I^-, SCN^-, and S^{-2}) by reaction with Ag^+, with which it forms a curdy white precipitate, soluble in NH_4OH. The $Ag(NH_3)_2^+$ so formed is reprecipitated as silver chloride with HNO_3. See Chapter 15 for reactions.

With the exception of SbOCl and the chlorides in Table 22–11, most are water soluble and all show increased solubility in solutions containing excess Cl^- due to complex ion formation. The chlorides of Pb^{+2}, Hg^{+2}, and Cd^{+2} are weak electrolytes.

TABLE 22–11. EQUILIBRIUM CONSTANTS FOR SOME CHLORIDE REACTIONS

Reactions (in order of decreasing [Cl^-])	*K*
$PbCl_2 = Pb^{+2} + 2Cl^-$	1.6×10^{-5}
$CuCl = Cu^+ + Cl^-$	3.2×10^{-7}
$BiOCl = BiO^+ + Cl^-$	7×10^{-9}
$AgCl = Ag^+ + Cl^-$	2.8×10^{-10}
$Hg_2Cl_2 = Hg_2^{+2} + 2Cl^-$	1.1×10^{-18}

There are many uses for chlorides such as NaCl and $CaCl_2$ and these are mentioned with discussions of the cations.

Quantitatively, chloride is determined by titration with standard $AgNO_3$ or by precipitation and weighing as AgCl.

M. Bromide Ion, Br^-

HBr is a colorless gas and like HCl is not very soluble in nonassociating solvents but dissolves in H_2O to give a strong acid. Anhydrous liquid HBr is no more ionized than is H_2O. Bromides are similar to chlorides in general properties; the bromides of the group 1 cations are less soluble, however, and Br^- is more readily oxidized than Cl^-. Bromides occur in natural brines and Br_2 is obtained by Cl_2 displacement commercially:

$$Cl_2 + 2Br^- = Br_2 + 2Cl^-$$

Other, more expensive oxidizing agents one could employ here include HClO, $Cr_2O_7^{-2}$, MnO_4^-, PbO_2, MnO_2, etc., in acid solution. The bromide–bromine partial is

$$2Br^- = Br_{2_{(aq)}} + 2e^- \qquad E^\circ = -1.09$$

HBr is not made from direct combination of elements because the low heat of formation (4.8 kcal/mole) precludes a good yield. It is best prepared by distillation from a mixture of bromide salt and H_3PO_4, the latter used for its high boiling point and nonoxidizing character. AgBr is used in some photographic emulsions and a few bromides are used in medicine. HBr finds little use.

Qualitatively, bromide is detected by precipitation as light yellow AgBr, which is soluble only in fairly concentrated NH_4OH or by oxidation to Br_2, which is extracted in CCl_4, giving a brown solution.

TABLE 22–12. EQUILIBRIUM CONSTANTS FOR SOME BROMIDE REACTIONS

Reactions (in order of decreasing $[Br^-]$)	K
$PbBr_2 = Pb^{+2} + 2Br^-$	4.6×10^{-6}
$CuBr = Cu^+ + Br^-$	6×10^{-9}
$AgBr = Ag^+ + Br^-$	5×10^{-13}
$Hg_2Br_2 = Hg_2^{+2} + 2Br^-$	1.3×10^{-22}

Quantitatively, bromide may be determined by precipitation with Ag^+ and weighing the AgBr, or by titration with standard Ag^+.

N. Iodide Ion, I^-

Iodide is a reducing agent in acid solution, where, depending upon the oxidizer's strength, it may give *iodine* or *iodate*. These partials are important in understanding the selective oxidation of I^- in the presence of other oxidizable substances:

$$2I^- = I_2 + 2e^- \qquad E^\circ = -0.54$$

$$I^- + 3H_2O = IO_3^- + 6H^+ + 6e^- \qquad E^\circ = -1.09$$

For instance Table A18 shows that HNO_2 is capable of oxidizing I^- but not Br^- or Cl^-. Reaction equations can be formulated accordingly:

$$2H^+ + 2HNO_2 + 2I^- = I_2 + 2\mathit{NO} + 2H_2O$$

The I_2 can be extracted with CCl_4 and the aqueous layer tested for other ions like Br^-.

Nonassociating solvents such as $CHCl_3$ and CCl_4 give purple solutions with iodine, others such as H_2O and alcohols give brown solutions containing triiodide ion, I_3^-. I_2 is quite soluble in aqueous I^- solution for that reason. Other iodides also form complexes with excess I^- which are soluble:

$$Hg^{+2} + 4I^- = \mathbf{HgI_{2_R}} + 2I^- = HgI^{-2}_{4_{Cl}}$$

With cupric ion, an oxidation-reduction takes place and iodine and cuprous iodide precipitate. If sulfite is present, the iodine is reduced to iodide again, leaving only the CuI precipitate.

$$SO_3^{-2} + 2OH^- + 2Cu^+ + 2I^- = \mathbf{2CuI_{\mathit{W}}} + SO_4^{-2} + H_2O$$

Iodine reacts slowly with water to give iodide and *hypoiodous acid*; the latter's decomposition is aided by light thus promoting I_2 hydrolysis.

$$I_2 + H_2O = I^- + HIO + H^+$$
$$2HIO = 2I^- + 2H^+ + O_2$$

Pure *hydriodic acid* is obtained by heating an iodide with concentrated phosphoric acid.

$$I^- + H_3PO_4 \overset{\Delta}{=} \mathit{HI} + H_2PO_4^-$$

The solubilities of the slightly soluble iodides are generally lower than the corresponding chlorides and bromides, but most iodides are fairly soluble.

TABLE 22-13. EQUILIBRIUM CONSTANTS FOR SOME IODIDE REACTIONS

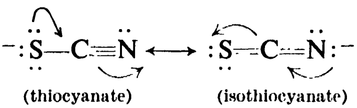
Reactions (in order of decreasing $[I^-]$)	K
$\mathbf{PbI_2} = Pb^{+2} + 2I^-$	8.3×10^{-9}
$\mathbf{CuI} = Cu^+ + I^-$	1.1×10^{-12}
$\mathbf{AgI} = Ag^+ + I^-$	8.5×10^{-17}
$\mathbf{Hg_2I_2} = Hg_2^{+2} + 2I^-$	4.5×10^{-29}

Iodides are isolated from sea plants and natural saline deposits from which the element is obtained by Cl_2 displacement. I_2 in alcohol is a standard antiseptic and sundry iodides are compounded in medicines. Some metals are purified via their iodides, see zirconium in Chapter 20, for instance.

Iodides are *determined quantitatively* by oxidation to I_2 and titration with standard $Na_2S_2O_3$, using starch indicator, or gravimetrically as AgI.

O. Thiocyanate (Sulfocyanate) Ion, —SCN^-

Resonance in this ion shows the possibility of attachment through either S or N and both series of salts are known. (See discussion of manner of attachment isomers, Chapter 4.)



In water solutions of thiocyanates, however, Raman spectrum shows only the triple bonded form. Pure HSCN is prepared by reaction between KSCN and $KHSO_4$ in cold solution, but is of little use. It polymerizes to a yellow solid upon heating and in aqueous solution is about as strong an acid as HCl. Thiocyanates are affected by heat and reducing or oxidizing agents. Products of SCN^- decomposition include C, S, NH_3, H_2S, NCO^-, HCN, SO_2, SO_3^{-2}, NH_4^+, SO_4^{-2}, CS_2, COS, CH_3NH_2, etc.

Most thiocyanates are water soluble and the slightly soluble ones increase in solubility with excess SCN^- by forming complexes.

TABLE 22-14. EQUILIBRIUM CONSTANTS FOR SOME THIOCYANATE REACTIONS

Reactions (in order of decreasing [SCN^-])	*K*
$Hg(SCN)_2 = Hg^{+2} + 2SCN^-$	4×10^{-9}
$AgSCN = Ag^+ + SCN^-$	1×10^{-12}
$CuSCN = Cu^+ + SCN^-$	4×10^{-14}
$Hg_2(SCN)_2 = Hg_2^{+2} + 2SCN^-$	3×10^{-20}

With Fe^{+3}, thiocyanate gives $Fe(SCN)^{+2}$ (and possibly other ions) whose red color is a good qualitative test for either Fe^{+3} or SCN^-. With Hg^{+2}, thiocyanate gives a white precipitate of $Hg(SCN)_2$ which expands greatly on heating due to polymer formation (fourth of July "snakes") and simultaneous gas release. With Co^{+2} and acetone, SCN^- yields a blue cobalt complex (test 17–10), and with Ag^+, white AgSCN precipitates. This, when heated with dilute HCl and Fe^{+3}, forms AgCl and the red ferric-thiocyanate color. Like $S_2O_3^{-2}$ and S^{-2}, SCN^- catalyzes the azide-iodide reaction (special experiment 6, part 5) which can also be used as a qualitative testing method.

Thiocyanates are prepared by heating cyanides with sulfur and as a by-product in coking. Their uses are limited.

With regard to *quantitative analysis*, thiocyanates are gravimetrically determined as $BaSO_4$ (after oxidation to SO_4^{-2}), by precipitation and weighing of AgSCN, or by colorimetry using the ferric complex.

P. Ferrocyanide [Hexacyanoferrate(II)] Ion, $[Fe(CN)_6^{-4}]$

This ion is a mild reducing agent, as ferrous iron is capable of losing an electron to yield the ferricyanide, hexacyanoferrate(III), ion containing ferric iron:

$$[Fe(CN)_6^{-4}]_{Y} = [Fe(CN)_6^{-3}]_{Or} + e^- \qquad E^\circ = -0.36$$

These cyano complexes are quite stable (K_{ins} for $Fe(CN)_6^{-4} = 10^{-42}$), except in the presence of hot alkalis or acids. The latter produce the weak acid HCN:

$$[Fe(CN)_6^{-4}] + 6H^+ = Fe^{+2} + 6HCN$$

$H_4[Fe(CN)_6]$ can be prepared by acidification of an alkali metal ferrocyanide solution, ether extraction, and solvent evaporation. It is a crystalline solid which decomposes in solution or moist air to yield some Fe^{+3} which reacts with the remaining ferrocyanide to produce a dark blue solid called "Prussian blue," $KFe[Fe(CN)_6]\cdot H_2O$. This reaction is utilized in blue-print paper, which contains ferric citrate and ammonium ferricyanide. Citrate reduces ferricyanide to ferrocyanide, which in turn combines with ferric ion when catalyzed by light.

The first two protons are readily ionizable from $H_4Fe(CN)_6$, whereas the last two show weaker acidity: $K_3 = 10^{-3}$, $K_4 = 5 \times 10^{-5}$.

Most ferrocyanides are colored and only slightly water soluble, the colors of salts of Hg_2^{+2}, Fe^{+2}, Fe^{+3}, Cu^{+2}, Cr^{+3}, Mn^{+2}, Co^{+2}, Ni^{+2}, Th^{IV}, Ti^{IV}, UO_2^{+2}, for example, being of value in identification of the cation present. $K_4[Fe(CN)_6]$, the most common ferrocyanide, is prepared as a by-product from coking. Many double salts like $K_2Zn[Fe(CN)_6]$ are made from it and are useful in precipitations for analytical separations. With Fe^{+2} and K^+, ferrocyanide yields a white precipitate of $FeK_2[Fe(CN)_6]$, which air oxidizes to Prussian blue; with Ag^+, ferrocyanide forms white $Ag_4[Fe(CN)_6]$ which is insoluble in ammonia but is converted to red $Ag_3[Fe(CN)_6]$ when heated gently with concentrated HNO_3, and that

TABLE 22–15. EQUILIBRIUM CONSTANTS FOR SOME FERROCYANIDE REACTIONS

Reactions (in order of decreasing $[Fe(CN)_6^{-4}]$)	K (approximate)
$CaK_2[Fe(CN)_6] = Ca^{+2} + 2K^+ + [Fe(CN)_6^{-4}]$	1.2×10^{-2}
$Mg(NH_4)_2[Fe(CN)_6] = Mg^{+2} + 2NH_4^+ + [Fe(CN)_6^{-4}]$	9.1×10^{-3}
$Ca(NH_4)_2[Fe(CN)_6] = Ca^{+2} + 2NH_4^+ + [Fe(CN)_6^{-4}]$	8.9×10^{-3}
$BaK_2[Fe(CN)_6] \cdot 5H_2O = Ba^{+2} + 2K^+ + [Fe(CN)_6^{-4}] + 5H_2O$	6.4×10^{-3}
$MgK_2[Fe(CN)_6] = Mg^{+2} + 2K^+ + [Fe(CN)_6^{-4}]$	6.2×10^{-3}

product is ammonium hydroxide soluble. All ferrocyanides are decomposed by heat; a possible reaction is

$$3K_4[Fe(CN)_6] \overset{\Delta}{=} 12KCN + 2(\mathit{CN})_2 + C + Fe_3C + \mathit{N}_2$$

The structure of heavy metal cyanides is still not certain. There is evidence that many exist as polymers, chains being built up probably by means of the cyano group using an unshared electron pair of N as a second valence:

$$-C{\equiv}N\rightarrow X-C{\equiv}N\rightarrow \quad \text{etc.}$$

This is resonance stabilized. Iron uses all its $3p$, $4s$, and $4p$ orbitals.

Laboratory Study of Group 3 Anions

★Test 22–33. Cl^- in the Presence of SCN^-, Br^- and I^-. The identification of AgCl by color and solub. is difficult in the presence of the insol. silver salts of these other ions so they are oxidized before AgCl is pptd.

(*a*) Three drops of each test soln. and 1 ml of glacial HAc are mixed in a beaker, then 100 mg of PbO_2 is added. The mixt is carefully evapd. in the hood until only a moist mass remains. If at this time the vapors still appear violet from I_2 or turn starch-iodide paper blue from Br_2, another half ml of HAc should be added and heating and testing continued. When completed, dil. the mixt. with 1.5 ml of H_2O, transfer to a tube, centrifuge, and test a little centrate with Ag^+ for Cl^-.

(*b*) If only SCN^- is present, it may be destroyed by simple evapn. of the sample in a crucible, baking until charring is over, cooling, then leaching with H_2O, centrifuging, and testing for Cl^-, as before.

Try the solub. of AgCl in dil. NH_4OH and the result of acidifying that mixt. with HNO_3. Explain with equations; see **silver**, Chapter 15.

★Test 22–34. I^- and Br^- Oxidations. Iodide is more easily oxidized than bromide so a selective oxidizing agent will eliminate I^- which would otherwise give reactions similar to Br^-.

(*a*) Mix 3 drops each of I^- and Br^- solns. with 5 drops of H_2O. Add 4-6 drops of CCl_4, and with shaking add drops of a dil. NaOCl soln. A violet color in the organic layer indicates I_2. Continue with good shaking to add drops of NaOCl until the I_2 has been oxidized to colorless IO_3^-. Only a little Br^- has been oxidized at this point. Acidify with 6 *M* H_2SO_4 and mix cautiously. Cl_2 is released and Br^- is oxidized to Br_2, and the organic layer shows this with a brown bromine color. Write the reaction equation showing iodine, hypochlorous acid, and water giving iodate, hydrogen ions, and chloride ions.

(*b*) Make the I^-–Br^-–CCl_4 mixt. as above. Add a few drops of sodium nitrite soln. and acidify with dil. HAc. Explain what happens in words and with equations.

(*c*) Make the test mixt. as above again. Add 3–4 drops of 3% H_2O_2 and a drop of 6 *M* H_2SO_4 and mix slowly. Does this reagent oxidize only I^- or both halide ions? Give equations.

★*Test 22–35. Br^- in the Presence of I^- and SCN^-.* (*a*) Put a few crystals or about a ml of sample in a small beaker. Add a ml of H_2O contg. about 50 mg of Fe^{+2}, then add satd. $CuSO_4$ soln. dropwise until no more cuprous iodide ppts.: $2Fe^{+2} + 2Cu^{+2} + 2I^- = 2CuI + 2Fe^{+3}$. Centrifuge and put half the centrate in the tube of the Gutzeit apparatus (Fig. 14–4). Mix in a few small crystals of $K_2Cr_2O_7$ and 4–5 drops of 6 *M* H_2SO_4 and assemble the rest of the apparatus as pictured. Put a drop of dil. alcoholic fluorescein on the indicator paper (in place of $AgNO_3$ used in the Gutzeit test) and add a drop of 50% alcohol to the paper. Heat the tube carefully. Both SCN^- and Br^- are oxidized but only Br_2 reacts with the reagent and turns it orange pink. See example 13, Chapter 12, p. 196.

$$14H^+ + Cr_2O_7^{-2} + 6Br^- \overset{\Delta}{=} 2Cr^{+3} + 7H_2O + 3Br_2$$

(*b*) *Preparation of fluorescein* (*optional*). In a 4-in. tube, heat this mixt. gently over a low flame for 3-4 min.: 100 mg of phthalic anhydride, 150 mg of resorcinol, and 4 drops of concd. H_2SO_4. Allow the mass to cool. Add a mixt. of 5 drops of 6 *M* NaOH and a ml of H_2O, rewarm, and discard the supernatant liq. Add a drop of 6 *M* NaOH and 3 ml of 95% alcohol and shake. The resulting yellow fluorescent soln. is bottled and used as in (*a*). It should be diluted enough to appear *light* yellow when spotted on the paper.

Test 22–36. Precipitation and Solubility of AgBr. To 4 drops of Br^- soln., add 10 drops of H_2O, 1 drop of 2 *M* HNO_3, and 5 drops of Ag^+. Note the color of AgBr. Centrifuge, wash, and try the solub. of the residue in dil. NH_4OH and compare with AgCl and AgI (tests 22–33 and 22–37). See also example 9–6.

Test 22–37. Some Heavy Metal Iodides. (*a*) Repeat test 22–36 using I^- instead of Br^-.

(*b*) To a few drops of I^- soln., add a few drops of Hg^{++} soln. What is the red ppt.? Add more I^-, mix, and describe the change. Write the equations.

(*c*) Prepare some PbI_2 from $PbAc_2$ and KI solns. Transfer to a beaker, boil with 30–40 ml of H_2O, and pour the clear supernatant liq. into another beaker. After the soln. has cooled and pptn. is complete, view one of the leafy crystals under magnification and describe it. Does it appear that some solids could be identified by this means alone?

(*d*) Try several other cations from the solns. for cation testing and report colors of any insol. iodides obtained.

Test 22–38. Formation of Cuprous Iodide. Add 2 drops of I^- to 15 drops of H_2O, then mix in 2 drops of Cu^{+2} soln. and 2 drops of SO_3^{-2} soln. What is the white ppt.? Br^- and Cl^- do not give this test.

Test 22–39. Starch Indicator for I_2. Mix a few drops of I^- soln. with a drop of 6 *M* H_2SO_4 and a drop of starch solution. Add a drop of some oxidizing agent and note the color of the starch-iodine complex. Neutralize the soln. with a drop of 6 *M* NaOH, then add a drop or two of $S_2O_3^{-2}$ soln. and note the sharp color change as iodine is reduced. These reactions are of prime importance in quant. analysis. (See section describing thiosulfate chem.) Starch-potassium iodide paper is used to indicate the presence of oxidizing agents. Explain how it might be prepd. and what one would observe in a positive test.

****Test 22–40. SCN^- in the Presence of $Fe(CN)_6^{-4}$ and I^-.*** Ferrocyanide and iodide give colors with Fe^{+3} which obscure the formation of $Fe(SCN)^{+2}$, an otherwise sensitive test for thiocyanate.

Arrange a tube for distillation and distillate collection (Fig. 14–7). Put 3 drops of each of these three test solns. in the distillation tube, and add a boiling chip and 5 drops of concd. HCl. Heat the mixt. and collect the distillate ($HCl + H_2O + HSCN$) in a test tube contg. 6 drops of 2 *M* NaOH and standing in a beaker of cold water. When several drops of distillate have come over, add 3 drops of 6 *M* HNO_3 to them and a drop of Fe^{+3} soln. A red color shows SCN^- in the mixt. The concn. limit is about 0.1 ppm of SCN^-.

Test 22–41. AgSCN and its Solubility. Repeat test 22–36 using SCN^- in place of Br^- and compare the results with previous work.

Test 22–42. Co^{+2}-acetone Test for SCN^-. Review test 17–10 and decide what modification is needed to make this an analytical method for thiocyanate. Write your method in the notebook and give experimental evidence that it will work. The concn. limit is about 20 ppm SCN^-.

****Test 22–43. [$Fe(CN)_6^{-4}$] in the Presence of SCN^-.*** Using the color of Prussian blue, one may determine ferrocyanide in the presence of thiocyanate in at least two ways:

(*a*) Mix 2 drops of each of these test solns. with 10 drops of H_2O and a drop of HCl. Add 3 drops of Fe^{+3} soln., shake, and centrifuge. A red supernatant color shows $Fe(SCN)^{+2}$, a blue ppt. is Prussian blue. Ferrocyanide *alone* may be detected at a concn. as low as 3 ppm by this test.

(*b*) Make the same mixt. as above but this time add 2 drops of *freshly prepd.*

Fe^{+2} soln. A white ppt. gradually turning blue is evidence that an iron ferrocyanide has formed.

Test 22–44. Heavy Metal Ferrocyanides. Prepare silver ferrocyanide using 3 drops of $[Fe(CN)_6^{-4}]$, 10 drops of H_2O, and 3 drops of Ag^+ soln. Centrifuge and try the solub. in NH_4OH. Account for the evidences of reaction with equations. Repeat using other heavy metal ions as suggested in the description of ferrocyanide general chem. As time permits, make several known dilns. of potassium ferrocyanide, put 2 drops of each on a different piece of filter paper, and add to each a drop of soln. of one or another heavy metal ion. Describe the procedure devised and discuss the results. Does this method seem to give a way to approx. the concn. of a ferrocyanide soln.?

THE GROUP 4 ANIONS

Q. Nitrate Ion, NO_3^-

The *oxidation state* of N is (V), the highest that element has, consequently nitrates (especially as concentrated HNO_3) can act only as oxidizers. NO_3^- may yield, upon being reduced, various products such as NO, NO_2, N_2O_3, N_2O_4, N_2, NH_4^+, NH_3, NO_2^-, NH_2OH (hydroxylamine), $H_2N—NH_2$ (hydrazine), etc. Some of the redox half reactions involving nitrate are:

$$NO + 2H_2O = NO_3^- + 4H^+ + 3e^- \qquad E^\circ = -0.96$$
$$NH_4^+ + 3H_2O = NO_3^- + 10H^+ + 8e^- \qquad E^\circ = -0.87$$
$$NO_2 + H_2O = NO_3^- + 2H^+ + e^- \qquad E^\circ = -0.81$$
$$N_2 + 6H_2O = 2NO_3^- + 12H^+ + 10e^- \qquad E^\circ = -1.24$$

The nitrate ion is planar and is stabilized by resonance among three equivalent forms; nitrogen oxides are similarly stabilized. Almost all nitrates are water soluble. Those of mercury and bismuth hydrolyze to precipitate basic salts, as $BiONO_3$, but the reactions are reversed with dilute HNO_3. Light metal nitrates give nitrites and oxygen when heated, heavy metal nitrates give a metal oxide, nitrogen dioxide and oxygen; ammonium nitrate, a special case, decomposes to nitrous oxide and water.

HNO_3 is prepared by heating Chile saltpeter (natural $NaNO_3$) with concentrated sulfuric acid or via the oxidation of NH_3 (Ostwald process). The commercial HNO_3 is 68% *nitric acid* by weight, but the oxidizing power may be increased by solution of nitrogen oxides in it to produce white and red fuming nitric acids. These are used as oxidants in liquid fueled rockets, being sprayed into a reaction chamber with a combustible material like gasoline, turpentine, or aniline. All such mixtures are spontaneously inflammable. Mixed H_2SO_4 and HNO_3 is used in organic reactions to introduce the nitro group, $—NO_2$, into certain organic molecules (trinitrotoluene, "T.N.T.") and to make nitrate esters with alcohols (glyceryl trinitrate, "nitroglycerine"). Nitro alkanes like nitromethane, CH_3NO_2, are used as solvents and in racing fuels. Inorganic nitrates such as NH_4NO_3 are used in explosives and as fertilizers. Four tests are described here for the analysis of nitrate.

(*a*) A brown ring forms at the liquid junction in a tube containing dilute $FeSO_4$ solution and nitrate on top of a layer of concentrated sulfuric acid, due to the presence of nitrosyl iron(II) ions:

$$NO_3^- + 3Fe^{+2} + 4H^+ = 3Fe^{+3} + \mathit{NO} + 2H_2O$$

$$\mathit{NO} + Fe^{+2} = Fe(NO)^{+2}$$

Interferences include other reducing, oxidizing, or complexing agents such as NO_2^-, I^-, Br^-, CrO_4^{-2}, $S_2O_3^{-2}$, SO_3^{-2}, SCN^-, $[Fe(CN)_6^{-4}]$. These can be precipitated, however, with Ag_2SO_4. Any remaining nitrite can be destroyed with sulfamic acid (see paragraph A, p. 375).

(*b*) NO_3^- gives a red color with a concentrated H_2SO_4 solution of brucine, one of a class of naturally occurring amines known as alkaloids. When the color fades, addition of Sn^{II} solution causes a violet color to appear.

(*c*) With hot H_2SO_4 and copper, nitrate gives brown NO_2 gas and a blue solution of cupric ions:

$$Cu + 4H^+ + 2NO_3^- = 2\mathit{NO}_2 + Cu^{+2} + 2H_2O$$

(*d*) Nitrate can be reduced in alkaline solution with Devarda's alloy (Zn-Al-Cu) or other active metals to yield ammonia:

$$8Al + 5OH^- + 18H_2O + 3NO_3^- \overset{\Delta}{=} 3\mathit{NH}_3 + 8Al(OH)_4^-$$

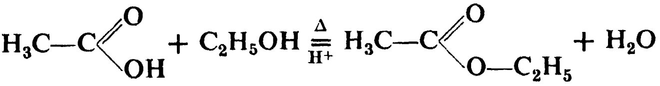
Other nitrogen-containing radicals, $Fe(CN)_6^{-4}$, SCN^-, NO_2^-, NH_4^+, must be removed first, as they give ammonia also.

Quantitatively, one measures nitrate content by reduction to NH_3 as described in (*d*) above. The NH_3 is distilled and trapped in boric acid, then standard acid is used to titrate the NH_4BO_2 formed. (Winkler modification of the Kjeldahl method.) This is possible because boric acid is much weaker as an acid than is ammonium hydroxide as a base.

R. Acetate Ion, $H_3C—CO_2^-$ (Ac^-)

Acetic acid is stable in water solution as well as in the pure state, the latter a water-white liquid that freezes to a solid resembling ice (hence the name "glacial" for the pure acid) at 16.6 C. The melting point is used as a purity criterion. HAc is a weak monoprotic acid, the H on the O being the only ionizable one. Almost all acetates are water soluble. (See Chapter 7 for problems dealing with acetate equilibria.)

When heated with dilute H_2SO_4, acetic acid is released from acetates and its characteristic vinegar odor detected. If an alcohol is added to the mixture, a pleasant smelling ester is distilled off (*ethyl acetate* here):



$$H_3C-C\begin{array}{l} /\!\!/O \\ \backslash OH\end{array} + C_2H_5OH \overset{\Delta}{\underset{H^+}{=}} H_3C-C\begin{array}{l} /\!\!/O \\ \backslash O-C_2H_5\end{array} + H_2O$$

With hot dilute solutions of Fe^{+3}, acetate precipitates at about pH 7 as basic ferric acetate, a possible formula being $Fe(OH)_2Ac$. Distilling an acetate with calcium carbonate yields acetone. Acetone in basic I_3^- solution is converted to triiodomethane, iodoform, whose distinctive odor is easily recognized:

$$2H_3C-CO_2Na \underset{CaCO_3}{\overset{\Delta}{=}} Na_2CO_3 + (H_3C)_2C=O$$

$$(H_3C)_2C=O + OH^- + I_3^- = HCI_3 + H_3C-CO_2Na$$

Another qualitative test for Ac^- is made by adding $La(NO_3)_3$, I_3^-, and NH_4OH to an acetate solution to precipitate basic lanthanum acetate whose surface adsorbs I_2 and gives a blue color. A concentration of about 500 ppm Ac^- is needed, which means the test is only about half as sensitive as the basic ferric acetate method. Ions that precipitate La^{+3} (OH^-, PO_4^{-3}, SO_4^{-2}) can be removed by pH adjustment to 7 and precipitation with Ba^{+2}.

Quantitatively, Ac^- is converted to HAc, distilled to purify, and titrated with standard base.

Laboratory Study of the Group 4 Anions

Test 22-45. Brown Ring Test for NO_3^-. Note in section *Q* part (*a*) the ions which interfere with this test and remove them accordingly if the soln. may contain them.

Put 2 drops of NO_3^- soln. in a tube, and add 8–10 drops of H_2O and 2 drops of fresh Fe^{+2} soln. Incline the tube and without homogenizing the mixt., let 3-4 drops of concd. H_2SO_4 run down the tube wall and form a layer on the bottom. A brown ring due to $FeNO^{+2}$ at the interface is indicative of nitrate. (See the similar test earlier described for nitrite.)

Test 22-46. Brucine Test for NO_3^-. Add a few crystals of brucine (POISON!) to 10 drops of concd. H_2SO_4 and stir to dissolve. On a spot plate place a drop of nitrate soln. and add two of brucine reagent. A red color shows nitrate (if nitrite has been previously shown absent). When the spot fades to yellow, a drop of $SnCl_4^{-2}$ turns it violet. A blank should be run. A slight reddish tint to the reagent is due to nitrate in the sulfuric acid. The exact formulas for the nitrated (?) brucine and its tin reduction products are not known. This test will detect NO_3^- in concns. as low as about 2 ppm.

★***Test 22-47. Reduction of NO_3^- to NH_3 and to HNO_2.*** Note the interferences to this test as explained in paragraph Q, p. 404.

(*a*) To 50 mg of Devarda's alloy add 6 drops of nitrate soln., 4 drops of 6 *M* NaOH, warm, then carefully note the odor of NH_3. Write the equation using Zn as the reacting metal. How could Nessler's reagent (test 19–9) be utilized? Invent a method and report on it.

(*b*) If NO_2^- is present, remove it via test 22–1 (*b*). Make soln. neut. with NH_4OH, then slightly acid with HAc. Make a mixt. of a drop of α-naphthylamine, a drop of sulfanilic acid, and a little Zn dust. Add the nitrate soln. to this and agitate it now and then during the next few min. A very definite color indicates NO_3^- was in the sample, since it has been reduced to HNO_2 which gives the Griess reaction (test 22–5).

Test 22–48. Acetate in the Presence of Interfering Ions. (*a*) When one attempts to identify Ac^- in the presence of group 1 anions, the odor tests on HAc and its esters fail because other volatiles like NO_2 and SO_2 mask them. One may ppt. all the ions except Ac^- with excess $AgNO_3$, then proceed with the centrate to test for acetate. In this method some nitrite escapes although the excess pptng. agent decreases the solub. of $AgNO_2$ and at the same time prevents the formation of the soluble silver thiosulfate complex, $Ag(S_2O_3)_2^{-3}$. Treatment of the centrate with sulfamic acid (see test 22–1 and paragraph A p. 382) destroys NO_2^- traces. The student should try this procedure on a known mixt. contg., for instance, SO_3^{-2}, NO_2^-, and Ac^-.

(*b*) Another procedure is to oxidize all the group 1 ions except Ac^- and CO_3^{-2} in a warm neutral or slightly acidic soln. with $KMnO_4$. One may then test the centrate for Ac^- by heating with H_2SO_4 to get the HAc odor or by one of the tests below. The student should also try this procedure on a known mixt.

Test 22–49. Basic Ferric Acetate. Put 4 drops of neutral Ac^- test soln. in a test tube, add 10 drops of H_2O, 3 drops of $FeCl_3$, and boil briefly. A red-brown color or ppt. is ferric hydroxy acetate. Interferences include S^{-2}, SO_3^{-2}, SCN^-, $Fe(CN)_6^{-4}$, and I^-, but they can be pptd. with Ag^+. The concn. limit is about 250 ppm Ac^-.

Test 22–50. Conversion of Acetate to Acetone and to Esters. (*a*) Heat a mixt. of about 100 mg of solid $CaCO_3$ with 20 drops of Ac^- soln. in a test tube and slowly evap. it to 2–4 drops. Connect a delivery tube and arrange to collect the distillate in another tube standing in a 50 ml beaker of cold H_2O (Fig. 14–7). Evaporate the mixt. and heat it strongly. To the distillate of acetone and water add a drop of 6 *M* NaOH and a drop of $KI–I_2$ soln. and shake. The appearance of a faint yellowish ppt. of iodoform accompanied by its easily recognized medicinal odor is a positive test for acetate. The sensitivity is about the same as for the preceding test. Group 1 anions should be removed prior to making the test.

(*b*) Acetic acid forms pleasant-scented esters when caused to react with alcohols, in the presence of a catalytic amount of mineral acid. To 10 drops of Ac^- soln., add 5 drops of an alcohol, a drop of 6 *M* H_2SO_4, and warm. Note the fruit-like odor of the ester. Write the equation.

Test 22–51. Lanthanum-Iodine Test for Acetate. Put 2 drops of Ac^- test soln. on a spot plate, add a drop of 5% lanthanum nitrate, a drop of 0.01 N I_3^- (I_2 in KI) and a drop of 2 M NH_4OH. Depending upon the [Ac^-] a blue color or ring develops. The concn. limit is about 500 ppm.

GENERAL INSTRUCTIONS FOR AN ANION UNKNOWN

(1) *If the sample is known to be only a mixture of soluble* Na^+ and K^+ salts of the 18 anions just listed, one should test small portions of it with the three group reagents (hot dilute H_2SO_4, Ca^{+2}–Ba^{+2}, and Ag^+) to determine if tests on individual ions within those groups are necessary. Group 4 ions, NO_3^- and Ac^-, must be tested for individually. (*It is assumed that explosively powerful oxidizing ions as* ClO_3^-, ClO_4^-, *and* $S_2O_8^{-2}$ *are absent.*) After deciding in which groups to make tests, one systematically runs individual tests, as described, using a fresh small portion of unknown each time unless a sequence is specified. Cognizance of interferences must be taken and such substances removed. Sometimes the first test for an ion will be conclusively positive or negative, sometimes several are needed. *The tests marked ★ listed after the description of the ion are recommended as the ones most likely free of difficulties.* Where the words "test solution" or "solution of that ion" appear, one substitutes the words "unknown solution," and proceeds as if repeating the preliminary work.

(2) *If the sample is soluble but cations other than* Na^+ *and* K^+ *are suspected,* they may interfere with anion tests. Such cations form insoluble carbonates and can be not only detected but eliminated in that way. Paragraph Y in this chapter, p. 411, gives the procedure.

S. Testing Anion Group 1

If the unknown is a soluble solid, dissolve about 200 mg in 5 ml of H_2O. (The solution should not be too concentrated since the tests are designed for small quantities.) Test the solution's pH by putting a drop on a spot plate and adding a drop of phenolphthalein; since group 1 anions hydrolyze, it is characteristic of their alkali metal salt solutions to have a high pH (PO_4^{-3}, BO_2^-, $C_2O_4^{-2}$, and Ac^- give the same reaction also). To several drops of solution, add 1–2 drops of 6 M H_2SO_4 and note the appearance of gas evolution. Warm and again observe the result, cautiously getting the odor above the tube. If the solution fizzes immediately and the gas is odorless, a **carbonate** or **bicarbonate** is probably present. The odor of SO_2 indicates a **sulfite** or **bisulfite** is present and a simultaneous fine yellow-white precipitate may be sulfur and indicates the possibility of a **thiosulfate**. The odor of H_2S is unmistakable and shows **sulfides** or

bisulfides and a brown gas is most likely NO_2, created when a **nitrite** decomposed. (Some HAc odor indicating **acetate** may be noted here if other odors are faint or missing.) If any of these evidences of group 1 anions is apparent, individual testing of appropriate ions according to the preliminary exercises is undertaken. This solution can be used to examine group 3 below (decomposition of NO_2^- gives NO_3^- in solution), if heating is continued to evolve all easily produced gases. If no gas evolution is noted, try the test again using concentrated HCl on some solid sample. The absence of gas release indicates the absence of group 1 anions, though nitrite should be checked by an independent test, and oxidizing agents may release Cl_2 from the HCl.

T. Testing Anion Group 2

To another small volume of unknown solution add 2 drops of 6 *M* HCl and warm the mixture to decompose and expel the decomposition products of group 1 ions. If no group 1 was present, HCl addition is omitted. Neutralize any HCl added with a drop or two of NH_4OH, add a drop of methyl orange and enough 2 *M* HAc to change the indicator red, and then add 3 drops more of HAc. Add a few drops of $CaCl_2$ solution; a white precipitate indicates the probable presence of F^- and/or $C_2O_4^{-2}$, and no precipitate indicates their absence. The solid can be dissolved in HCl and tested for the two anions, remembering that $C_2O_4^{-2}$ must be destroyed before F^- is analyzed colorimetrically.

Treat the centrate with just enough 3 *M* NH_4OH to turn the indicator yellow then heat the tube in a water bath and add several more drops of $CaCl_2$ and several of $BaCl_2$. A yellow precipitate indicates CrO_4^{-2}, a fine white precipitate possibly shows SO_4^{-2}, and bulkier white precipitates may be the barium salts of BO_2^- or PO_4^{-3}. Add 4 drops of dilute HCl and reheat, with stirring. If a precipitate remains it is $BaSO_4$, if it only slowly dissolves, it may be $Ba_3(PO_4)_2$. If no precipitate formed with the barium-calcium mixture, then appreciable amounts of PO_4^{-3}, SO_4^{-2}, CrO_4^{-2}, F^-, $C_2O_4^{-2}$, and BO_2^- are absent. If only small quantities are suspected present then those tests which are most sensitive should be tried. Of these residues, borate is most soluble and must be tested for even if no group 2 precipitate comes down.

U. Testing Anion Group 3

The solution from the H_2SO_4 testing of group 1 is centrifuged if any residue is present, and the centrate examined further. To a portion, add 2 drops of 6 *M* NH_4OH, 5 drops of 6 *M* HNO_3, and enough Ag^+ to complete precipitation of group 3 ions. Group 2 anions will not yield insoluble silver salts in the presence of HNO_3 but group 3 ions will. A yellow precipitate is probably AgI, a white or faintly yellow precipitate may be any or all of the silver salts of Cl^-, Br^-, SCN^-, and $[Fe(CN)_6^{-4}]$.

Try the solubility of the precipitate in 0.3 *M* NH_4OH. If it readily dissolves and SCN^- is shown to be absent, Cl^- was probably the only anion present (though test 22–33 should be used to check). Addition of dilute HNO_3 to that solution reprecipitates white AgCl. The other ions are tested in the remaining portion of solution from group 1, using tests 22–34, 22–35, 22–40, and 22–43 on separate parts.

V. Testing Anion Group 4

No general reagent is available for this. Groups 1, 2, and 3 are first eliminated, then group 4 tests are made. To a small portion of unknown solution add $Ag_2(SO_4)$ solution to complete precipitation of all ions giving insoluble silver salts. Centrifuge. Treat the centrate with the $CaCl_2$–$BaCl_2$ mixture to complete precipitation of other ions (except Cl^- and group 4). Centrifuge and test the centrate for Ac^- and NO_3^- as described in tests 22–47 and 22–49. These tests are not obscured by Cl^- introduced with the calcium-barium solution.

W. Testing for oxidizing Agents

If strong oxidizing anions are present in the unknown then strong reducing anions are absent. The extent to which these react with one another is chiefly dependent upon the distance of separation of their oxidation potentials and the solution *p*H; in general a considerable difference in E° values and a low *p*H give optimum reaction conditions. Thus at high *p*H, SO_3^{-2} and S^{-2} do not react with each other, but if the mixture is acidified, sulfur and water result. One checks for oxidizing and reducing ions, consequently, not only to find what is in the sample but also to get a clue as to what is not. A *negative test* can be almost as helpful as a positive one.

To 4 drops of unknown solution, add 2 drops of 12 *M* HCl and 6 drops of saturated $MnCl_2$ in HCl, and warm the tube in a water bath. A brown precipitate of MnO_2 indicates that NO_2^-, CrO_4^{-2}, and/or NO_3^- are in the sample. After the residue settles, the supernatant solution may be green due to Cr^{+3}, from a chromate, or yellow, due to dissolved nitrogen oxides from a nitrite or nitrate. Nitrate gives the poorest response in this test and should be checked again as described in paragraph V.

X. Testing for Reducing Agents

If oxidizing agents were not present, reducing ions may be.

To 6 drops of sample solution, add 4 drops of H_2O and 2 drops of 6 *M* H_2SO_4. Mix and cool. Now add 2 drops of 0.01 *M* $KMnO_4$.

A bleaching of the color shows that at least one of these is present: SO_3^{-2}, I^-, Br^-, S^{-2}, NO_2^-, and SCN^-. No bleaching at room temperature or below means that these ions are probably absent. Continue adding oxidizing agent with mixing until a definite red color remains. Now heat the tube in a water bath. If more bleaching takes place, $C_2O_4^{-2}$ is probably the cause, or appreciable quantities of Cl^- are present. Test further for these ions if the reaction was positive.

A further useful test for reducing agents is described by Lundin (references). Drops of solution are put on starch-iodate paper and the paper turns blue if reducing ions are present which can act on iodate to liberate iodine. Reported sensitivities in mg/ml of the ions are

S^{-2} 0.1, SO_3^{-2} 0.1, $S_2O_3^{-2}$ 10, $[Fe(CN)_6^{-4}]$ 10, I^- 0.1, NO_2^- 10, SCN^- 0.05

Y. Insoluble Samples For Anion Analysis

If the unknown is not already in solution and gives evidence of slow or low solubility in H_2O and dilute acids, a portion should be powdered in an etched spot plate depression, using a blunt stirring rod as a pestle. A little of this material is tested for carbonate using test 22–15, then the rest is transposed by boiling with sodium carbonate solution or by fusion with the solid in a platinum crucible. For example:

$$Ba_3(PO_4)_2 + 3Na_2CO_3 \overset{\Delta}{\rightleftharpoons} 2Na_3PO_4 + 3BaCO_3$$

In this way the anions are put into solution, since the sodium salts formed are water soluble.

With stirring in a 20-ml beaker, boil a mixture of 300 mg of sample with 1200 mg of cp anhydrous Na_2CO_3 and 8 ml of H_2O, or use proportionate amounts on available sample. Continue to keep the mixture hot for at least 10 minutes, and replace water as it evaporates. Rinse the mixture into two tubes, centrifuge, and save both centrates and residues. Wash the residues and combine washings with centrates. Use small portions of the centrate and make individual ion examinations as already described.

The residue may contain carbonates and hydroxides of the first four cation groups, plus Mg^{+2}, as well as some untransposed F^-, S^{-2}, Cl^-, Br^-, I^-, and PO_4^{-3}. If these ions are found in the centrate, they need not be analyzed again here, since enough was solubilized for testing purposes before. If the residue contains carbonates only, it should be soluble in warm 3 M HAc and if this is found, then only the centrate above requires anion analysis. If some of the residue remains after HAc addition, portions are used as directed below.

1. *Fluoride.* To a portion of residue contained in a 4-inch test tube,

add, in order, a few granules of powdered glass, 2 ml of 6 *M* H_2SO_4, and finally 25–50 mg of solid Ag_2SO_4, and arrange to distill (**CAUTION!**) and collect the distillate. The silver salt precipitates some of the ions and prevents their distillation as volatile acids. The glass reacts with HF giving H_2SiF_6, which distills. Collect about 1 ml of distillate in a tube cooled in a beaker of water and test it colorimetrically for fluoride. Compare with a blank and a known. See test 22–27.

2. *Sulfide.* To a separate portion of residue, add a few mg of Zn and a ml of 6 *M* HCl. Test for H_2S release by $PbAc_2$ paper.

3. *Halides of silver.* To a separate portion of residue, add 2 ml of 3 *M* HNO_3 and boil. Cool and centrifuge. Save the centrate for part 4, below. To the residue add 1 ml of 0.3 *M* H_2SO_4, 6–10 drops of CH_3CSNH_2, and heat in the water bath. Silver halides are converted to black Ag_2S and soluble halide ions. Centrifuge. The centrate contains the halides, sulfate, and acetic acid (from thioacetamide). Cl^-, Br^-, and I^- are then tested by procedures given in this chapter, such as tests 22–33, 22–34, and 22–35.

4. ***Phosphate.*** To the centrate from 3, above, test for phosphate with molybdate and nitric acid (test 22–16).

Z. Further Aid in Anion Analysis

If the analysis of the cations in the sample has been made prior to anion analysis, considerable aid is given the analyst in the table of solubilities (back cover), for he can eliminate some cations and suspect the presence of others by solubility behavior of the sample. This gives the student the opportunity to use his ingenuity, acquired knowledge of chemical facts, and application of principles.

The analysis of the general unknown for cations is given in Chapter 21, including treatment of slightly soluble samples. Note there also the information to be gained by dry ignition of the sample, as some of the observations apply directly to anions.

PROBLEMS

1. Use the table of oxidation potentials to answer the following.

(*a*) A solution of sodium nitrite and potassium chromate is acidified. What happens?

(*b*) Can H_2O_2 oxidize Br^- to Br_2 in acid solution?

(*c*) Will sulfite bleach permanganate at low *p*H?

(*d*) In acid solution can MnO_4^- oxidize I^- to IO_3^-, or only to I_2?

(*e*) Will $Cr_2O_7^{-2}$ selectively oxidize I^- and not Br^-?

(*f*) PbO_2 is heated with hydrochloric acid. Is chlorine gas released?

(*g*) In basic solution, can zinc metal reduce $Fe(OH)_3$?

(*h*) May Fe^{+3} be used to selectively oxidize I^- and not Br^-?

(*i*) $H_2O_2 + H_2Cr_2O_7 =$

(*j*) Why does addition of chlorine water (Cl_2 in H_2O) to a mixture of KBr in H_2O and CCl_4 give a brown CCl_4 layer?

2. (*a*) Why is I_2 essentially insoluble in H_2O but quite soluble in aqueous KI?

(*b*) Why is I_2 in KI solution brown, but in CCl_4, purple?

(*c*) What color would you expect I_2 to be in CH_3OH solution? In CS_2? In chloroform, $CHCl_3$? Why? What color is Br_2 in each solution?

3. What simple test(s) will distinguish between the following pairs if each is in a different container?

(*a*) AgI and AgCl (*b*) $CaCrO_4$ and $BaCrO_4$ (*c*) AgCl and AgSCN (*d*) $NaNO_3$ and $NaNO_2$ (*e*) $H_4[Fe(CN)_6]$ and HSCN (*f*) $Ag_4[Fe(CN)_6]$ and AgBr (*g*) $Na_2S_2O_3$ and Na_2SO_3 (*h*) K_2SO_3 and K_2SO_4 (*i*) $(NH_4)_3PO_4$ and NH_4NO_3 (*j*) CaF_2 and CaC_2O_4.

4. A general unknown is a mixture of white salts and is water soluble. It is found to contain Pb^{+2}, Ba^{+2}, and Na^+. Which negative ions are probably not present in appreciable quantities?

5. A general unknown is water soluble and found to contain Cl^-, SO_4^{-2}, and S^{-2}. What cations should one test for?

6. A white solid is a single simple salt; it is not soluble in water but reacts with H_2SO_4 to give an odorless gas and another white residue. What might the sample have been? Explain.

7. What anions are possibly present in moderate quantity in a water soluble unknown which is analyzed first for cations and found bearing Ag^+, Ca^{+2}, Ba^{+2}, NH_4^+, Li^+, and K^+.

8. A certain water soluble sample is partially analyzed and Br^-, SO_4^{-2}, NO_2^-, and PO_4^{-3} are found. What cations and anions are probably not present? Give a reason for each choice.

9. (*a*) A solution of $FeSO_4$ that has been on the shelf for some months gives a dark red color when KSCN is added. Give a theory to account for this.

(*b*) A solid mixture containing $NaNO_2$ and NaI slowly turns dark. Explain.

(*c*) An old sample of $NaNO_2$ gives the brucine test. Explain.

10. J. P. Slipshod offers helpful hints on handling a solution that may contain any combination of these ions: Cl^-, Br^-, SO_4^{-2}, SCN^-, NO_2^-, and SO_3^{-2}:

"Divide the solution among six tubes and proceed with six spot tests to blanket the entire problem:

Tube 1: add H_2SO_4 and heat; a gas release proves sulfite.

Tube 2: add Ag^+; a white precipitate proves chloride.

Tube 3: add Fe^{+2}; a red color is thiocyanate.

Tube 4: add chlorine water, H_2SO_4 and CCl_4; a brown upper layer proves bromide.

Tube 5: add a $KMnO_4$ crystal; decolorization shows nitrite.

Tube 6: add Ba^{+2} solution; a gelatinous, white precipitate proves sulfate."

Which points in the Slipshod methods are specious?

11. Balance and decide in which direction these go:

(*a*) $H_2Cr_2O_7 + Br^- =$

(*b*) $H^+ + Cl^- + IO_3^- =$

(*c*) $I_2 + Fe(CN)_6^{-4} =$

(*d*) $ClO_3^- + H_2SO_3 = Cl^- + H^+ + HSO_4^-$

(*e*) $Cr^{+3} + S + H_2O = S^{-2} + CrO_4^{-2} + H^+$

12. One runs the transposition reaction according to paragraph Y, p. 411, with 10 ml of 1 *M* Na_2CO_3 on solid CaC_2O_4.

(*a*) Find the ratio $[C_2O_4^{-2}]/[CO_3^{-2}]$ at equilibrium with Ca^{+2}.

(*b*) What weight of CaC_2O_4 is transposed if CO_3^{-2} is added as fast as it is used up, and $[CO_3^{-2}]$ is maintained at 1 *M*?

13. Air contaminated with NO_2 (nitrogen dioxide) may be stripped of that component by bubbling it through aqueous base or even plain water:

$$2NO_2 + H_2O = HNO_2 + H^+ + NO_3^- \qquad K_{eq.} \cong 10^5$$

You are called in by an air pollution commission to devise a sensitive method for the detection of NO_2 in the air. Explain your complete solution to this problem including sketch of an air sampling device. How might the method be made quantitative?

14. (*a*) Boron at a concentration as low as 2–5 ppm in irrigation water is known to kill citrus trees. You are asked to recommend a method or methods capable of indicating borates under these conditions. Could a person with no chemical background be taught to run the test in the field?

(*b*) (*Library*) Chromates are sometimes added to industrial water as corrosion preventatives for iron pipes. Explain how this might work. Look up the diphenylcarbazide method and summarize its use as a Cr^{VI} reagent including equation, sensitivity, and evidence of positive reaction.

(*c*) Sulfites are sometimes added to industrial water to prevent iron corrosion by acting as an "oxygen scavenger." Explain. You are asked to devise a test capable of detecting small amounts (~ 10 ppm) of residual sulfite in the water. The water contains only the other usual ions. What may happen if considerable sodium sulfite is added to a recirculating water system over a long period of time?

(*d*) A wine sample is dark red and tastes particularly sour. How could you test it for acetic acid?

(*e*) Someone proposes a method for cutting up a certain variety of sea weed, boiling it in water, filtering, evaporating the filtrate, and getting iodide salts from it. You are asked for an iodide test. Considerable NaCl is known present. What is your test?

15. (*a*) Copper pot cleaners frequently contain oxalic acid, which forms soluble copper complexes, and an abrasive, such as, diatomaceous earth, which is essentially SiO_2. How would you proceed to prove that a sample corresponded to this formulation?

(*b*) A solid, white mixture put out for the purpose of silver plating brazed joints in electric circuits, contains AgCl, NaCl, $NaHCO_3$, and bentonite (clay). How would one analyze the product?

(*c*) A green-colored solid mixture which is sprinkled on fireplace fires to produce colored flames is made from $CuSO_4 \cdot 5H_2O$ and KCl. Why isn't $CuSO_4 \cdot 5H_2O$ used alone, or why not use $CuCl_2$? How could the mixture be analyzed? Could one use NaCl in place of the more expensive KCl?

(*d*) A solid, grey mixture, meant to be sealed in plastic bags with shaved ice, is on the market for incorporation in short air shipments of perishable items. The product contains asbestos fiber, fuller's earth (an absorbant clay), and potassium chloride. What is the function of each ingredient? How would one analyze the sample? How would a microscope aid the investigation?

(*e*) Restaurants may cut up potatoes for frying several days in advance, but if not properly preserved, they turn dark or become slimy even in the refrigerator. An aqueous solution sometimes used to keep potatoes white contains $NaHSO_3$, $NaHCO_3$, and citric acid. How could one analyze a sample?

16. (*a*) A solution is suspected of containing $S_2O_3^{-2}$, PO_4^{-3}, Br^-, and SCN^-. Give two methods for analyzing the sample.

(*b*) An unknown solution gives no gas when heated with dilute H_2SO_4. It gives a white precipitate with the Ca^{+2}–Ba^{+2} reagent, and the precipitate is insoluble in 6 *M* HCl. The sample also gives a white precipitate with Ag^+ plus HNO_3. This is soluble in NH_4OH and if that solution is acidified with HNO_3 and then treated with chlorine water and CCl_4, no reaction is apparent. What anions might be present?

(*c*) To a few mg of Ag_2CrO_4, one adds a 2 *M* NH_4Cl solution. Explain what happens and why. If 2 *M* NH_4NO_3 were added instead, what would the result be? (Hint: consider the chromate-dichromate equilibrium and the hydrolysis of the ammonium ion.)

17. (*a*) With respect to the base F^-, which acts as the stronger acid in aqueous solution: HF or H_2O? Explain.

(*b*) Calculate the concentration of each of these in 0.5 *M* HF: H^+, F^-, HF, HF_2^-.

18. (*a*) Organic chemists have found that when esters are formed according to the reaction described in the section on acetate (p. 406) the oxygen in the water formed came from the acid and not the alcohol. How could one prove this?

(*b*) In making chromate precipitates like $BaCrO_4$, laboratory directions usually specify approximately neutral solutions to which are added sodium acetate. Why does this procedure insure a good yield of the chromate?

19. Tell what complications one encounters in the following and how they are circumvented:

(*a*) Analyzing Ac^- in the presence of NO_2^-.
(*b*) Detecting SO_3^{-2} in the presence of $S_2O_3^{-2}$ and SO_4^{-2}.
(*c*) Finding Br^- in a mixture of I^- and Cl^-.

20. (*Library*) Common anions sometimes tested in a beginning course in addition to those mentioned in this chapter include CN^-, ClO_3^-, ClO^-, AsO_4^{-3}, and $C_4H_4O_6^{-2}$ (tartrate). Find a good test for each and describe it, including interferences, elimination of interferences, and sensitivity, if possible.

21. (*a*) Why is the azo dye test for nitrite better than the test involving bleaching of permanganate?

(*b*) Why is the acetone–iodoform reaction better for acetate detection than the ester–odor test?

(*c*) Why is the zirconyl–alizarin test superior to the etching test for fluoride analysis?

22. In one test for carbonate and bicarbonate, acid is added to the sample and the gas evolved is bubbled through a dilute Na_2CO_3–phenolphthalein solution. The fading of the indicator color is taken as evidence of a positive test. Explain, including equations.

23. $C_2O_4^{-2}$ and F^- both give a yellow color with the alizarin-zirconyl fluoride reagent. Suggest how to rid a solution of oxalate without distillation so one can test for fluoride. Include equations for destruction of oxalate, remembering that the solution prepared for F^- determination must not contain any colored ions which might mask the F^- test.

24. Which of the following oxidizing agents in acid solution will oxidize I^- but not Br^-? Which will oxidize I^- and Br^- but not Cl^-? Which is/are capable of oxidizing all these halide ions? (*a*) F_2 (*b*) HNO_2 (*c*) O_2 (in going to H_2O) (*d*) $Cr_2O_7^{-2}$ (*e*) Fe^{+3} (*f*) MnO_4^- (in going to Mn^{+2}).

25. The solubility of lead thiocyanate is about 0.45 g/liter. Place it in Table 22–14.

26. (*a*) Various nitrate reduction products are listed in paragraph Q. What is the oxidation state of N in each?

(*b*) Give balanced equations showing what happens when the following are heated: NH_4NO_3, NH_4NO_2, $NaNO_3$, $Pb(NO_3)_2$, HNO_3.

(*c*) One has a mixture of NH_4^+ and NO_3^-. How could it be analyzed for each ion quantitatively by the Kjeldahl method? Give equations and explain.

27. Note the interferences in test 22–49. Explain with equations why each hinders the test.

28. A certain ink for marking glassware contains ammonium bifluoride and barium sulfate. Explain. How could one analyze it?

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23

SPECIAL EXPERIMENTS: SOME PRINCIPLES AND APPLICATIONS OF QUALITATIVE TESTING

The following experiments are roughly divided into two types: the first four illustrate principles such as equilibrium constants, *p*H, and buffers; the last nine are practical applications of qualitative analysis and an introduction to the use of such analysts' tools as the spectroscope, ultraviolet radiation, electrography, chromatography, etc. These experiments may be used as lecture demonstrations or given to students as extra-credit material, or simply assigned to the class as regular laboratory exercises. It is felt that this section broadens the student's concept of the area of chemical analysis and serves as a summation to the course with its human interest value, practicality, and spirit of discovery. Related topics for general interest reading are listed in a short compilation of references following the experiments.

SPECIAL EXPERIMENT 1—USING THE CONDUCTIVITY BRIDGE

Investigation of a Typical Weak Electrolyte

1. The degree of ionization or dissociation of a weak electrolyte in water solution may be measured by three methods discussed in previous chapters: (*a*) from freezing and/or boiling point data (*b*) from voltages of properly constituted cells, and (*c*) from measurement of electric conductivity. The last method as described below is simple, rapid, and productive of good results.

A conductivity cell and laboratory-constructed Wheatstone bridge circuit are satisfactory for the experiment, or one may use a commercially available bridge and dipping cell.*

From the electrical resistance of a solution one may calculate its conductance and, from the known concentration of the solution, the solute's equivalent conductance. From handbook data and application of Kohlrausch's law one may find the equivalent conductance of the solute at infinite dilution, and, by comparison of this with the value obtained experimentally, the solute's degree and percent of dissociation can be calculated. The calculation is illustrated in Chapter 5.

2. Assemble the particular apparatus as instructed.

3. Various student groups may be assigned different concentrations of some weak electrolyte on which to gather data and make calculations. A table of class data can be then assembled on the board for copy in the laboratory notebook with comments on the experiment and answers to the questions. A suitable system for study is acetic acid–water in the concentration range 0.4–0.0001 *M*.

If solutions are not already prepared at the various concentrations, make 250 ml of the particular concentration assigned from a stock bottle of HAc and distilled water, using a cylinder or pipets and a volumetric flask as directed. If small conductivity cells are employed, smaller volumes are used. Adjust the temperature of the solution to some predetermined value like 25 C so the class data will be consistent, rinse the cell twice with small volumes of the solution, then measure the resistance of the solution and calculate the other values. At 25 C, Λ_0 for HAc = 372 (see Table 5–2). The cell should be rinsed with distilled water and the apparatus made available for the next group. *Always treat the cell and bridge carefully.*

4. Copy the class data from the board. From your individual measurements, calculate and contribute the following to the table: (*a*) Molarity of solution. (*b*) Specific resistance. (*c*) Specific conductance. (*d*) Volume in ml needed to contain 1 g equivalent weight of solute. (*e*) Equivalent conductance (from your data). (*f*) Equivalent conductance at infinite dilution (from reference data). (*g*) Degree of ionization. (*h*) Per cent of ionization. (*i*) Theoretical per cent of ionization as calculated from the book value of the ionization constant. (*j*) K_{ion} (experimental). (*k*) Plot a graph of per cent ionization versus concentration from the entire data collection, and explain.

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* A good instrument for this purpose is the type RC conductivity bridge manufactured by Industrial Instruments, 17 Pollock Ave., Jersey City 5, New Jersey. The dipping cell should have a cell constant of about unity, and should be given by the instructor to save lab time.

TABLE 23-1. TYPICAL STUDENT DATA FOR HAc IN SPECIAL EXPERIMENT 1

N HAc	R 25 C	1/R $\times 10^{-4}$	ml/equiv. wt. $\times 10^3$	Λ_N (experiment)	Λ_N/Λ_0	Per Cent Ioniz. (experiment)	Per Cent Ioniz. (theory)
0.2	1410	7.09	5.0	3.55	0.0091	0.91	0.93
0.1	1,800	5.55	10.0	5.55	0.0159	1.59	1.36
0.05	2,750	3.64	20.0	7.28	0.0209	2.09	1.93
0.02	4,760	2.10	50.0	10.5	0.0301	3.01	3.04
0.01	6,350	1.58	100.0	15.8	0.0452	4.52	4.30
0.005	8,700	1.15	200.0	23.0	0.0661	6.61	6.11
0.001	21,000	0.476	1000.0	47.6	0.122	12.2	12.5

5. Questions: (*l*) Why does dilution change the per cent ionization but not K_{ion}?

(*m*) Which contains more H^+ and Ac^- ions: 1 liter of 0.01 M HAc or 1 liter of 0.001 M HAc? Show calculations.

(*n*) What factors affect the cell constant? Why doesn't one always assume its value is unity?

(*o*) Could one readily check the last table value for per cent ionization by a freezing point method? Explain.

(*p*) Draw a diagram of the cell used. Label parts.

(*q*) Draw and briefly explain a Wheatstone bridge circuit. For what is it specifically used here? (See any physics text.)

(*r*) What results would you expect by conducting the same experiment on NH_4OH solutions to determine the degree of dissociation at different concentrations?

(*s*) Conductivity measurements are used industrially to check such things as the extent of carbonation in soft drinks, purity of distilled water, operation of ion exchangers and the mineral content of boiler feed waters. Explain how this simple, rapid method of quality testing applies.

Investigation of Typical Strong Electrolytes (Optional)

6. Make several dilutions of HCl in the range 0.2–10^{-3} M, from a

stock solution of dilute acid. Repeat the experiment and calculate parts (*a*) through (*k*) in paragraph 4. Explain the differences noted.

7. Make several dilutions of some salt like KCl in the range 0.2–10^{-4} M and measure the conductivities. Prepare a graph of specific conductance versus concentration and extrapolate to zero concentration (infinite dilution) to find the limiting equivalent conductance. Check this answer by applying Kohlrausch's law to appropriate handbook data.

8. Measure the conductivity of solutions of each of the following at the same temperature and concentration, say 25 C and 0.02 M: KCl, K_2SO_4, $MgCl_2$, $MgSO_4$, $Pb(NO_3)_2$, $BaAc_2$, and $PbAc_2$. Compare these figures. Explain why the last salt gives a figure greatly different from the others. How does this help to explain why, in cation group 2 analysis, $PbSO_4$ is soluble in NH_4Ac?

See references at the end of Chapter 5.

SPECIAL EXPERIMENT 2—DEDUCTIONS FROM *p*H DETERMINATIONS

If a *p*H meter is to be used, its construction and operation will be briefly discussed by the instructor. If indicators are to be used, a list of them similar to appendix A17 will be given. A series of buffer solutions (see a handbook) will be furnished with the indicators. Since various meters may be used, no effort is made here to give specific operating instructions.

A. Finding K_A for a Weak Acid

1. Various student groups may be assigned the task of preparing solutions of a weak acid like HAc as in special experiment 1. More or less solution will be needed depending upon the method used but 50 or 100 ml is satisfactory.

(*a*) *If a meter is employed*, adjust the temperature of the solution to 25 C and, after balancing the meter with a suitable buffer or standard,* measure the *p*H of the acid solution, where this dissociation has taken place:

$$HA = H^+ + A^-$$

If one knows the concentration of H^+ (by conversion of the *p*H reading), he may assume the A^- concentration is the same, and the HA concentration is the original solution molarity minus the quantity dissociated as

---

* Two solutions for *p*H reference at 25 C are 0.030 M potassium hydrogen tartrate, *p*H 3.57, and 0.050 M potassium hydrogen phthalate, *p*H 4.00. *p*H does not vary much with small temperature changes.

represented by either [H^+] or [A^-]. This is enough data to calculate K_A, or with K_A given to calculate the per cent dissociation as in special experiment 1. Class data may again be assembled from group contributions. Note that this instrumental measurement has again led to a means for determining such fundamentals as ion constants and dissociation percentages. Table 23-2 is data gathered by this method.

(*b*) *If indicators are used*, trial and error experimentation is used to get the *p*H roughly, and a more accurate approximation is obtained by comparing the hue of the particular indicator with the sample and with buffers in the same *p*H range. A "universal indicator" can also be employed as another check. (See the reference below.)

TABLE 23-2. TYPICAL STUDENT DATA FOR HAc IN SPECIAL EXPERIMENT 2

M HAc	*p*H 25 C	[H^+] $M \times 10^{-3}$	Per Cent Dissoc. (experiment)	Per Cent Dissoc. (theory)	K_A (experiment) ($\times 10^{-5}$)
1.0	2.35	4.48	0.45	0.41	2.02
0.1	2.90	1.26	1.26	1.34	1.59
0.01	3.48	0.332	3.32	4.25	1.10
0.001	5.00	0.010	10.0	13.4	1.10

B. Further Experiments (Optional)

2. Measure the *p*H of a salt such as NH_4Cl in the concentration range 0.3–0.01 *M* and calculate K_{ion} for the weak electrolyte produced in the hydrolysis. Compare *p*H to the calculated *p*H.

3. To 100 ml of one of the HAc solutions used above, add a weighed amount of NaAc and measure the *p*H of the buffer solution. Compare it to the calculated value. Account for any difference.

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SPECIAL EXPERIMENT 3—THE K_{SP} OF CaF_2

If one is able to find the molar concentration, X, of fluoride ion in a standard CaF_2 solution, it follows that the solubility product constant can be determined by

$$[Ca^{+2}][F^-]^2 = (X/2)(X)^2 = X^3/2$$

Fluoride may be determined to an accuracy of ±0.1 ppm in the range in the two flames and to get product colors corresponding to various oxidation states of the metal. These colors sometimes are different when the bead is hot or cold, and hence a number of ways of differentiation of metallic ions is available with one simple method. This finds use in the geological field, since many minerals will respond to fusions, whereas they are not easily solubilized for wet chemical reactions.

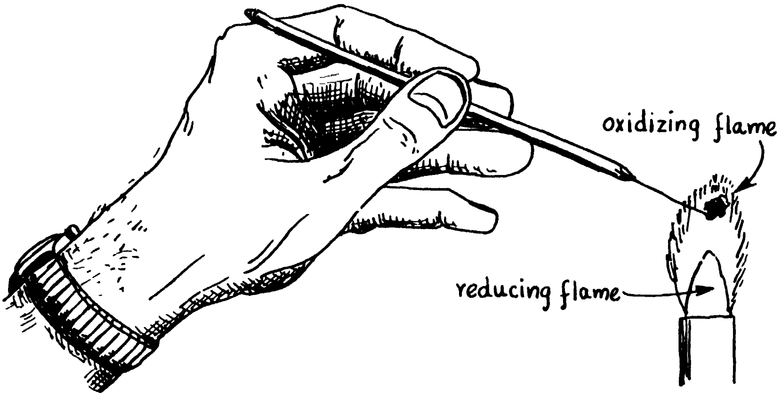

FIG. 23-1. Making a bead test. Sample and flux are transferred from a watch glass via Pt wire to the Bunsen flame.

Several minerals or salts should be tried as follows: touch a little of the material to be tested to the hot, clear bead and heat in the appropriate flame until the fusion mixture appears homogeneous. If minerals are not available, sulfides like CoS, as prepared in the cation procedures, or oxides like Cr_2O_3 from the side shelf or stockroom may be used with good results. See Table 23-3.

Other compounds may be used instead of borax for fusions, two common ones being soda ash, Na_2CO_3, and microcosmic salt, $NaNH_4(HPO_4)$. Colors developed with several less familiar elements are listed below. A typical formula for a compound formed in this method is $NaCoPO_4$ (blue). (Color abbreviations refer to A27.) The student may gather data to fill in the blanks of Tables 23-3 and 23-4.

2. Blowpipe Analysis—Charcoal Reductions

(*a*) *Minerals.* As usually practiced, one mixes 50 to 100 mg of powdered mineral with 100 to 200 mg of Na_2CO_3 and a drop or two of water. This paste is put in a shallow depression dug in a charcoal block. A *reducing* flame directed from the Bunsen flame via a blowpipe fuses the

Table 23-3. Borax Bead Colors

Element Contained in Mineral	Borax Bead Color					
	Oxidizing Flame			Reducing Flame		
	Hot	Cold	Corresponding Oxide	Hot	Cold	Corresponding Oxide or Metal
Cr	*Br*	*Gr*	CrO_3		*Gr*	Cr_2O_3
U	*Br*	*Y*	UO_3		*Y–Gr*	U_2O_3
Fe	*Br*	*Y*	Fe_2O_3		*Gr*	FeO
Ni	*Pu*	*Br*	NiO		opaque *Gy*	Ni
Cu	*Gr*	*Bu–Gr*	CuO		opaque *R*	Cu_2O, Cu
Mn	*Pu*	*R*	Mn_2O_3		*Cl–P*	MnO
Co	*Bu*	*Bu*	CoO	*Bu*	*Bu*	CoO
Ag, Zn, Mg, Si, Al, Ca, Ba	*Cl*	*Cl*	SiO_2, etc.	*Cl*	*Cl*	SiO_2, etc.

Table 23-4. Microcosmic Salt Bead Colors

Element Contained in Mineral	Microcosmic Salt Bead Color			
	Oxidizing Flame		Reducing Flame	
	Hot	Cold	Hot	Cold
W				*Bu*
U	*Br*		*Gr*	
Ti	*Cl*	*Cl*	*Y*	*Pu*
Mo	*Gr*		*Gr*	

mass. As the mixture tends to melt into the block, more carbonate is added and melted as before. This acts as a fluxing material for the gangue, leaving the metal oxide to be reduced by the combined action of the reducing flame and hot carbon. The result with reducible oxides is beads of metal suitable for microscopic or other examination (after washing them free of extraneous matter). Powdered minerals or appropriate oxides from the stock shelf may be used. Further tests to identify the metals are made after preliminary study with the microscope. Some simple cases are listed in Table 23–5. See also Chapter 21, on dry ignitions.

TABLE 23–5. CHARCOAL REDUCTION OF SOME OXIDES

Free Metal Obtained	Color	Further Test on Free Metal to Identify It
Ag	*W*	Soluble HNO_3; precipitates with HCl. (AgCl)
Au	*Y*	Insoluble HNO_3
Bi	*Gy*	Brittle
Cu	*R*	Soluble HNO_3; deep blue with NH_4OH. $[Cu(NH_3)_4^{+2}]$
Pb	*Gy*	Soft
Sn	*W*	White precipitate with HNO_3. (H_2SnO_3)

(*b*) *Sulfur-containing radicals.* A specific application and variation of the technique is this blowpipe method for sulfur-containing compounds. Concentrate a solution suspected of containing S^{-2}, SO_3^{-2}, $S_2O_3^{-2}$, SCN^-, or SO_4^{-2} (the last particularly, since good tests for sulfate are less numerous than for the others). Heat several drops of this with a little Na_2CO_3 on a charcoal block, directing the *reducing* flame to the mixture with a blowpipe. When well fused to a bead, let it cool, then transfer the bead to a spotplate and pulverize it with a stirring rod. If sulfur was present in the unknown, sulfide is now present in the powder and any sensitive method for S^{-2} is usable. The student should try several of his own design and report the results. One commonly used is to put the powder on a shiny, cleaned copper or silver coin with a drop of 1 *N* HCl; a dark spot indicates sulfide. The test should be repeated using a precipitate of $BaSO_4$ in place of test solution. In this manner one confirms the barium precipitate for sulfate. The reactions are:

$$SO_4^{-2} + 2C \overset{\Delta}{=} S^{-2} + 2\mathit{CO_2}$$

$$S^{-2} + 2H_2O = 2OH^- + \mathit{H_2S}$$

$$\mathit{H_2S} + Cu = CuS_B + 2H^+$$

3. Examinations With Ultraviolet Light

(*a*) Many minerals emit light upon excitation by ultraviolet radiation ("black light") and are segregated by this means for mining, testing, or actual identification. If light is emitted only while ultraviolet radiation is falling on the sample, the sample is said to be *fluorescent*; if emitted after the radiation source is removed, the sample is *phosphorescent*. The first phenomena are more generally observed, but the processes are similar in mechanism. Other means of excitation are also usable but less common in the field. These include heat (thermoluminescence), visible light (photoluminescence), X-rays (X-ray fluorescence), sound waves, neutron bombardment, etc. Chemicals produced for their fluorescence and phosphorescence are used in fluorescent lights, television tubes, advertising paints, etc. Some various commercially-coated tubes, minerals, semi-precious stones (sometimes identifiable from imitations by this means) and chemicals should be studied under ultraviolet illumination and a tabulation like Table 23–6 made. Fairly inexpensive ultraviolet lights may be purchased, or hand made ones, employing an argon bulb and filter, constructed. The former are available in so-called short wave length (2537 A) and long wave length (3660 A). The short is used for mineral inspection, the long for petroleum investigations.

TABLE 23–6. FLUORESCENCE OF SOME MINERALS

Mineral	Mineral Formula	Color under Natural Light	Color under 2537 Å Ultraviolet Light
Calcite	$CaCO_3$	*W*	*P*
Scheelite	$CaWO_4$	*W*	*W–Bu*
Opal	$SiO_2 \cdot nH_2O$	various	various
Sapphire	Al_2O_3	*Bu*	*Y–O, R*
Willemite	$2ZnO_2 \cdot SiO_2$	*W*	*Y*
Swartzite	$CaMg(UO_2)(CO_3)_3 \cdot 12H_2O$	*Gr*	*Y–Gr*
Manganapatite	$CaF \cdot Ca_3Mn(PO_4)_3$	*Gr*	*Y*
Fluorite	CaF_2	*W*	*Bu*
Diamond	C	*Cl*	*Bu*
Wernerite	$(CaCO_3 \cdot 3CaAl_2Si_2O_8)_x \cdot$ $(NaCl \cdot 3NaAlSi_3O_8)_Y$	*W*	*Y*

(*b*) Sometimes fusions are made with minerals to enhance fluorescence for the identification of small amounts. The following field test for ***uranium*** is illustrative of this method. A mixture of 20 parts of NaF, 400 of Na_2CO_3, and 400 of K_2CO_3 is fused (m.p. 730 C) in a small nickel or iron dish to give a glass 1–3 mm deep. (In the field, beer bottle caps function as reaction vessels but these are perhaps not as familiar to chemists as to geologists.) When cool, one sprinkles a few grains of mineral to be tested on the glassy surface, spacing the grains a few millimeters apart. The mass is then reheated until the mineral particles just begin to fuse with the flux, then it is allowed to cool. The surface is examined under the ultraviolet lamp, using the short wave length filter. If the grains contain U, a yellow fluorescence is noted. Some rare earths like cerium and a few metals like vanadium if present in large amounts will quench the fluorescence, but generally speaking this test gives reliable and rapid results. A blank run should also be made, using the reagents only. If many samples are to be run the fluxes are prepared in the lab and the finished fusions are labeled and brought back from the field for closer examination. Alternately, a flux of 10% NaF—90% $NaHCO_3$ may be used.

(*c*) If a *Geiger counter* is available its sensitivity should be compared with the above test, using for the fusion only an amount of uranium mineral which will just give a good fluorescent reaction. It will be found that the fusion–ultraviolet test will out perform the usual laboratory radioactivity demonstration instrument.

4. Crystal Types

The interested student with some background in geology should review the section in Chapter 13 on crystals and obtain a standard reference work on minerology like Dana's *Manual.* With a hand lens study some well-defined chemical compounds and try to identify the crystal symmetry. Refer to a chemical handbook for confirmation of decisions. Study some minerals in the same way and refer to the handbook on minerology. Note in this the variations of the basic types of crystal symmetry and how the geologist is able to use them in connection with other simple observations like color, hardness, etc. in practical quality analysis. Conventional chemical methods do not produce results as rapidly.

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SPECIAL EXPERIMENT 5—FLAME TESTS AND THE SPECTROSCOPE

1. Flame Tests

(*a*) These tests are used to aid the detection of Cu^{+2}, Sn^{+2}, Ba^{+2}, Ca^{+2}, Sr^{+2}, Na^+, K^+, Li^+, and BO_2^- among the ions listed in this text for testing. Such tests are usually made by concentrating 1–2 ml of solution to about one quarter of its original volume, adding several drops of concentrated HCl, dipping in a clean platinum or nichrome wire loop, and holding it in the flame and observing the color imparted to the Bunsen flame. (Tests for tin and borate are modifications and are described earlier with other examination of these ions.) In order to give a longer duration flame one may wind the wire around a little Gooch asbestos fiber and moisten with the solution. One should note the color of the flame, the time elapsed before the color becomes apparent, and the duration of the color. Sodium should be tested last since its flame is most persistent.

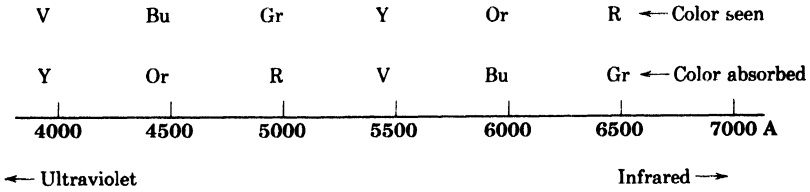

FIG. 23–2. The visible spectrum. See also Fig. 3–1.

Using Pt wire or wire-asbestos, run flame tests on test solutions of the ions listed above that have not been done previously. If solutions of Rb^+ and Cs^+ are available, add these and any others of interest. Report results in the notebook.

(*b*) Brilliant flames can be produced by spraying atomized solutions (hand bulb or compressed air) into a bunsen flame (**HOOD!**).

(*c*) *Potassium in the presence of sodium* can be detected upon filtering the mixed flame color by viewing it through a sheet or two of cobalt glass, the violet-blue glass absorbing the yellow Na^+ color and transmitting the K^+ color as a reddish violet. Suggest ways in which Li^+

could be seen in the presence of Na^+ and how a small amount of Na^+ might be seen in the presence of a large amount of K^+ or Li^+ or Rb^+. If available, a Di no. 512 filter from Corning Glass Co. is excellent to eliminate the Na^+ flame so others may be seen.

2. The Spectroscope

This instrument is used to make refined observations on flame tests. A glass prism separates the light by refraction into its different wavelength components which appear as colored lines called *spectral lines*. The whole visible field may reveal a number of lines for a given heated element, compound, or ion and this spectrum is distinctive of the element and consequently is a means of qualitative analysis. Each monochromatic image of the slit appears to the observer as a narrow, vertical line superimposed on an illuminated scale. The scale may read in wavelengths, but more often laboratory demonstration instruments contain an arbitrary

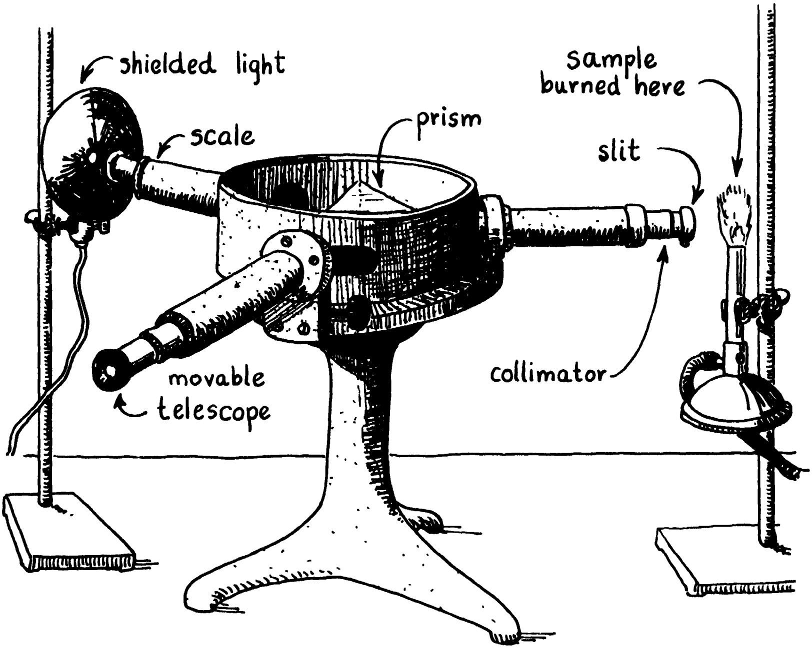

FIG. 23–3. A spectroscope. The cover has been removed to show the prism. A sample in solution is introduced into the flame on a Pt wire loop. The telescope is moved to scan the scale upon which are superimposed the spectra.

scale. This is calibrated using known substances in the flame and comparing the arbitrary scale numbers corresponding to the position of their strong spectral lines with handbook data that lists actual spectral position of these lines. One such instrument containing a scale reading from 0 to 180 in divisions of one unit gave the typical data in Table 23–7, using a Bunsen burner and the simple method described in part 1.

TABLE 23–7. CALIBRATION OF A TYPICAL STUDENT MODEL SPECTROSCOPE

Chloride of	Scale Observation (0–180)	
	Lines	Bands
Na^+	29	—
K^+	4.4, 112	—
Li^+	15.5	—
Ca^{+2}	38	22–24
Sr^{+2}	13.5, 26	16–19
Ba^{+2}	—	32–45
Cu^{+2}	—	39–42

The wavelengths corresponding to some of these readings are listed in Table 23–8.

The use of the spectroscope described above was to study *emission spectra.* Another use is the analysis of *absorption spectra,* which are also characteristic of the substances involved. If a beam of white light is the source of illumination before the slit in Fig. 23–3, the observer sees a continuous ("rainbow") spectrum. If, interposed between the light and the slit, is a thick gas layer, a crystal, or a column of solution, the observer now sees a discontinuous spectrum, certain black lines appearing since energy of those wavelengths, typical of the interposed substance, is being absorbed. In general, these dark lines appear where bright, colored lines would show if the interposed material had been burned to produce its emission spectra. (Using a powerful telescope and refined spectroscope in this manner, spectra of the sun have been observed and the composition of the absorbing gas envelope around it deduced.)

TABLE 23-8. SPECTRAL LINE WAVE LENGTHS

Element	Prominent Lines, A	Remarks
Cu	3274, 3248	Color due to compound used, not ion itself
Sn	3262, 3175	Color due to compound used, not ion itself
Ba	5536, 4554	Color due to oxide, not ion itself
Ca	4227, 3968, 3933	Color due to oxide, not ion itself
Sr	4607, 4078	Color due to oxide, not ion itself
Na	5896, 5890	Color due to ion itself
K	4047, 4044, 7665	Color due to ion itself
Li	6707, 6103, 3233	Color due to ion itself
Rb	7800, 4202	Color due to ion itself
Cs	4593, 4555	Color due to ion itself

Interpose solutions of some colored salts like $CuSO_4$, K_2CrO_4, $CrCl_3$, etc. between a white light source and the slit. Record the observations. Could unknown samples be identified in this manner if the behaviors of known materials were previously catalogued?

Look up descriptions of the spectrograph, flame photometer, and spectrometer and give schematic sketches of them with brief descriptions. Show their similarity and difference with the simple spectroscope.

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SPECIAL EXPERIMENT 6—SIX EXAMPLES OF QUALITY ANALYSIS FROM THE COMMERCIAL LABORATORY

A commercial laboratory advertising itself as performing analyses and/or duplicating formulations receives a variety of samples for both qualitative and quantitative examination. While such jobs are generally not as lucrative as the long-term contracts for routine analyses, the little diversified investigations are compensated for by the interest they create and the "know-how" background the chemist derives from them. Examples of these are the type wherein a customer wants to test his swimming pool water for free chlorine, another wants to check if a certain filling station is actually selling him gasoline containing tetraethyl lead, another person has read that coffee contains potassium and is curious enough to find out if this is true, a woman wants to verify an advertisement that a certain beer contains no sugars, another woman wants to find out if the dress she bought is wool as purported, or a cotton imitation, still another desires to know if an antiperspirant contains metals like zinc or aluminum toward which she is allergic, etc. The following six applications of qualitative analysis treat the problems just mentioned.

1. Free Chlorine in Water

This test is used to test for "free" or "residual" chlorine as found in municipally treated drinking water, swimming pools, bottle rinsing solutions, etc. The usual Cl_2 source is sodium hypochlorite or elemental chlorine. Other oxidizing agents like Fe^{+3}, Mn^{IV}, and NO_2^- interfere with the test by oxidizing the reagent and changing its color (see example 12, Chapter 12, p. 196), but they are not likely to be present in significant quantity in ordinary water samples.

Dissolve 14 mg of *o*-tolidine, or an equivalent quantity of its dihydrochloride, in 5 ml of H_2O and add this, with stirring, to a mixture of 3.5 ml of H_2O and 1.5 ml of concentrated HCl.

To 5 ml of water to be tested and contained in a 4-inch test tube, add 5 drops of reagent, mix well and allow to stand in the dark for 2 minutes. Examine it at that time for a yellow to red color. When running samples, one should always compare them with a blank made with distilled water, and viewing should be vertically through the longest column of solution.

The method can be made quantitative by comparison to color standards made from Cr^{VI} solutions. See reference 7, p. 436.

2. Tetraethyl Lead in Gasoline

$(C_2H_5)_4Pb$ has been used in gasoline for a long time to moderate the combustion of hydrocarbons, thus decreasing motor knock due to too rapidly exploding fuel.

Extinguish all flames in the vicinity. One milliliter of gasoline is shaken with 100 mg of decolorizing carbon, centrifuged, and retreated if not colorless. A few drops of colorless centrate are put on a spot plate or filter paper and allowed to evaporate in the sun.

While this is taking place, prepare a solution of dithizone (see example 2, Chapter 12) by dissolving one crystal in a few milliliters of cp CCl_4 (redistilled over NaOH preferably) to yield a moderately dark green solution.

Spot the residue with a drop or two of dithizone. The appearance of a red color indicates lead in concentrations as low as 0.02 ppm. The color intensity gives an estimate of concentration. (Zinc gives the same reaction.)

Lead may also be determined quantitatively in gasoline by precipitating it as $PbCrO_4$, dissolving in H_2SO_4, reacting the $Cr_2O_7^{-2}$ formed with excess KI, and titrating the I_3^- liberated with standard thiosulfate. What are the reactions?

3. Potassium in Coffee

Potassium is contained in coffee in easily measurable amounts. In the human system potassium is needed to activate certain heart muscles.

Put a gram of ground or powdered coffee in 20–25 ml of H_2O and boil it well. Divide the solution between two tubes, centrifuge, recombine centrates, and boil with 200–400 mg of decolorizing carbon. Stir to prevent superheating and bumping. Centrifuge and retreat the centrate with carbon if it has not been rendered colorless or light yellow. Boil the solution down to 2–3 ml and centrifuge again if any sediment remains suspended. To 1 ml of cooled, concentrated centrate, add 2 drops of 1 *N* HNO_3 and 10 drops of $Na_3[Co(NO_2)_6]$. Mix and note the slow formation of yellow dipotassium sodium hexanitrocobaltate, indicative of a sample containing K^+. The method can be made quantitative by centrifuging and reacting the residue with $K_2Cr_2O_7 + H_2SO_4$. The compound reduces dichromate to Cr^{+3} and the green color of the latter is matched with a series of standards.

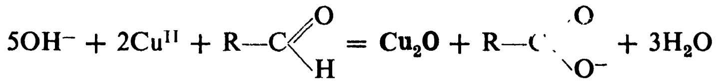
4. Reducing Sugars in Beer

In the production of beer, starch (*A*) in the fermenting malt (wort) is hydrolyzed by water and the enzyme diastase to the disaccharide maltose (*B*), which in turn is hydrolyzed in water by the catalytic action of another enzyme, maltase, to yield the simple sugar dextrose, also called glucose (*C*):

$$\underset{(A)}{(C_6H_{10}O_5)_x} \xrightarrow[\Delta]{H_2O} \underset{(B)}{x/2C_{12}H_{22}O_{11}} \xrightarrow[\Delta]{H_2O} \underset{(C)}{xC_6H_{12}O_6}$$

Beers contain 0.9–2.6 g of sugar, expressed as maltose, per 100 ml. Both these sugars are classed as reducing sugars; that is, they are capable of working reductions (not on the waistline, however) and become oxidized in the process. Both contain aldehyde groups which readily oxidize to acids.

With Fehling's solution, a basic copper tartrate complex, Cu^{II}, is reduced to Cu^{I}, which is not complexed and precipitates in the hot basic solution as red Cu_2O. The appearance of this precipitate is indicative of a reducing sugar in this case, and the method is quantitative if one weighs the sample, uses excess reagent, and weighs the cuprous oxide. The generalized reaction is



$$5OH^- + 2Cu^{II} + R{-}C\left\langle\begin{matrix}O\\H\end{matrix}\right. = Cu_2O + R{-}C\left\langle\begin{matrix}O\\O^-\end{matrix}\right. + 3H_2O$$

Mix 2 ml each of Fehling's solutions *A* and *B* (see reagents, A13) and stir to dissolve any $Cu(OH)_2$ temporarily formed. Now add 2 ml of beer and let the tube stand in a hot-water bath for 5–20 minutes. At the same time run a known, using a dilute glucose (but not sucrose) solution and a blank, using distilled water. The tubes (labeled) are best observed while being simultaneously heated in the same bath.

5. Vegetable and Animal Fibers Compared

Vegetable fibers like cotton are composed of only C, H, and O, whereas animal fibers like wool contain S and N as well. A sensitive test for —SH groups in animal protein (as well as sulfur in the form of S^{-2}, $S_2O_3{}^{2}$, and SCN^-) is a sulfur-catalyzed reaction between iodine and azide ion. A positive reaction gives nitrogen gas bubbles which are observable in small concentrations:

$$2N_3^- + I_2 = 3N_2 + 2I^-$$

In one spot plate depression put a clean wool thread, in another a clean cotton thread. Add to each, 2 drops of H_2O and 3 drops of NaN_3—I_2 reagent (reagent list, appendix), and after a minute or two observe which fiber has a cluster of bubbles around it. (The cotton may become dyed by the I_2.)

6. Aluminium and Zinc in Antiperspirants

These metallic ions are used in antiperspirant cosmetics because of their ability to close skin pores and prevent excretion.

Heat to boiling about 200 mg of sample with 6 drops of 6 *M* HCl and 3-4 ml of H_2O. Stir well, squashing out any greasy lumps to free soluble salts. Cool and centrifuge or decant. Divide the clear solution between two tubes:

Tube 1: Add 1 drop of phenolphthalein, then 3 *M* NH_4OH until barely pink. Add 1 drop of glacial HAc and rinse the solution into a small beaker with 3–4 ml of H_2O, and heat in a water bath to 80 C. Add 1 ml of 8-hydroxyquinoline solution (see example 4, Chapter 12 and A15). Then add 2 ml of 2 *M* NH_4Ac and keep the mixture hot for 2 minutes. A white flocculent precipitate indicates Al^{+3}, Zn^{+2}, and/or Mg^{+2} among the common metals precipitating under these conditions. Further testing is necessary to show which is present, but a positive test at least indicates that further work is needed and also illustrates the use of this important organic reagent.

Tube 2: The student is invited to devise his own procedure for the detection of Al^{+3} and/or Zn^{+2}. Such might be based upon the fact that one gives a precipitate with excess NH_4OH, whereas the other forms a soluble ammine complex, etc. Report the results.

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SPECIAL EXPERIMENT 7—THREE EXAMPLES OF QUALITY ANALYSIS FROM THE FIELD OF CRIMINOLOGY

The scientific criminologist must have a broad background and working knowledge of many subjects, and because of the importance and consequence of his court testimony, he must be an exceedingly cautious and painstaking worker. He is frequently called upon to identify and test synthetic and inorganic substances as well as materials of plant and animal origin and must be versed not only in chemical analysis, but also in physics, biology, botany, pharmacology, toxicology, geology, microscopy, etc. It is a fascinating application of qualitative testing. The following tests are illustrative.

1. Testing Inks

Ink types, similarities, differences, composition, ages, etc. may sometimes be determined by a combination of chemical analysis for the elements present and a microscopical examination of the surface appearance of the ink and paper. Such work would be likely on questioned documents of the type where erasures, fill-ins, additions, counterfeiting, etc. are suspected. Thus although two samples of writing may appear alike, one may fluoresce under ultraviolet light because of the dye used, and the other may not. Or in another case, one ink may contain an iron pigment, and the second specimen may contain a copper pigment. Since earliest times inks have been compounded and used and thousands of mixtures made. It is quickest to demonstrate some differences in two samples as a means of telling them apart and qualitative testing is the tool for doing this.

(*a*) *Testing for iron and the age of inks.* Most older inks were made from mixtures of ferrous sulfate and two organic weak acids, tannic and gallic, with which iron gives a color-fast blue complex. Most newer inks are made from organic dyes, glycerine, gums, and water. The older the writing with iron inks, the more difficult it is to bleach, thus analyses for iron and for bleaching time will aid in characterizing a specimen of writing.

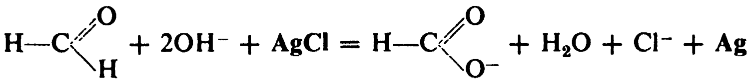
Put a small piece of paper containing some writing to be examined on a watch glass and submerse it in 1% NaOCl. Note the length of time needed to bleach the writing. If writing samples of several ages are available (as one might collect from old letters and envelopes) the bleaching times should be measured and compared. Experimental procedures, including temperature, should be identical.

The hypochlorite treatment (basic) will cause Fe^{+3} to be precipitated as $Fe(OH)_3$ where the writing was. If the paper is then washed with a 5% $Na_2S_2O_3$ solution, and next with H_2O, one may test for the presence of iron. The faded writing is spotted with a solution made by dissolving 0.5 g of NH_4SCN in 5 ml of 2 *M* HCl. Red $Fe(SCN)^{+2}$ is the evidence one looks for. Blank paper should be run in the same way. Why?

(*b*) *Testing for chloride.* Prepare some $AgNO_2$ by adding 8 ml of Ag^+ test solution to 3 ml of NO_2^- test solution. Decant and discard the supernatant liquid, wash the residue with a little H_2O, and discard the liquid again. Dissolve the light yellow residue of silver nitrite in 10 ml of 3 *M* HNO_3.

Cut out a small sample of writing, place it on a watch glass and submerse it in the silver reagent just prepared. Any chloride in the ink will be converted to AgCl and fixed on the paper where the writing was. (Some cheaper papers may themselves contain chloride and may mask the next reaction.) When the writing has faded, wash the paper with H_2O, let it soak 5 minutes in 0.1 *M* HNO_3, then rinse it with H_2O again. Now reduce the AgCl to metallic silver by spotting the writing (or immersing the paper) with a solution made by mixing 5 drops of 35% formaldehyde (formalin) in 2.5 ml of 0.5 *M* NaOH. Again wash the paper in H_2O

and if Cl^- was present in the ink, the writing is visible as a tracing of dark silver.



$$H{-}C\begin{matrix}{\scriptstyle \nearrow}O\\ \searrow H\end{matrix} + 2OH^- + AgCl = H{-}C\begin{matrix}{\scriptstyle \nearrow}O\\ \searrow O^-\end{matrix} + H_2O + Cl^- + Ag$$

Blank paper is tested in the same way.

2. Testing Marihuana

A cooperative police department may furnish a few grams of this common narcotic or at least enough for one or two tests to be viewed by larger groups. Pictures of the growing plants may also be available. The international problem of stopping the illicit narcotics trade has been attacked in various ways, not the least important of which is the work of analytical chemists whose methods enable law enforcement agencies to test and identify microscopic amounts of such materials. While marihuana (Indian hemp, *cannibus sativa*) does not give the addict the violent withdrawal symptoms that opium derivatives do, it is a frequent precursor to the use of more powerful narcotics and its insidious character in this respect is not to be underestimated.

(*a*) *Microscopical examination.* Under low magnification one looks for oval-shaped seeds of light-brown color with tracings in darker brown over the surface. Leaf particles will show a surface covered with curved pubescent hairs and a few patches of dark resin and pimple-like excrescences called globule protuberances. These features are highly characteristic of the plant.

(*b*) *The hydrochloric acid test.* Under the microscope, find a globule on a leaf surface and pick it apart with a needle. In many of these are found crystals of $CaCO_3$, hence the name "stone cells" is given to them. Add from a capillary glass pipet, made by pulling out a piece of tubing, a micro drop of dilute HCl and note the fizzing as CO_2 is released.

(*c*) *The Ducanois* (*Megm*) *test.* Make a solution of 0.2 g of vanillin, 3 drops of acetaldehyde, and 10 ml of 95% methyl alcohol. Grind a bit of marihuana on a spot plate with a blunt stirring rod. Add a few drops of petroleum ether and grind again; then let the solvent evaporate. Scrape out the larger particles and discard, leaving the extraction stain intact. Add 2 drops of 6 *M* HCl to this residue, then 4 drops of reagent. A positive reaction, which apparently is specific for marihuana, is the development over the next 5–20 minutes of a series of colors predominantly blue and violet.

If the three above tests were all positive, the material examined was marihuana, and evidence based on similar procedures is being presented daily in courts. If other dried plants are available, they should be studied as outlined and differences noted. Among those which show some microscopical similarities is catnip.

3. Testing Blood

In testing spots, stains, solutions, etc. for blood, one first covers all the suspected areas with rapid preliminary tests, then restudies those pieces of evidence that gave a positive test with methods that are specific, but more time consuming.

(*a*) *The benzidine test—a preliminary.* Mix about 0.1 g of benzidine base (the free diamine) with 2 ml of glacial HAc and stir well. Add 4 drops of 3% H_2O_2 and stir again. To a speck of material suspected of being or containing blood and placed on a spot plate, add a few drops of reagent. The appearance of a blue-green color is a positive reaction and will detect as little blood as 1–2 ppm. The reaction will even work on dried blood samples several years old. Try the test on various samples. Some suggested ones are: dried nonhuman blood, rust, MnO_2, PbO_2, NaOCl, NaCl, $NaNO_3$, cloth, perspiration, and hair. Report the results. Refer to example 8, Chapter 12.

(*b*) *The Teichmann test—a confirmation.* A reagent is made from 0.1 g each of KI, KBr, and KCl in 10 ml of glacial HAc. A smear of water-loosened material (as a stain soaked out of a cloth) is put on a glass slide and dried below 100 C. Two drops of reagent are added to the smear, a cover glass put on, and the preparation warmed over a low flame until the liquid begins to bubble. Then the flame is turned off. Another drop of reagent is put alongside the cover slip and allowed to seep under. After allowing the slide to cool, examination under about 100× magnification will reveal yellow to brown rhomohedra of hemin chloride. If both tests (preliminary and confirmatory) were positive, the sample is blood.

Further testing is possible, the biological precipitin test verifying the sample to be human blood and giving its type: A, B, AB, or O. Experts in the field are able to group samples even more specifically and some feel that in time enough will be known about blood and its analysis so that blood samples will become as distinctive as fingerprints in human identification.

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SPECIAL EXPERIMENT 8—QUALITATIVE TESTING OF SOME INORGANIC IONS BY FLUORESCENCE

1. Boron

A test for boron which can detect that element at low concentrations is reported by White. The method involves making a derivative of boron (as borate) with benzoin and checking the fluorescence under the ultraviolet light.

Prepare 1 ml samples, using borax as a source of boron, to contain 0.5, 5.0, 10, 50, and 100 ppm B. To each add 1 drop of 0.25 *M* NaOH, then 8 ml of 95% ethyl alcohol, and 1 ml of 0.4% benzoin in alcohol. Shake each and compare the strengths of fluorescence in a dark room with ultraviolet radiation. A green–white color is specific for boron. Does it appear from these samples that one could make the method semiquantitative?

2. Aluminium

A similar method is usable for metallic ions that yield 8-hydroxyquinoline (oxine) derivatives. (See example 4, Chapter 12, and special experiment 6, part 6.)

Put 2 drops of Al^{+3} test solution on a piece of filter paper, add 2 drops of an alcoholic 8-hydroxyquinoline solution, and show that the spot fluoresces only weakly. Now hold the paper over an open NH_4OH bottle. Reaction takes place between the oxine and metallic ion and the spot becomes strongly fluorescent. Wash the spot with a little H_2O, then hold over an open bottle of glacial HAc. The spot is still fluorescent, showing the stability of the Al–oxine chelate.

Repeat the experiment with various quantities of the metal and note the effect on the fluorescence.

Repeat with Mg^{+2} instead of Al^{+3}. What difference is noted? Does this give one a method for determining which chelate is more stable? Postulate a reason for the stability differences.

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SPECIAL EXPERIMENT 9—DEMONSTRATIONS OF CHROMATOGRAPHIC METHODS

Chromatography is a method of separating one or several dissolved components of a mixture by distributing them between two immiscible phases, one of which is moving past the other. Separations can be made in *columns* (*Twsett*, 1906) packed with insoluble materials like alumina, silica, starch, carbon, etc. over which the solution is poured, or made on *paper strips* (*Goppelsroeder*, 1906) over which the solution moves capillarily. In either case, under proper conditions the separable components will concentrate in different areas and will appear as variously colored zones or bands, either by themselves or by color-developing reagents or radiations. The components may be bound chemically or physically to the adsorbing surface and since the various components have different abilities to do this, separations are possible which might be difficult by other means. Considerable opportunity for original work in this technique exists.

1. Separation of Two Dyes—a Quick Preliminary Illustration

Dissolve a few crystals of salts of methyl orange and malachite green in several milliliters of H_2O contained in a 7- or 8-inch test tube. Cut a strip of filter paper $\frac{1}{2}$ in. wide and long enough to reach to the liquid from the tube's mouth. Fix the strip at the top by some method, such as a staple and cork, so that it hangs free in the center of the tube with its bottom about 1 cm below the level of the dye mixture. Observe over the next few hours that the methyl orange rises much more readily than the green dye and that a separation is effected. In practice one would cut the strip in two at the color boundary and *elute* each component from the paper with proper solvents. When the solvent boundary has almost reached the top, calculate the R_f *value* (ratio of fronts) for each dye: R_f = distance the component traveled on the strip divided by the distance the solvent traveled.

2. Separation by Partition on Paper of Group 1 Cations

Cut a strip of filter paper about 30 cm long and 1.5 cm wide. Put 3 drops of each group 1 test solution on one spot about 5 cm from the bottom of the strip and dry it over a low flame. Suspend the strip from a cork in a cylinder which contains at the bottom, in contact with the strip, a few milliliters of a mixture containing 15% H_2O, 10% ethylacetoacetate, 75% *n*-butanol, and enough glacial HAc to make the *p*H 3.5–4. After the liquid boundary has reached the top, remove the strip and let it dry. Spray the strip with a dilute K_2CrO_4 solution and from the colors of the group 1 chromates discovered in the preliminary experiments in Chapter 15, identify each zone. Calculate R_f for each ion. Wash the strip with H_2O then dry it and label its areas. See reference 1, p. 443.

Many references may be found giving similar methods for the other anion and cation groups. The separations may be made quantitative by dissolving the adsorbed substance from the paper and then titrating, electroplating and weighing, ashing and weighing, etc.

3. Separation in a Column of Group 1 Cations

Prepare a dry column as illustrated in Fig. 23–4. Start moderate suction with the aspirator, add 2 ml of H_2O, and press the cotton wad down well to keep air moving ahead of the water, excluding entrained bubbles from the column. Adjust the aspirator so that the water boundary falls quite gradually. Add in order, 1 ml of glacial HAc, 1.5 ml of 5% K_2CrO_4, 2 ml of H_2O, 3 ml of solution containing 1 ml of each group 1 test solution, Ag^+, Pb^{+2}, Hg_2^{+2}, and then 3 ml of H_2O.

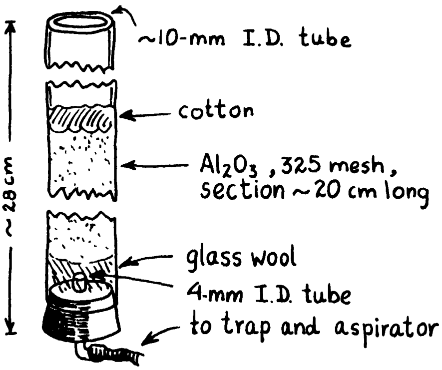

FIG. 23–4. A chromatographic column.

Bands of colored chromates will form in the column at different distances from the top. Note the order and compare it to the paper method. The column may be pushed out with a plunger, the colored segments cut out with a spatula, the metallic chromates dissolved in HNO_3, and those solutions further tested. Outline a method for testing to verify the presence of each metallic ion. See reference 6, p. 443.

4. Group 2 by Paper Chromatography

Cut a strip of Whatman no. 1 filter paper about a foot long and ½ in. wide. Put a ¼ in. streak of solution containing several group 2 ions across the width of strip and about 1 in. from the bottom. Dry it by waving over the Bunsen flame. Hang the strip from a cork in a 12-in. tube which contains enough developing solvent (95 volumes of tert-butanol and 5 volumes of glacial HAc) to submerge about ½ in. of the strip below the streak. *Do not get solvent above the streak.* Stand the tube aside for 6–12 hours. Remove the paper when the solvent boundary reaches the top, and allow the strip to air or oven dry. Moisten the strip with H_2O, using a fine atomizer or steam bath, and then expose it to H_2S gas until all the colored sulfide zones have appeared. One may cut the individual areas out, dissolve them in HCl or HNO_3 and run spot tests to determine their identity, or one may identify them simply by reference reading, then dry the strip, label the zones, and preserve the preparation with clear varnish.

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SPECIAL EXPERIMENT 10—USE OF DITHIZONE AS A SPOT REAGENT FOR SEVERAL METALLIC IONS

Dithizone (diphenylthiocarbazone) was prepared by the great organic chemist Emil Fischer in 1878, but its use as a color reagent for small amounts of metallic ions did not become generally known until almost 50 years later. It is soluble in several common organic solvents and with many metal ions forms inner complexes which are also soluble in these solvents. If the organic solvent is immiscible with H_2O, it affords a method of extraction, and, since the complexes of the metals form at various *p*H's, and the colored dithizonates lend themselves to quantitative colorimetry, considerable use of the reagent has been evidenced during recent years. Dithizone is a sensitive reagent for Mn, Fe, Cu, Ni, Co, Zn, Pd, Ag, Cd, In, Sn, Pt, Au, Hg, Tl, Pb, and Bi. Good technique is needed, of course, since its wide reactivity makes any specific reaction subject to question. See example 2, Chapter 12.

1. As an Indicator Paper

Make about 10 ml of a saturated solution of dithizone in acetone. Soak a circle of filter paper with the solution and when the solvent evaporates, cut the paper into small squares, each suitable for a single test. To succeeding squares, add a drop of the following, and record the colors produced initially and when dry: 1 *M* HCl, 1 *M* NaOH, 1 *M* NH_4OH, and ion test solutions of Zn, Pb, Sn, Hg_2, Hg, Cu, Ag, and Bi. See reference 2 below.

2. As a CCl_4 Solution

The reagent may be prepared as a 0.001 wt/volume per cent solution in cp CCl_4 or $CHCl_3$. To test an aqueous solution, 2 ml of solution are shaken with 10 drops of dithizone reagent and the color in the dithizone layer noted. In practice, a buffer is also added to aid specific extractions. Working in this way, as little as 0.0016 ppm Zn^{+2} has been reported detectable, which is comparable to spectrographic analysis and is one of the most sensitive chemical tests known. Water from galvanized pipes easily shows this test and distilled water which has been condensed in copper tubing gives a test for copper. The reagent is so sensitive in fact that, in inexperienced hands, almost any aqueous sample gives a positive reaction of some sort.

Dilute the same test solutions used in paragraph 1 by 10-fold and run them as mentioned here, without buffers, and report the colors obtained in the CCl_4 layer.

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SPECIAL EXPERIMENT 11—DIFFERENTIATION OF Ca^{+2} AND Sr^{+2} USING CHEMICAL MICROSCOPY

There are many examples of the identification of substances by microscopical study of the crystal habit of reaction products. This general method is used particularly with complex substances like natural products which do not yield to other simple tests. One drawback is that a given material may, under slightly different conditions of temperature, concentration, etc., yield differently shaped crystalline products and one may misinterpret the evidence, so experience in handling the technique is all important.

In group 4, calcium and strontium are often confused because of their chemical similarities. The following method is one means of differentiation and is typical of the use of the microscope in this behalf. See reference 3 below.

1. Clean a glass slide thoroughly with scouring powder, rinse it under tap and distilled water, then let it dry.
2. Near one end of the slide put a drop of Ca^{+2} solution containing 5–6 mg Ca^{+2} per milliliter and with a clean Pt wire spread the drop a bit.
3. Near this drop put a drop of 10% HIO_3 and draw the cleaned wire from it to the first drop, making a thread of connecting reagent between the two. Tilt the slide only slightly to allow the acid to flow. This more dense solution will mix on the bottom of the calcium drop and with crystallization starting there, crystals will show their well-defined features toward the observer.
4. After the spot has been prepared, it is examined under low power, 25–150×, and the crystal growth and habit described in the notebook.
5. Repeat 1–4 using strontium at the same concentration at the other end of the slide. Note the differences in the two preparations. Comment on this specific method and on the general approach to qualitative analysis.
6. As an alternate precipitating agent in the same general manner, use 6 *M* H_2SO_4 and warm the slide gently until crystals begin to appear at the edges. Note the characteristic bundles of needles exhibited by $CaSO_4 \cdot 2H_2O$.

The use of the microscope illustrated in this experiment is only one of the ways in which the analyst utilizes this important instrument. Further applications are in finding the index of refraction of small samples (which is an identification means) and in observations using polarized light, under which crystals show several identifying characteristics. The uses of the microscope in metallurgy, criminology, and petrography are invaluable.

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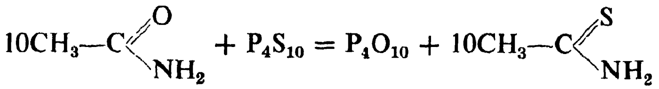
SPECIAL EXPERIMENT 12—PREPARATION OF THIOACETAMIDE

One gram-mole of acetamide (CH_3CONH_2, mol wt = 59) and 0.12 g-mole of powdered phosphorous pentasulfide (P_4S_{10}, mol. wt = 444) are refluxed in a liter flask (steam bath) containing a few boiling chips and 500 ml of dry benzene, for about a half hour. The reflux column should carry a $CaCl_2$ tube at the top. The solution is decanted from the residue into another flask, refluxed with several boiling chips and 5–6 g of decolorizing carbon, then filtered hot. The flask is connected to a condenser via a 10-mm I.D. goose neck and excess solvent distilled, using the steam bath until crystallization of product appears imminent. The hot solution is poured into a beaker and allowed to crystallize (hood) over night. The thioacetamide is filtered off on a suction assembly and the mother liquor either concentrated to obtain a second, small crystal crop, or returned to the original flask with the distilled benzene and residue from the first refluxing. This flask is recharged with more solids and solvent as needed to give approximately 500 ml, and the process repeated. After the final run, the gummy residue in the reaction flask is removed with *small* portions of dilute HNO_3 and later heating. **(HOOD! CAUTION!)** The yield is about 30% of theoretical. The reaction is



$$10\mathrm{CH_3{-}C}\Big\langle^{\mathrm{O}}_{\mathrm{NH_2}} + \mathrm{P_4S_{10}} = \mathrm{P_4O_{10}} + 10\mathrm{CH_3{-}C}\Big\langle^{\mathrm{S}}_{\mathrm{NH_2}}$$

Good ventilation must be provided as moisture will cause some hydrolysis liberating hydrogen sulfide.

$$\mathrm{P_4S_{10}} + 16\mathrm{H_2O} = 10\mathrm{H_2S} + 4\mathrm{H_3PO_4}$$

The 8% aqueous student solutions need not be filtered prior to use if a residue appears.

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Also see references at the end of Chapter 16.

SPECIAL EXPERIMENT 13—ELECTROGRAPHIC TECHNIQUE

Another simple and useful technique in qualitative testing is the electrographic method first described by *H. Fritz* in 1929. The sample under test is anodically eroded onto a piece of filter paper charged with a moist inert electrolyte solution like KCl or K_2SO_4. The paper is then spotted with a reagent and the sample identified by the color produced. Typical reagents are the same ones used in the laboratory to give color reactions with the common ions: dimethylglyoxime, silver nitrate, acid–thioacetamide, ammonium sulfide, potassium ferrocyanide, potassium chromate, etc. The apparatus is shown in Fig. 23–5. A desirable addition is a means for exerting pressure on the electrode–sample system.

Any d-c source (from a flashlight battery to a small rectifier) is satisfactory and other metals than those indicated may be used for electrodes. The anode is a rod, and the cathode is a sheet. The sample is a metal, conducting mineral, or even powder. The meter is any low current-consuming ammeter or voltmeter, but it is not absolutely necessary. A little experimentation will reveal the conditions of time and solution concentrations that give best results with a particular device and sample. As with the rest of qualitative testing, the method is open for improvement and ingenuity by the person with the scientifically inquisitive mind.

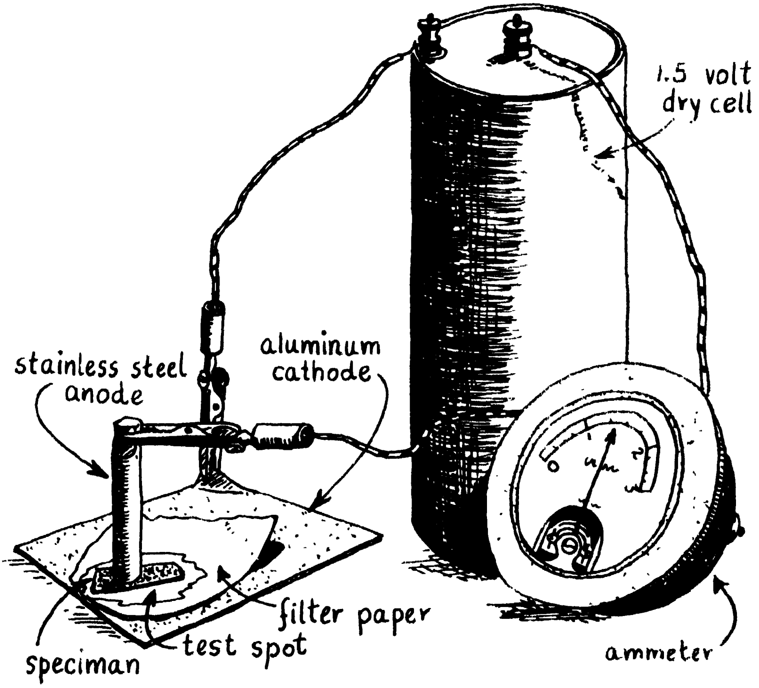

FIG. 23 5. The electrographic setup. Pressure must be put on the anode to obtain a good print. Contact is maintained a minute or more For serious work, a regular press is used to produce pressures up to 1000 psi.

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APPENDIX

A1. Review of Exponential Numbers

Very large and very small numbers are common in chemistry. They are best expressed and mathematically handled by writing them as one decimal numbers times 10 to a power (exponent). For transposing numbers larger than 10 into this form, one moves the decimal point to the left the requisite number of places to still leave one place to the left of the point, and the resulting exponent is a positive integer expressing the number of places the decimal was moved. Thus

$115 = 1.15 \times 10^{2}$ (decimal point moved two places)
$6{,}000{,}000 = 6.00 \times 10^{6}$ (decimal point moved six places)
$3717 = 3.717 \times 10^{3}$ (decimal point moved three places)

One may round off the third figure, as slide rule accuracy is sufficient in problem solving in this course. The last number then becomes 3.72×10^{3}.

In expressing numbers smaller than 1 in this system, the decimal is moved to the right to give a one-decimal number. The exponent again expresses the number of places moved but is negative this time:

$0.156 = 1.56 \times 10^{-1}$ (decimal point moved one place)
$0.00326 = 3.26 \times 10^{\ 3}$ (decimal point moved three places)
$0.000000407 = 4.07 \times 10^{-7}$ (decimal point moved seven places)

Common mathematical operations are speeded in the following ways.

(1) *Multiplication*

Numbers are written in exponential form as described above. The numbers preceding the "times" signs are multiplied on the slide rule (see slide rule section) in the normal fashion. The exponents are added algebraically. The answer is finally written as a one-decimal number times 10 to a power. Thus

$$(2 \times 10^3)(4 \times 10^4)(3 \times 10^{-2}) = 24 \times 10^5 = 2.4 \times 10^6 \quad (\textit{Ans.})$$

(2) *Division*

The decimal parts are divided on the slide rule in the usual manner. The sign of the exponent in the denominator is reversed and the exponents in numerator and denominator then added algebraically:

$$5.75 \times 10^{-5}/7.21 \times 10^3 = 0.798 \times 10^{-8} = 7.98 \times 10^{-9} \quad (\textit{Ans.})$$

(3) *Addition and subtraction*

The numbers are rewritten (if necessary) so that all exponents are alike in magnitude and sign. The decimal parts are then added or subtracted in normal fashion and the answer has the same exponent on 10 as did all the preceding 10's in the problem:

$$\begin{aligned} &2.00 \times 10^2 + 3.00 \times 10^1 + 1.00 \times 10^3 \\ &\qquad = 0.200 \times 10^3 + 0.0300 \times 10^3 + 1.00 \times 10^3 \\ &\qquad = 1.23 \times 10^3 \quad (\textit{Ans.}) \end{aligned}$$

(4) *Squaring*

Square the decimal part using the slide rule, then multiply the exponent by 2 and rewrite the answer in one decimal exponential form:

$$(4000)^2 = (4.00 \times 10^3)^2 = 16.0 \times 10^6 = 1.60 \times 10^7 \quad (\textit{Ans.})$$

(5) *Cubing*

Cube the decimal part using the slide rule, then multiply the exponent by 3 and rewrite the answer in one decimal exponential form:

$$(300)^3 = (3.00 \times 10^2)^3 = 27.0 \times 10^6 = 2.70 \times 10^7 \quad (\textit{Ans.})$$

(6) *Square root (the ½ power)*

Rewrite the number so the decimal part is a number between 1 and 100 and the exponent is divisible by 2. Find the root of the decimal part using the slide rule in the usual way, then divide the exponent by 2. The answer will always contain a decimal number between 1 and 10 and may be left as found:

$$\sqrt[2]{2500} = (2500)^{\frac{1}{2}} = (25.0 \times 10^2)^{\frac{1}{2}} = 5.00 \times 10^1 = 5.00 \times 10 \quad (\textit{Ans.})$$

(7) *Cube root* (*the* $\frac{1}{3}$ *power*)

Rewrite the number so that the decimal part is a number between 1 and 1000 and the exponent is divisible by 3. Find the root of the decimal part using the slide rule, then divide the exponent by 3. The answer will always contain a decimal number between 1 and 10 (why?) and may be left as found:

$$\sqrt[3]{0.000722} = (722 \times 10^{-6})^{\frac{1}{3}} = 8.98 \times 10^{-2} \quad (\textit{Ans.})$$

A2. Review of the Slide Rule

The following general rules constitute only the briefest summary of the operation of those scales on the slide rule that are necessary for working problems encountered in this course. The student is referred to the library for books giving more detail and worked examples. Consult these or your instructor regarding questions arising from markings on nonstandard slide rules, special scales, etc. It is assumed the student is able to read the scales on the rule; i.e., he can locate given numbers and can read the answer. It is best if the numbers in the problem be rewritten in exponential form (see preceding section), the answer approximated mentally (since the slide rule only gives the numbers in the answer and does not directly give decimal points), and then the actual answer found with the rule. Thus

$$\begin{aligned} &\sqrt{406}(28.4)/(31.6)(0.0150) \\ &\qquad = (4.06 \times 10^2)^{\frac{1}{2}}(2.84 \times 10)/(3.16 \times 10)(1.50 \times 10^{-2}) \\ &\qquad \cong (2 \times 10)(3 \times 10)/(3 \times 10)(1.5 \times 10^{-2}) \\ &\qquad \cong 2 \times 10/1.5 \times 10^{-2} \cong 1.3 \times 10^3 \quad (\textit{Approx. ans.}) \end{aligned}$$

The number one gets on the slide rule is 121. The actual answer must be 1.21×10^3. The 10-in. slide rule gives 3-place accuracy, and that will be sufficient for our purposes. If the student is in doubt as to the interaction of any two scales, he may always check his methods by trying a problem (involving those scales) whose answer is known.

(1) *Multiplication*

To multiply x by y, put the *index* of the C scale (the 1's at the ends of the scale are the indexes) over x on the D scale. Slide the *wire* (also called the *cursor*) over y on the C scale, and read the answer under the wire on the D scale. In case the answer does not fall on the rule, having used the left C index, the right C index is used, thus permitting any number of numbers to be multiplied together without running out of room on the rule or having to write down any intermediate answers.

(2) *Division*

To divide x by y, (x/y), put wire over x on D scale. Slide y on C scale under wire. Read answer under the C index on the D scale.

(3) *Logs and Antilogs*

(More detail is given in the section following, which is devoted to this topic.) Most rules work in this manner: to find the mantissa of the logarithm of x, put wire over x on D scale, read the mantissa under wire on the L scale. To find the antilog of y, put wire over y on L scale, read antilog under wire on D scale.

(4) *Squaring*

To square x, (x^2), rewrite x as a one-decimal exponential number, put wire over x on D scale, and read square under wire on A scale; multiply the exponent by 2. Note that the A scale is a double one, going from 1 through 10 to 100. Thus 2^2 is 4, but 6.33^2 is 40.0 and $(6.33 \times 10^4)^2$ is 40.0×10^8 or 4.00×10^9.

(5) *Cubing*

To cube x, (x^3), write x as a one-decimal exponential number, put wire over x on D scale, and read cube under wire on K scale; multiply exponent by 3. Notice that the K runs from 1 through 10 and 100 to 1000 in a triple scale. Thus 2^3 is 8, 4.31^3 is 80.0, and 9.29^3 is 800.

(6) *Square root*

To take the square root of x, $(\sqrt{x}$ or $x^{\frac{1}{2}})$, write x as a number between 1 and 100 times 10 to an even exponent. Put wire over x on A scale, read root under wire on D scale; divide exponent by 2.

$$\sqrt{650} = \sqrt{6.50 \times 10^2} = 2.55 \times 10; \text{ and } \sqrt{6500} = \sqrt{65.0 \times 10^2} = 8.07 \times 10 \quad (\textit{Ans.})$$

(7) *Cube root*

To take the cube root of x, $(\sqrt[3]{x}$ or $x^{\frac{1}{3}})$, write x as a number between 1 and 1000 times 10 to a power divisible by 3. Put the wire over x on the K scale, read root under wire on D scale; divide exponent by 3.

$$\sqrt[3]{5} = 1.71;\ \sqrt[3]{500} = 7.94;$$

$$\sqrt[3]{50{,}000{,}000} = (50.0 \times 10^6)^{\frac{1}{3}} = 3.69 \times 10^2 \quad (\textit{Ans.})$$

Other scales will find little use in this course. If desired, they can be mastered by use of a manual on the slide rule.

A3. Review of Logarithms

If one understands the foregoing section on exponential numbers, he should have little difficulty with logarithms. In this course, only logs to the base 10 will be used. The following development summarizes their use. See also A30.

The logarithm of any number is the power to which 10 must be raised to equal that number:

Number	Number Exponentially	Logarithm
100,000.	10^5	5
100.	10^2	2
10.	10^1	1
1.	10^0	0
.1	10^{-1}	-1
.0001	10^{-4}	-4

For numbers like 75, which cannot be expressed as an even power of 10 and handled mentally, one uses log tables or the L and D scales on the slide rule. Obviously the log of 75 must lie between 1 and 2 (10^1 and 10^2) and is 1.875.

Each log is made of two parts: the *characteristic*, which is to the left of the decimal point and establishes the decimal places in the actual number the log represents; and the *mantissa*, which is to the right of the point and establishes the integers in the actual number the log represents. It is seen above that the characteristic is 1 less than the number of decimal places in the actual number. Example: Find the log of 6750. One rewrites this as 6.750×10^3. The characteristic is 3 and the log of 6.750 is found in a table to be 0.829, so the log of 6750 is 3.829. The operation is the addition of two logs: $\log 6.750 + \log 10^3 = 0.829 + 3 = 3.829$. As we added exponents in the previous section on multiplication, so we will add logs to carry out the same process. Using most slide rules, one sets the slide wire over 675 on the D scale and reads 829 under the wire on the L scale. (Some models operate differently.)

The log of a number less than 1 has a negative value. Find the log of 0.006750. This is rewritten $6.750 \times 10^{-3} = \log 6.750 + \log 10^{-3} = 0.829 - 3 = -2.171$. If one has this log given and is asked to find the decimal number it represents, the process is a little more complicated since one has to convert $10^{-2.171}$ to the number desired, and log tables do not provide for negative mantissae. The mantissa is made positive by rewriting as a product of a plus and a minus exponent such that their addition gives the negative exponent in question. Thus $10^{-2.171} = 10^{-3} \times 10^{0.829}$. This becomes $10^{-3} \times \text{antilog } 0.829 = 6.750 \times 10^{-3}$.

Examples: (*a*) Using logs find the product $(0.0215)(6.31 \times 10^{5})(227)$.

$$= \log(2.15 \times 10^{-2}) + \log(6.31 \times 10^{5}) + \log(2.27 \times 10^{2})$$
$$= (0.332 - 2) + (0.800 + 5) + (0.356 + 2)$$
$$= -1.668 + 5.800 + 2.356 = 8.156 - 1.668 = 6.488$$
$$10^{6.488} = 10^{6} \times 10^{0.488} = 10^{6} \times \text{antilog } 0.488 = 3.08 \times 10^{6} \quad (\textit{Ans.})$$

(*b*) Find x: $x = \log(1/2.56 \times 10^{-7})$

The problem is simplified slightly by making part of the indicated division first, then subtracting the two logs to carry out the next division:

$$= \log(10^{7}/2.56) = \log 10^{7} - \log 2.56 = 7 - 0.408 = 6.592 \quad (\textit{Ans.})$$

(This is typical of *p*H problems, Chapter 6.)

(*c*) Find r using logs: $r = \sqrt[3]{0.0175}$

$$= 1/3 \log(1.75 \times 10^{-2}) = 1/3\,(0.242 - 2)$$
$$= -1.758/3 = -0.586$$
$$10^{-0.586} = 10^{-1} \times 10^{0.414} = 10^{-1} \times \text{antilog } 0.414 = 2.60 \times 10^{-1} \quad (\textit{Ans.})$$

Checking on the slide rule: does $(2.60 \times 10^{-1})^{3} = 1.75 \times 10^{-2}$ (D and K scales.) Note again the relationship between exponential handling and working with logs.

Students having slide rules with *LL scales* may use those to take numbers to powers and use logs to check, or vice versa. For instance, $3.80^{2.75}$: set left index of C scale over 3.80 on LL3 scale. Put wire on 275 on C scale, and read 39.3 under wire on LL3 scale. How are logs used to check this?

It is handy to learn a few logs of numbers to aid in estimating answers. These are easy to remember: $\log 1 = 0$, $\log 10 = 1$, $\log 2 = 0.3$, $\log 5 = 0.7$. Other identities follow; as, $2 \times 2 = 4$, meaning that $\log 2 + \log 2 = \log 4$, and since $\log 2 = 0.3$, then $0.3 + 0.3 = 0.6 = \log 4$; etc.

For practice in using logs and the slide rule, the student should review problems in his lecture notes and those worked in the text so he has answers to check his computations.

What was stated previously regarding the handling of exponential numbers in multiplication, division, extracting roots, squaring and cubing may now be applied to logs. Thus:

$$\log (A \cdot B) = \log A + \log B$$

$$\log (A/B) = \log A - \log B$$

$$\log A^x = x \cdot \log A$$

$$\log \sqrt[x]{A} = (1/x) \log A$$

To find the actual number in question after the above operations are done, one refers to a table of antilogs or uses his slide rule in reverse order to that used before: the mantissa is located under the wire on the L scale and the corresponding number (antilog) is read under the wire on the D scale. One then places the decimal point as dictated by the characteristic.

See appendix A28 for a log table.

A4. SUGGESTED STUDENT LOCKER EQUIPMENT

Item	Quantity	Volume Milliliters	Item	Quantity	Volume Milliliters
Beaker	2	150	Stirring rod, glass	3	
Beaker	2	100	Stoppers, assorted	4	
Beaker	2	50	Test tube	6	4
Beaker	2	20	Test tube	10	8
Beaker	2	10	Test tube holder	1	
Bottles, dropping	6	30	Triangle	1	
Bottles, dropping	18	15	Tubing, rubber, 2 ft	2	
Bottles, glass stoppered	5	30	Watch glass, 1½ in.	1	
			Wire, Pt, 2 in.	1	
Bottles, wide-mouth, screw cap	14	30			
Burner, micro	1				
Cover, water bath	1				
Crucible and cover	1	15			
Cylinder	1	10	*Nonreturnables:*		
Droppers	4	2	Brush, test tube	1	
Forceps	1		Charcoal block	1	
Flask, Erlenmeyer	2	125	Corks, assorted	6	
Rack, bottle, (15 ml)	1		Gauze, wire	1	
Rack, bottle, (30 ml)	1		Labels, box	1	
Rack, test tube	1		Matches, box	1	
Ring, iron	1		Towel	1	
Spot plate	1		Wire, nichrome, 2 in.	6	
Spatula, micro	1				

A5. SOLIDS* FOR WIDEMOUTH BOTTLES IN STUDENT LOCKERS

Quantity	Description	Quantity	Description
5 g	NH_4Cl	5 g	$H_2C_2O_4 \cdot 2H_2O$
5 g	NH_4NO_3	10 pcs.	Nichrome wire, 26 gage
2 g	Cu (turnings)	15 g	Na_2CO_3
25 pcs.†	$PbAc_2$ paper	2 g	$NaBiO_3$
25 pcs.†	Methyl violet paper	2 g	NaCN or $Na_2S_2O_4 \cdot 2H_2O$
100 pcs.	Litmus paper (red)	5 g	$Na_2B_4O_7 \cdot 10H_2O$
100 pcs.	Litmus paper (blue)	5 g	Zn, pure, granular

* Supplies will vary with sections selected from text. This list covers most of the standard experiments.

† Students prepare these by dipping filter paper into side shelf solutions, drying over a burner, and cutting into strips.

A6. SUGGESTED SOLUTIONS* FOR 15 ML DROPPING BOTTLES IN STUDENT LOCKERS

Concentration	Description	Concentration	Description
3 *M*	NH_4Ac	1.5%	Dimethylglyoxime
2 *M*	$(NH_4)_2CO_3 \cdot H_2O$	Sat'd.	$HgCl_2$
5%	NH_4Cl	1%	Phenolphthalein
1 *M*	NH_4NO_3	0.3 *M*	$K_4Fe(CN)_6 \cdot 3H_2O$
0.25 *M*	$(NH_4)_2C_2O_4 \cdot H_2O$	1 *M*	KSCN
1 *M*	$(NH_4)_2SO_4$	0.1 *M*	$AgNO_3$ (dark bottle)
1 *M*	$BaCl_2 \cdot 2H_2O$	0.2 *M*	$Na_2HPO_4 \cdot H_2O$
0.5	$CaAc_2 \cdot H_2O$	Sat'd.	Na_2CO_3
100%	CCl_4	0.2 *M*	$SnCl_2 \cdot 2H_2O$

* These are described in Tables A13 and A15.

A7. SUGGESTED SOLUTIONS FOR 30 ML DROPPING BOTTLES IN STUDENT LOCKERS

Concentration	Description	Concentration	Description
6 *M*	NH_4OH	0.5 *M*	K_2CrO_4
8%	CH_3CSNH_2	6 *M*	NaOH
6 *M*	KOH		H_2O, distilled

A8. Suggested Solutions* for Glass-Stoppered Bottles in Student Lockers

Concentration M	Description	Concentration M	Description
6	HAc	6	H_2SO_4
6	HCl	3%	H_2O_2 (dark bottle)
6	HNO_3		

* Concentrated acids and bases are not recommended in the lockers. Hydrogen peroxide and acetic acid are put in glass-stoppered bottles since they cause rapid deterioration of rubber.

A9. Laboratory Bench Acid and Base Solutions

Concentration, M	Description	Molecular Weight*	Concentration, M	Description	Molecular Weight*
6	HAc	60.05	6	H_2SO_4	98.08
17	(glacial) HAc		18	(concentrated) H_2SO_4	
6	HCl	36.47	6	NH_4OH	35.06
12	(concentrated) HCl		15	(concentrated) NH_4OH	
6	HNO_3	63.02	6	KOH	56.10
15	(concentrated) HNO_3		6	NaOH	40.00
6	H_3PO_4	98.00			

* Molecular and ionic weights are given in these tables as an aid in problem solving.

A10. Side Shelf Test Solutions

Test solutions for preliminary experiments on cations contain 10 mg of the ion per milliliter. The cations are Ag^+, Hg_2^{+2}, Pb^{+2}, Hg^{+2}, Bi^{III}, Cu^{+2}, Cd^{+2}, As^{III}, Sb^{III}, Sn^{II}, Sn^{IV}, Mn^{+2}, Fe^{+3}, Al^{+3}, Cr^{+3}, Zn^{+2}, Co^{+2}, Ni^{+2}, Ba^{+2}, Sr^{+2}, Ca^{+2}, Mg^{+2}, Na^+, K^+, and NH_4^+.

Test solutions for preliminary experiments on anions contain 10 mg of the ion per milliliter. The anions are, NO_2^-, S^{-2}, SO_3^{-2}, $S_2O_3^{-2}$, CO_3^{-2}, PO_4^{-3}, SO_4^{-2}, CrO_4^{-2}, BO_2^-, F^-, $C_2O_4^{-2}$, Cl^-, Br^-, I^-, SCN^-, $Fe(CN)_6^{-4}$, NO_3^-, and Ac^-.

Solutions of the above ions are conveniently made in concentrations of 50 mg of ion/milliliter and diluted from stock bottles. These are described in A11.

A11. STOCK SOLUTIONS FOR DILUTION, IN ORDER OF USE IN CATION PRELIMINARY EXPERIMENTS

Ion	Ionic Weight	Salt	Molecular Weight	Grams Salt/Liter = 50 mg Ion/Milliliter
Ag^{+}	107.880	$AgNO_3$	169.89	78.5
$^*Hg_2^{+2}$	401.22	$Hg_2(NO_3)_2 \cdot 2H_2O$ (in 2 *M* HNO_3)	561.26	70
$^*Pb^{+2}$	207.21	$Pb(NO_3)_2$	331.23	80
Hg^{+2}	200.61	$Hg(NO_3)_2 \cdot \frac{1}{2}H_2O$	333.63	83
Bi^{III}	209.00	$Bi(NO_3)_3 \cdot 5H_2O$ (in 2 *M* HNO_3)	485.10	117
Cu^{+2}	63.54	$Cu(NO_3)_2 \cdot 3H_2O$	241.63	190
Cd^{+2}	112.41	$Cd(NO_3)_2 \cdot 4H_2O$	308.49	139
As^{III}	74.91	As_2O_3 (in 4 *M* HCl)	197.82	26.4 (= 20 mg/ml)
Sb^{III}	121.76	$SbCl_3$ (in 4 *M* HCl)	228.13	94
$^*Sn^{II}$	118.70	$SnCl_2 \cdot 2H_2O$ (in 2 *M* HCl)	225.65	94
Sn^{IV}	118.70	$SnCl_4 \cdot 5H_2O$ (in 3 *M* HCl)	350.61	147
Mn^{+2}	54.94	$MnCl_2 \cdot 4H_2O$	197.91	180
Fe^{+3}	55.85	$FeCl_3 \cdot 6H_2O$	270.32	241
Al^{+3}	26.98	$AlCl_3 \cdot 6H_2O$	241.44	450
Cr^{+3}	52.01	$CrCl_3 \cdot 6H_2O$	266.48	255
Zn^{+2}	65.38	$Zn(NO_3)_2 \cdot 6H_2O$	297.49	228
Co^{+2}	58.94	$Co(NO_3)_2 \cdot 6H_2O$	291.05	250
Ni^{+2}	58.69	$Ni(NO_3)_2 \cdot 6H_2O$	290.80	250
Ba^{+2}	137.36	$BaCl_2 \cdot 2H_2O$	244.31	89.5
Sr^{+2}	87.63	$Sr(NO_3)_2 \cdot 4H_2O$	283.71	162
Ca^{+2}	40.08	$Ca(NO_3)_2 \cdot 4H_2O$	236.16	295
Mg^{+2}	24.32	$Mg(NO_3)_2 \cdot 6H_2O$	256.43	530
Na^{+}	22.991	$NaNO_3$	85.01	186
K^{+}	39.100	KNO_3	101.10	129
NH_4^{+}	18.040	NH_4Cl	53.50	147

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* A little free metal is put in the bottle to hinder oxidation of the lower valence state.

A12. STOCK SOLUTIONS FOR DILUTION, IN ORDER OF USE IN ANION PRELIMINARY EXPERIMENTS

Ion	Ionic Weight	Salt	Molecular Weight	Grams Salt/Liter = 50 mg ion/milliliter
NO_2^-	46.008	$NaNO_2$	69.01	75
S^{-2}	32.066	$Na_2S \cdot 9H_2O$	240.19	150 = 20 mg/ml
SO_3^{-2}	80.066	Na_2SO_3	126.05	78.5
$S_2O_3^{-2}$	112.132	$Na_2S_2O_3 \cdot 5H_2O$	248.19	111
CO_3^{-2}	60.011	K_2CO_3	138.20	87
PO_4^{-3}	94.975	Na_2HPO_4	141.98	75
SO_4^{-2}	96.066	$(NH_4)_2SO_4$	132.14	69
CrO_4^{-2}	116.01	K_2CrO_4	194.20	83.5
BO_2^-	42.82	$Na_2B_4O_7 \cdot 10H_2O$	381.43	111 (as BO_2^-)
F^-	19.00	NaF	42.00	44 = 20 mg/ml
$C_2O_4^{-2}$	88.022	$(NH_4)_2C_2O_4 \cdot H_2O$	142.12	32.5 = 20 mg/ml
Cl^-	35.457	KCl	74.56	105
Br^-	79.916	KBr	119.01	74.5
I^-	126.91	KI	166.02	65.5
SCN^-	58.085	$KSCN$	97.17	83.5
$Fe(CN)_6^{-4}$	211.96	$K_4Fe(CN)_6 \cdot 3H_2O$	422.39	99
NO_3^-	62.008	KNO_3	101.10	81.5
$C_2H_3O_2^-$	59.046	$NaC_2H_3O_2 \cdot 3H_2O$	136.09	115

A13. SIDE SHELF SOLUTIONS

Concentration	Compound	Molecular Weight	Grams Needed for 1 Liter of Solution
*3 M	$NH_4C_2H_3O_2$	77.06	231
*2 M	$(NH_4)_2CO_3 \cdot H_2O$	114.11	228 g in 1.2 M NH_4OH
*5%	NH_4Cl	53.50	50
20%	NH_4Cl	53.50	240
*0.07 M	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	1235·95	90 g in 40 ml 15 M NH_4OH; dil. to 500. Add 220 g NH_4NO_3, dil. to 1 liter
*1 M	NH_4NO_3	80.05	80
*0.25 M	$(NH_4)_2C_2O_4 \cdot H_2O$	142.12	35.5
*0.2 M	$(NH_4)_2HPO_4$	132.07	26.4
*1 M	$(NH_4)_2SO_4$	132.14	132
*7%	$(NH_4)_2S$	68.14	350 ml of light $(NH_4)_2S$ (20–24%) diluted to 1 liter with 5 M NH_4OH
*50 mg Sb/ml	$SbCl_3$	228.13	95.5 g in 4 M HCl

A13.—*Contd.*

Concentration	Compound	Molecular Weight	Grams Needed for 1 Liter of Solution
*0.5 *M*	$Ba(C_2H_3O_2)_2 \cdot H_2O$	273.46	136
*1 *M*	$BaCl_2 \cdot 2H_2O$	244.31	244
Saturated	$Ba(OH)_2 \cdot 8H_2O$	315.50	36
*100 mg Bi/ml	$BiCl_3$	315.37	150 g in 3 *M* HCl
*Saturated	Br_2	159.83	(H_2O solution)
*0.5 *M*	$Ca(C_2H_3O_2)_2 \cdot H_2O$	176.20	88
*Saturated	$Ca(OH)_2$	74.10	3
Saturated	CaF_2	78.08	1
*0.5 *M*	$Co(NO_3)_2 \cdot 6H_2O$	291.05	15
1 *M*	$CuSO_4 \cdot 5H_2O$	249.71	250
*3%	H_2O_2	34.02	3% as purchased
10%	HIO_3	175.93	100 g + 900 ml H_2O
20%	HF	20.01	
	Fehling's A		70 g $CuSO_4 \cdot 5H_2O$
	Fehling's B		346 g $NaKC_4H_4O_6 \cdot 4H_2O$ + 100 g NaOH
0.2 *M*	$FeCl_3 \cdot 6H_2O$	270.32	54 g in 0.1 *M* HCl
0.5 *M*	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	379.35	190
5%	$La(NO_3)_3 \cdot 6H_2O$	433.04	50
Saturated	$HgCl_2$	271.52	80
	Magnesia mixture		56 g $MgCl_2 \cdot 6H_2O$ + 140 g NH_4Cl in 500 ml H_2O. Add 130 ml 15*M* NH_4OH, dil. to 1 liter.
*	$Mg(C_2H_3O_2)_2$—$3UO_2(C_2H_3O_2)_2$		37.5 g $UO_2Ac_2 \cdot 2H_2O$ + 150 ml H_2O + 125 ml glac. HAc. Heat to dissolve, then add 275 ml glac. HAc. Dissolve 186 g $MgAc_2 \cdot 4H_2O$ in hot 50 ml H_2O + 400 ml glac. HAc. Mix the warm solns. Filter after 24 hrs. Discard residue.
Saturated	$MnCl_2 \cdot 4H_2O$	197.91	700 g in 6 *M* HCl
	Nesser's solution		50 g KI + least amount cold H_2O to dissolve. Add satd. soln. $HgCl_2$ to get slight permanent ppt. Add 400 ml 50% KOH; dil. to 1 liter.
*2 *M*	KCl	74.56	149
*0.5 *M*	K_2CrO_4	194.20	97

A13.—*Contd.*

Concentration	Compound	Molecular Weight	Grams Needed for 1 Liter of Solution
0.012 *M*	$KFeIO_6$	317.86	120 ml 0.1 *M* $FeCl_3 \cdot 6H_2O$ in 0.2 *N* HCl, + 100 ml 2 *M* KOH + 400 ml H_2O contg. 23 g KIO_6. Dil. to 1 liter with 2 *M* KOH. Polyethylene bottle.
*0.3 *M*	$K_4Fe(CN)_6 \cdot 3H_2O$	422.39	127
*0.3 *M*	$K_3Fe(CN)_6$	329.25	99
*0.5 *M*	KI	166.02	83
0.1 *M*	KI_3	419.8	166 g KI + 25.4 g I_2
*5 *M*	KNO_2	85.10	424
*0.1 *M*	$KMnO_4$	158.03	15.8
*1 *M*	KSCN	97.17	97
*0.1 *M*	$AgNO_3$	169.89	17
*50%	$AgNO_3$	169.89	100 g $AgNO_3$ + 100 g H_2O. No dilution; ≅ 120 ml soln.
Saturated	Ag_2SO_4	311.82	8
*Saturated	$Na_2CO_3 \cdot 10H_2O$	286.16	250
	NaN_3, I_2		25.4 g I_2 + 20 g KI + 30 g NaN_3
1 *M*	NaF	42.00	42
*0.3 *M*	$Na_2HPO_4 \cdot H_2O$	138.01	41.4
*0.3 *M*	$NaH_2PO_4 \cdot 7H_2O$	268.09	80.4
0.5 *M*	$Na_3Co(NO_2)_6$	403.98	202
*5%	NaOCl	74.75	5% as purchased (household bleach)
5%	$NaHCO_3$	84.01	50
1 *M*	$NaBF_4$	109.82	110
0.1 *M*	$NaKC_4H_4O_6 \cdot 4H_2O$	282.23	28.2
*0.2 *M*	$SnCl_2 \cdot 2H_2O$	225.65	45 g in 3 *M* HCl + piece of metallic Sn. Ion in soln. is $SnCl_4^{-2}$.

* More important reagents; used in analysis of the common cations and anions.

A14. SIDE SHELF SOLIDS

Substance	Molecular Weight	Description
Al_2O_3	101.94	325 mesh alumina for chromatography
*Al	26.98	Granular
*NH_4Cl	53.50	
*NH_4NO_3	80.05	
$(NH_4)_2C_2O_4 \cdot H_2O$	142.12	
NH_4SCN	76.12	
$(NH_4)_2SO_4$	132.14	
As_2O_3	197.82	
Asbestos	—	Gooch grade
$BaCO_3$	197.37	Powder
C	12.011	Norite decolorizing carbon
$CaCl_2$	110.99	Anhydrous
$CaCO_3$	100.09	Powder
CaF_2	78.08	Chemically pure, not mineral grade
$Co(NO_3)_2 \cdot 6H_2O$	291.05	
*Cu	63.54	Fine turnings or fine wire
$CuSO_4 \cdot 5H_2O$	249.71	Small crystals
Cotton	—	
Devarda's metal	—	Granular
*Fe	55.85	Filings or powder
*$FeSO_4 \cdot 7H_2O$	278.02	
$Fe_2(SO_4)_3$	399.88	
FeS	87.91	Pea lump
Glass Wool	—	
PbO_2	239.21	
Mg	24.32	Powder
MnO_2	86.93	
$HgCl_2$	271.52	
*$H_2C_2O_4 \cdot 2H_2O$	126.07	
K_2CO_3	138.20	
KCl	74.56	
$KClO_3$	122.56	
KI	166.02	
KNO_3	101.10	
KNO_2	85.10	
$K_2Cr_2O_7$	294.21	
KHF_2	78.10	
$NaNH_4HPO_4 \cdot 4H_2O$	209.09	(Microcosmic salt)
$NaC_2H_3O_2$	82.04	
*$NaBiO_3$	280.00	
*Na_2CO_3	106.00	
NaCN	49.02	
NaCl	58.45	

A14.—*Contd.*

Substance	Molecular Weight	Description
$NaBO_3 \cdot H_2O$	99.83	(Sodium perborate)
NaF	42.00	
*$Na_2C_4H_4O_6 \cdot 2H_2O$	230.10	(Sodium tartrate)
*$Na_2B_4O_7 \cdot 10H_2O$	381.43	(Borax)
$Na_2S_2O_4 \cdot 2H_2O$	210.15	(Sodium hyposulfite)
Na_2O_2	77.99	
$NaNO_3$	85.01	
S	32.066	Flowers
*Zn	65.38	Granular, arsenic-free
ZnO	81.38	Powder

* See footnote p. 460.

A15. SIDE SHELF ORGANIC REAGENTS

Reagent	Preparation
*Acetone	
Acetaldehyde	
*Alizarin, $ZrOCl_2$	0.42 g alizarin red S in 100 ml H_2O. Pour this into 100 ml H_2O contg. 0.25 g $ZrOCl_2 \cdot 8H_2O$. Add 500 ml H_2O contg. 59 ml con. H_2SO_4. Dilute to 1 liter
*Aluminon	1 g of ammonium salt of aurin tricarboxylic acid per liter of H_2O
*Benzidine	Solid; and also a soln. contg. 2 g in 100 ml of glac. HAc
*n-Butanol	
Benzoin	Solid
Brucine sulfate	Solid
*Carbon tetrachloride	
Carmine	0.1 g in 100 ml concd. H_2SO_4
*Chloroform	
*Diethyl ether	
*Dimethyl glyoxime	1.5 g in 100 ml of 95% ethanol
Diisopropyl ether	
Dithizone	Solid
Ethanol	95%
Formaldehyde	35%
Hydroquinone	Solid
8-hydroxyquinoline	3 g in 100 ml 95% ethanol
*Methanol	

A15.—*Contd.*

Reagent	Preparation
*Methyl violet	1 g in 1 liter 95% ethanol. Impregnate filter paper with soln., dry, cut in strips for indicator paper in group 2 analysis
α-naphthylamine	3 g in a mixt. of 300 ml glac. HAc + 700 ml H_2O
α-nitroso-β-naphthol	3 g in 50 ml glac. HAc; dil. to 100 with H_2O
**p*-nitrobenzeneazoresorcinol	0.5 g in 100 ml of 1% NaOH soln.
Phthalic anhydride	Solid
Potassium xanthate	Solid
Quinalizarin	0.1 g in 100 ml con. H_2SO_4
Resorcinol	Solid
Rhodamine-B	0.01 g in 100 ml H_2O
Sodium diethyldithiocarbamate	0.1 g in 100 ml H_2O
Sulfanilic acid	10 g in a mixt. of 250 ml glac. HAc + 750 ml H_2O
Starch	Grind paste of 3 g soluble starch in 3 ml H_2O. Add to boiling mixt. of 100 ml H_2O + 100 ml glycerine.
Strychnine sulfate	Solid
*Thioacetamide	8% in H_2O. Polyethylene bottle
Thiourea	5 g in 100 ml H_2O; and also solid reagent should be available
o-Tolidine	Solid
Turmeric	Make satd. ethanol soln.; dil. with 4 vol. of ethanol.
Vanillin	Solid

* See footnote p. 460.

A16. ADDITIONAL SIDE SHELF SOLIDS FOR LESS FAMILIAR ELEMENTS*

Substance	Molecular Weight	Substance	Molecular Weight
Exhibit of metal samples: Li, Be, Ti, Zr, V, Mo, W, U	—	$ZrOCl_2 \cdot 8H_2O$ NH_4VO_3	322.26 116.99
Exhibit of mineral samples of these elements	—	$SnCl_2 \cdot 2H_2O$ MoO_3	225.65 143.95
LiCl	42.40	NaF	42.00
$BeSO_4 \cdot 4H_2O$	177.14	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	1235.95
$Na_2(C_4H_4O_6) \cdot 2H_2O$	230.10	$H_2WO_4 \cdot H_2O$	267.95
$TiCl_4$ (liq.)	189.73	KHF_2	78.10
TiO_2	79.90	$UO_2(C_2H_3O_2)_2 \cdot 2H_2O$	424.19
$KHSO_4$	136.16	$UO_2(NO_3)_2 \cdot 6H_2O$	502.18

* See Chapter 20.

A17. SIDE SHELF SOLUTIONS OF INDICATORS

Indicator	*Eastman No.	*p*H Range	†Colors	Preparation
Malachite green oxalate	1264	0.2–1.8 11.4–13.0	*Y-G* *BG-Cl*	0.2% in water
§Methyl violet	1309	0.2–2.0 5.0–6.0	*Y-BuV* *BuV-V*	0.02% in water
m-Cresol purple	2118	1.2–2.8 7.4–9.0	*R-Y* *Y-Pu*	‡26.2 ml
Thymol blue	753	1.2–2.8	*R-Y*	‡21.5 ml
Benzopupurin 4B	1021	1.2–4.0	*V-R*	0.1% in water
Cresol red	744	2.0–3.0	*Or-Am*	‡26.2 ml
2,4–Dinitrophenol	102	2.6–4.4	*Cl-Y*	Saturated in water
Bromphenol blue	752	3.0–4.7	*Y-Bu*	‡14.9 ml
Congo red	770	3.0–5.0	*Bu-R*	0.1% in water
§Methyl orange	432	3.2–4.4	*R-Y*	0.1% in water
Bromcresol green	1782	3.8–5.4	*Y-Bu*	‡14.3 ml
Methyl red	431	4.2–6.3	*R-Y*	0.02% in 70% ethanol
Bromthymol blue	839	6.0–7.6	*Y-Bu*	‡16.0 ml
Phenol red	541	6.8–8.4	*Y-R*	‡28.2 ml.
Curcumin	1179	7.4–8.6 10.2–11.8	*Y-R* *R-Or*	0.2% in 95% ethanol
Thymol blue	753	8.0–9.6	*Y-Bu*	‡21.5 ml.
o-Cresolphthalein	774	8.2–9.8	*Cl-R*	0.05% in 95% ethanol
§Phenolphthalein	202	8.3–10.0	*Cl-R*	0.5% in 75% ethanol
Thymolphthalein	1091	9.4–10.6	*Cl-Bu*	0.5% in 95% ethanol
1,3,5-Trinitrobenzene	639	12.0–14.0	*Cl-Or*	0.3% in 95% ethanol

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[*] Eastman Organic Chemicals Div., Rochester 3, New York. (Adapted by permission.)

† See A27 for color code.

‡ Grind 0.1 g of indicator in a mortar with this volume of 0.01 *N* NaOH, then dilute to 250 ml with water.

§ More important indicators; used in analysis of the common cations and anions.

A18. STANDARD OXIDATION-REDUCTION POTENTIALS*

ACIDIC SOLUTIONS

(Ions at Unit Activity, E° in Volts, Temperature 25 C)

Half-Cell Reaction	E°
$K = K^{+} + e^{-}$	2.925
$Ba = Ba^{+2} + 2e^{-}$	2.90
$Sr = Sr^{+2} + 2e^{-}$	2.89
$Ca = Ca^{+2} + 2e^{-}$	2.87
$Na = Na^{+} + e^{-}$	2.714
$Mg = Mg^{+2} + 2e^{-}$	2.37
$Al = Al^{+3} + 3e^{-}$	1.66
$Mn = Mn^{+2} + 2e^{-}$	1.18
$Zn = Zn^{+2} + 2e^{-}$	0.763
$Cr = Cr^{+3} + 3e^{-}$	0.74
$AsH_3 = As + 3H^{+} + 3e^{-}$	0.60
$SbH_3 = Sb + 3H^{+} + 3e^{-}$	0.51
$Fe = Fe^{+2} + 2e^{-}$	0.440
$Cr^{+2} = Cr^{+3} + e^{-}$	0.41
$Cd = Cd^{+2} + 2e^{-}$	0.403
$Pb + 2I^{-} = PbI_2 + 2e^{-}$	0.365
$Pb + SO_4{}^{2} = PbSO_4 + 2e^{-}$	0.356
$Pb + 2Br^{-} = PbBr_2 + 2e^{-}$	0.280
$Co = Co^{+2} + 2e^{-}$	0.277
$Pb + 2Cl^{-} = PbCl_2 + 2e^{-}$	0.268
$Ni = Ni^{+2} + 2e^{-}$	0.250
$Cu + I^{-} = CuI + e^{-}$	0.185
$Ag + I^{-} = AgI + e^{-}$	0.151
$Sn = Sn^{II} + 2e^{-}$	0.136
$Pb = Pb^{+2} + 2e^{-}$	0.126
$Hg + 4I^{-} = HgI_4^{-2} + 2e^{-}$	0.04
$H_2 = 2H^{+} + 2e^{-}$ (Standard hydrogen)	0.000
$Ag + 2S_2O_3{}^{2} = Ag(S_2O_3)_2{}^{3} + e^{-}$	−0.01
$PH_3 = P + 3H^{+} + 3e^{-}$	−0.06
$H_2S = S + 2H^{+} + 2e^{-}$	−0.141
$Sn^{II} = Sn^{IV} + 2e^{-}$	−0.15
$Cu^{+} = Cu^{+2} + e^{-}$	−0.153
$Bi + H_2O + Cl^{-} = BiOCl + 2H^{+} + 3e^{-}$	−0.16
$Ag + Cl^{-} = AgCl + e^{-}$	−0.222
$2Hg + 2Cl^{-} = Hg_2Cl_2 + 2e^{-}$ (Normal calomel)	−0.2825
$Cu = Cu^{+2} + 2e^{-}$	−0.337
$Fe(CN)_6^{-4} = Fe(CN)_6^{-3} + e^{-}$	−0.36
$2Ag + CrO_4^{-2} = Ag_2CrO_4 + 2e^{-}$	−0.446
$Cu = Cu^{+} + e^{-}$	−0.521
$2I^{-} = I_2 + 2e^{-}$	−0.5355

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* For values involving Li, Be, Ti, Zr, V, Mo, W, U, see Chapter 20. These lists are adapted by permission from W. H. Latimer, *Oxidation Potentials*, 2nd ed., Prentice-Hall, New York (1952).

A18.—*Contd.*

Half-Cell Reaction	E^o
$3I^- = I_3^- + 2e^-$	−0.536
$MnO_4^{-2} = MnO_4^- + e^-$	−0.564
$H_2O_2 = \mathit{O}_2 + 2H^+ + 2e^-$	−0.682
$Fe^{+2} = Fe^{+3} + e^-$	−0.771
$2Hg = Hg_2^{+2} + 2e^-$	−0.789
$Ag = Ag^+ + e^-$	−0.7991
$Hg = Hg^{+2} + 2e^-$	−0.854
$Hg_2^{+2} = 2Hg^{+2} + 2e^-$	−0.920
$HNO_2 + H_2O = NO_3^- + 3H^+ + 2e^-$	−0.94
$\mathit{NO} + 2H_2O = NO_3^- + 4H^+ + 3e^-$	−0.96
$\mathit{NO} + H_2O = HNO_2 + H^+ + e^-$	−1.00
$2Br^- = Br_2 + 2e^-$	−1.0652
$\frac{1}{2}I_2 + 3H_2O = IO^- + 6H^+ + 5e^-$	−1.195
$2H_2O = \mathit{O}_2 + 4H^+ + 4e^-$	−1.229
$Mn^{+2} + 2H_2O = MnO_2 + 4H^+ + 2e^-$	−1.23
$2Cr^{+3} + 7H_2O = Cr_2O_7^{-2} + 14H^+ + 6e^-$	−1.33
$2Cl^- = \mathit{Cl}_2 + 2e^-$	−1.3595
$Pb^{+2} + 2H_2O = PbO_2 + 4H^+ + 2e^-$	−1.455
$Mn^{+2} + 4H_2O = MnO_4^- + 8H^+ + 5e^-$	−1.51
$PbSO_4 + 2H_2O = PbO_2 + SO_4^{-2} + 4H^+ + 2e^-$	−1.685
$MnO_2 + 2H_2O = MnO_4^- + 4H^+ + 3e^-$	−1.695
$2H_2O = H_2O_2 + 2H^+ + 2e^-$	−1.77
$Co^{+2} = Co^{+3} + e^-$	−1.82
$\mathit{O}_2 + H_2O = \mathit{O}_3 + 2H^+ + 2e^-$	−2.07
$2F^- = \mathit{F}_2 + 2e^-$	−2.8
$HF = \mathit{F}_2 + 2H^+ + 2e^-$	−3.06

A19. STANDARD OXIDATION-REDUCTION POTENTIALS

BASIC SOLUTIONS

(Ions at Unit Activity, $E°$ in Volts, Temperature 25 C)

Half-Cell Reaction	$E°$
$Ca + 2OH^- = Ca(OH)_2 + 2e^-$	3.03
$Sr + 2OH^- + 8H_2O = Sr(OH)_2 \cdot 8H_2O + 2e^-$	2.99
$Ba + 2OH^- + 8H_2O = Ba(OH)_2 \cdot 8H_2O + 2e^-$	2.97
$Mg + 2OH^- = Mg(OH)_2 + 2e^-$	2.69
$Al + 4OH^- = Al(OH)_4^- + 3e^-$	2.35
$Zn + S^{-2} = ZnS + 2e^-$	1.44
$Cr + 3OH^- = Cr(OH)_3 + 3e^-$	1.3
$Zn + 4OH^- = Zn(OH)_4^{-2} + 2e^-$	1.216
$Cd + S^{-2} = CdS + 2e^-$	1.21
$Zn + 4NH_3 = Zn(NH_3)_4^{+2} + 2e^-$	1.03
$Fe + S^{-2} = FeS_{(\alpha)} + 2e^-$	1.01
$SO_3^{-2} + 2OH^- = SO_4^{-2} + H_2O + 2e^-$	0.93
$Fe + 2OH^- = Fe(OH)_2 + 2e^-$	0.877
$Ni + S^{-2} = NiS_{(\alpha)} + 2e^-$	0.83
$H_2 + 2OH^- = 2H_2O + 2e^-$	0.828
$Hg + S^{-2} = HgS + 2e^-$	0.72
$AsO_2^- + 4OH^- = AsO_4^{-3} + 2H_2O + 2e^-$	0.67
$Cd + 4NH_3 = Cd(NH_3)_4^{+2} + 2e^-$	0.597
$Fe(OH)_2 + OH^- = Fe(OH)_3 + e^-$	0.56
$S^{-2} = S + 2e^-$	0.48
$Ag + 2CN^- = Ag(CN)_2^- + e^-$	0.31
$Cr(OH)_3 + 5OH^- = CrO_4^{-2} + 4H_2O + 3e^-$	0.13
$Mn(OH)_2 + 2OH^- = MnO_2 + H_2O + 2e^-$	0.05
$NO_2^- + 2OH^- = NO_3^- + H_2O + 2e^-$	−0.01
$Co(NH_3)_6^{+2} = Co(NH_3)_6^{+3} + e^-$	−0.1
$2Ag + 2OH^- = Ag_2O + H_2O + 2e^-$	−0.344
$Ag + 2NH_3 = Ag(NH_3)_2^+ + e^-$	−0.373
$4OH^- = O_2 + 2H_2O + 4e^-$	−0.401
$Ni(OH)_2 + 2OH^- = NiO_2 + 2H_2O + 2e^-$	−0.49
$MnO_2 + 4OH^- = MnO_4^- + 2H_2O + 2e^-$	−0.60
$Cl^- + 2OH^- = ClO^- + H_2O + 2e^-$	−0.89
$O_2 + 2OH^- = O_3 + H_2O + 2e^-$	−1.24

A20. IONIZATION CONSTANTS OF WEAK ACIDS

Acid	Formula Weight	K_A	Acid	Formula Weight	K_A
$H(C_2H_3O_2)$	60.05	1.85×10^{-5}	$HClO$	52.47	3.2×10^{-8}
H_3AsO_4 (K_{A-1})	141.93	2.5×10^{-4}	HNO_2	47.02	4.5×10^{-4}
$H_2AsO_4^-$ (K_{A-2})	140.92	5.6×10^{-8}	$H_2C_2O_4$ (K_{A-1})	90.04	3.8×10^{-2}
$HAsO_4^{-2}$ (K_{A-3})	139.91	3×10^{-13}	$HC_2O_4^-$ (K_{A-2})	89.03	5.0×10^{-5}
HBO_2	43.83	6.0×10^{-10}	H_3PO_4 (K_{A-1})	98.00	7.5×10^{-3}
H_2CO_3 (K_{A-1})	62.03	4.16×10^{-7}	$H_2PO_4^-$ (K_{A-2})	96.99	6.2×10^{-8}
HCO_3^- (K_{A-2})	61.02	4.84×10^{-11}	HPO_4^{-2} (K_{A-3})	95.98	$\sim 10^{-12}$
HSO_4^- (K_{A-2})	97.07	*1.26×10^{-2}	H_3PO_3 (K_{A-1})	82.00	1.6×10^{-2}
$HClO_2$	68.47	1.1×10^{-2}	H_2SO_3 (K_{A-1})	82.08	1.25×10^{-2}
$HCNO$	43.00	2.0×10^{-4}	HSO_3^- (K_{A-2})	81.07	5.6×10^{-8}
$H(CHO_2)$	46.03	2.1×10^{-4}	$H_2(C_4H_4O_6)$ (K_{A-1})	150.09	1.1×10^{-3}
HCN	27.03	4×10^{-10}	$H(C_4H_4O_6)^-$ (K_{A-2})	149.08	6.9×10^{-5}
HF	20.01	6.71×10^{-4}	$Al(OH)_3$	77.99	4×10^{-13}
H_2O_2 (K_{A-1})	34.02	2.4×10^{-12}	$Cr(OH)_3$	103.03	1×10^{-16}
H_2S (K_{A-1})	34.08	1.0×10^{-7}	$Pb(OH)_2$	241.23	2×10^{-16}
HS^- (K_{A-2})	33.07	1.3×10^{-13}	$Hg(OH)_2$	234.63	1×10^{-15}
$HBrO$	96.92	2.06×10^{-9}	$Sn(OH)_2$	152.72	4×10^{-15}

* Varies widely with concentration.

A21. IONIZATION CONSTANTS OF WEAK BASES

Base	Mol.wt	K_B
NH_4OH	35.03	1.81×10^{-5}
$CH_3—NH_3OH$	49.06	5×10^{-4}
$(CH_3)_2—NH_2OH$	63.08	7.4×10^{-4}
$(CH_3)_3—NHOH$	77.11	7.4×10^{-5}
$(—C_6H_4—NH_3OH)_2$	238.25	†9.3×10^{-10}
$HONH_3—(C_6H_4)_2—NH_3$	221.26	*5.6×10^{-11}
$C_2H_5—NH_3OH$	63.08	5.6×10^{-4}
$C_6H_5—NH_3OH$	111.12	4.6×10^{-10}
$HONH_3—NH_3OH$	68.05	†9.8×10^{-7}

* (K_{B-2}). † (K_{B-1}).

A22. SOLUBILITY PRODUCT AND INSTABILITY CONSTANTS

(Page referrals are to tables, in the order of cation and anion analysis)

Ion	Page	Ion	Page	Ion	Page
Ag^+	233	Ni^{+2}	288	CO_3^{-2}	381
Pb^{+2}	235	Mn^{+2}	290	PO_4^{-3}	386
Hg_2^{+2}	237	Zn^{+2}	292	SO_4^{-2}	387
Hg^{+2}	238	Ba^{+2}	307	CrO_4^{-2}	388
Bi^{+3}	248	Sr^{+2}	308	BO_2^-	389
Cu^+	250	Ca^{+2}	310	F^-	391
Cu^{+2}	250	Mg^{+2}	321	$C_2O_4^{2}$	392
Cd^{+2}	252	K^+, Na^+, NH_4^+	325	Cl^-	396
Sn^{+2}	255	S^{-2}	377	Br^-	397
Fe^{+2}	284	SO_3^{-2}	378	I^-	398
Fe^{+3}	284	$S_2O_3^{-2}$	380	SCN^-	399
Co^{+2}	286			$Fe(CN)_6^{-4}$	401

A23. NOMINAL CHEMICAL COMPOSITION OF SOME COMMON ALLOYS*

Alloy	Approximate Per Cent Composition							
	C	Si	Ni	Cu	Fe	Cr	Mn	Other
Alcoa 24S		0.5		4.4	0.5	0.1	0.5	Mg 1.5, rest Al
Beryllium copper				97.4				Be 2.25, Co 0.25, or Ni 0.35
Brass, naval				60				Zn 39, Sn 0.75
Brass, yellow				65				Zn 35
Bronze, leaded				88.5				Pb 1.5, Sn 10
Bronze, manganese				59	0.8		0.5	Zn 39, Sn 0.75
Constantan	0.05	0.25	44	54.5	0.25		1	
Dowmetal H							0.2	Al 6, Zn 3, rest Mg
Durimet T	0.05	1	22	1	Rest	19		
Hastelloy B	0.1	1	62		6		1	Mo 30
Hastelloy C	0.1	1	55		6		1	Mo 17, W 5
Hastelloy D		10	85	3			1	Al 1
Inconel	0.08	0.25	78.5	0.2	6.5	14	0.25	
Invar			36		Rest			
Monel	0.15	0.1	67	30	1.4		1	
Nickel silver, 20%			20	65				Zn 6, Pb 5, Sn 4
Ni-resist type I	2.8	1.8	14.5	6	Rest	2	1.3	
Steel, aluminum nitriding	0.25	0.25			Rest	1.15	0.5	Al 1.15, Mo 0.2
Steel, mild (SAE 1020)	0.2	0.25			Rest		0.45	

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* Adapted by permission from The International Nickel Co. Inc., see footnote p. 366. For other data, particularly on stainless steels, see Chapter 21.

A24. MAIN OXIDATION STATES OF ELEMENTS*

Element	Symbol	Main Oxidation States	Approximate† Atomic Weight	Element	Symbol	Main Oxidation States	Approximate Atomic Weight
Aluminum	Al	III	27.0	Magnesium	Mg	II	24.3
Antimony	Sb	III, V	122	Manganese	Mn	II, IV, VII	54.9
Arsenic	As	III, V	74.9	Mercury	Hg	I, II	201
Barium	Ba	II	137	Molybdenum	Mo	III, VI	96.0
Beryllium	Be	II	9.01	Nickel	Ni	II	58.7
Bismuth	Bi	III, V	209	Nitrogen	N	—III, III, V	14.0
Boron	B	—III, III	10.8	Oxygen	O	—II	16.0
Bromine	Br	—I, V	79.9	Phosphorous	P	—III, III, V	31.0
Cadmium	Cd	II	112	Potassium	K	I	39.1
Calcium	Ca	II	40.1	Silicon	Si	—IV, IV	28.1
Carbon	C	—IV, IV	12.0	Silver	Ag	I	108
Chlorine	Cl	—I, I, III, V, VII	35.5	Sodium	Na	I	23.0
Chromium	Cr	III, VI	52.0	Strontium	Sr	II	87.6
Cobalt	Co	II, III	58.9	Sulfur	S	—II, IV, VI	32.1
Copper	Cu	I, II	63.5	Tin	Sn	II, IV	119
Fluorine	F	—I	19.0	Titanium	Ti	IV	47.9
Hydrogen	H	I	1.01	Tungsten	W	VI	184
Iodine	I	—I, V, VII	127	Uranium	U	III, IV, VI	238
Iron	Fe	II, III	55.9	Vanadium	V	V	51.0
Lead	Pb	II, IV	207	Zinc	Zn	II	65.4
Lithium	Li	I	6.94	Zirconium	Zr	IV	91.2

* For complete listings, see sections dealing with the individual elements.

† Three-place accuracy for slide rule problem solving.

A25. VALENCES OF COMMON ANIONS*

Name	Formula; Valence	Name	Formula; Valence
Acetate	$H_3CCO_2^-$	Nitrate	NO_3^-
Aluminate (meta)†	AlO_2^-	Nitrite	NO_2^-
Antimonate (ortho)†	SbO_4^{-3}	Nitrosylsulfate	$O_2NSO_3^-$
Antimonate (pyro)†	$Sb_2O_7^{-4}$	Oxalate	$C_2O_4^{-2}$
Arsenate (ortho)†	AsO_4^{-3}	Perborate	BO_3^-
Arsenite (ortho)†	AsO_3^{-3}	Perchlorate	ClO_4^-
Azide	N_3^-	Periodate (para)	$H_3IO_6^{-2}$
Bismuthate (meta)†	BiO_3^-	Permanganate	MnO_4^-
Borate (meta)†	BO_2^-	Peroxide	O_2^{-2}
Borate (ortho)†	BO_3^{-3}	Peroxychromate	CrO_8^{-3}
Borate (tetra)	$B_4O_7^{-2}$	Peroxydisulfate	$S_2O_8^{-2}$
Bromate	BrO_3^-	Phosphate (ortho)	PO_4^{-3}
Carbamate	$H_2NCO_2^-$	Phosphate (meta)	PO_3^-
Carbonate (meta)	CO_3^{-2}	Phosphate (hexameta)	$P_6O_{18}^{-6}$
Chlorate	ClO_3^-	Phosphate (pyro)	$P_2O_7^{-4}$
Chlorite	ClO_2^-	Phosphate (tripoly)	$P_3O_{10}^{-5}$
Chlorosulfonate	SO_3Cl^-	Phosphite (meta)	PO_2^-
Chromate	CrO_4^{-2}	Plumbate (ortho)	PbO_4^{-4}
Chromite†	CrO_2^-	Plumbite	PbO_2^{-2}
Cyanate	OCN^-	Silicate (meta)	SiO_3^{-2}
Cyanide	CN^-	Silicate (ortho)	SiO_4^{-4}
Dichromate	$Cr_2O_7^{-2}$	Stannate (meta)†	SnO_3^{-2}
Dithionate	$S_2O_6^{-2}$	Stannite†	SnO_2^{-2}
Dithionite	$S_2O_4^{-2}$	Sulfamate	$H_2NSO_3^-$
Ferricyanide	$Fe(CN)_6^{-3}$	Sulfate (meta)	SO_4^{-2}
Ferrocyanide	$Fe(CN)_6^{-4}$	Sulfide (hydro)	SH^-
Fluoaluminate	AlF_4^-	Sulfite	SO_3^{-2}
Fluoborate	AlB_4^-	Sulfite (pyro)	$S_2O_5^{-2}$
Fluoride ("acid")	HF_2^-	Superoxide	O_2^-
Fluosilicate	SiF_6^{-2}	Tetrathionate	$S_4O_6^{-2}$
Hydroxide	OH^-	Thioantimonate	SbS_4^{-3}
Hypochlorite	ClO^-	Thioantimonite	SbS_3^{-3}
Hyponitrite	$N_2O_2^{-2}$	Thioarsenate (meta)	AsS_3^-
Iodate	IO_3^-	Thioarsenite	AsS_3^{-3}
Iodide (tri)	I_3^-	Thiocyanate	SCN^-
Isocyanate	NCO^-	Thiostannate (meta)†	SnS_3^{-2}
Isothiocyanate	NCS^-	Thiosulfate	$S_2O_3^{-2}$
Manganate(VI)	MnO_4^{-2}	Zincate†	ZnO_2^{-2}

* Common names are given. For Werner nomenclature and list of coordinating groups, see Chapter 4. See also Table 20-3 for radicals derived from the less familiar metals of Chapter 20.

† These anions are thought to exist only in complexes or infinitely extended structures. Anions composed of a single element like chloride, Cl^-, are omitted and can be deduced from the previous table. Closely related anions to those above can also be deduced; thus PO_4^{-3} is (ortho) phosphate, HPO_4^{-2} will be mono hydrogen (ortho) phosphate; CO_3^{-2} is carbonate, HCO_3^- is hydrogen carbonate or bicarbonate, etc.

A26. ABBREVIATIONS OF COMMON CHEMICAL TERMS

Abbreviation	Term	Abbreviation	Term
Addn.	Addition	Insol.	Insoluble
Alk.	Alkaline	K	Kilo
Amt.	Amount	Lab.	Laboratory
Approx.	Approximately	Mmol.	Millimole
Aq	Aqueous	Math.	Mathematical
Atm.	Atmosphere	Max.	Maximum
Av.	Average	Meq.	Milliequivalents
B.p.	Boiling point	Mg	Milligram
Cal	Calorie	Min.	Minimum
Calc.	Calculate	Mixt.	Mixture
Compd.	Compound	Mol.wt	Molecular weight
Cm	Centimeter	M.p.	Melting point
Compn.	Composition	No.	Number
Conc(d).	Concentrat(ed)	Ox.	Oxidation, oxidize(d)
Contg.	Containing	Pos.	Positive
Cp	Chemically pure	Powd.	Powdered
Cryst.	Crystalline	Ppm	Parts per million
Decompn.	Decomposition	Ppt(d).	Precipitate(d)
Detmd.	Determined	Pptn.	Precipitation
Diam.	Diameter	Prepd.	Prepared
Dil.	Dilute	Qual.	Qualitative
Dissocd.	Dissociated	Quant.	Quantitative
Emf	Electromotive force	Red.	Reduction, reduce(d)
Eq.	Equation	Resp.	Respectively
Equil.	Equilibrium	Satd.	Saturated
Equiv. wt	Equivalent weight	Sep.	Separate
Estd.	Estimated	Sol.	Soluble
Evapd.	Evaporated	Soln.	Solution
Examd.	Examined	Soly.	Solubility
Expt.	Experiment	Sp. gr.	Specific gravity
Form. wt	Formula weight	Tech.	Technical (grade)
F.p.	Freezing point	Temp.	Temperature
G	Gram	Vol.	Volume
In.	Inch	Wt	Weight

A27. ABBREVIATIONS OF COLORS

Color	Symbol	Color	Symbol	Color	Symbol
Black	*B*	Green	*G*	Purple	*Pu*
Brown	*Br*	Grey	*Gy*	Red	*R*
Blue	*Bu*	Light	*L*	Violet	*V*
Colorless	*Cl*	Orange	*Or*	White	*W*
Dark	*D*	Pink	*P*	Yellow	*Y*

A28. COMMON LOGARITHMS

	0	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396

A28.—*Contd.*

	0	1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996

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SOLUBILITIES

ANIONS	CATION GROUP 1			CATION GROUP 2A				CATION GROUP 2B			
	Ag^{+}	Hg_2^{+2}	Pb^{+2}	Hg^{+2}	Bi^{+3}	Cu^{+2}	Cd^{+2}	As^{+3}	Sb^{+3}	Sn^{+2}	Sn^{+4}
GROUP 1											
1. NO_2^-	W$_{Y}$	W	W$_{Y}$	W	W	W$_{Bu}$	W				
2. S^{-2}	A$_{B}$	A$_{B}$	A$_{B}$	A$_{B}$	A$_{B}$	A$_{B}$	A$_{Y}$	I$_{Y}$	A$_{Or}$	A$_{Br}$	A$_{Y}$
3. SO_3^{-2}	WA	A	A	A	A	A$_{Bu}$	A				
4. $S_2O_3^{-2}$	WA	A	I				W				
5. CO_3^{-2}	A$_{Y}$	A$_{Br}$	A	A	A	A$_{G}$	A				
GROUP 2											
6. PO_4^{-3}	A$_{Y}$	A	A	A$_{Y}$	I	A$_{Bu}$	A				I
7. SO_4^{-2}	S	SA	I	S	H	W$_{Bu}$	W		H	WH	H
8. CrO_4^{-2}	A$_{R}$	A$_{Or}$	A$_{Y}$	A$_{R}$	H$_{R}$	A$_{Br}$	A$_{Y}$			A$_{Br}$	H$_{Br}$
9. BO_2^-	A		A		A	A$_{Bu}$	A			A	
10. F^-	W$_{Y}$	SA$_{Y}$	A	SA	H	A$_{Bu}$	W	H	H	H	H
11. $C_2O_4^{-2}$	A	A	A	A	A	A$_{Bu}$	A		A	A	
GROUP 3											
12. Cl^-	I	I	S	W	H	W$_{G}$	W	H	H	WH	H
13. Br^-	I$_{Y}$	I$_{Y}$	I	S	H	W$_{B}$	W	H$_{Y}$	H	WH$_{Y}$	H
14. I^-	I$_{Y}$	I$_{Y}$	I$_{Y}$	A$_{R}$	H$_{Br}$		W$_{Br}$	H$_{R}$	H$_{R}$	SA$_{Or}$	H$_{Y}$
15. SCN^-	I	SA	A	W		A$_{B}$	SA				W
16. $Fe(CN)_6^{-4}$	I$_{Y}$	A$_{Y}$	SA$_{R}$	I$_{Br}$	SA	I$_{Br}$				A	I$_{G}$
GROUP 4											
17. NO_3^-	W	WH$_{Y}$	W	WH	H	W$_{Bu}$	W		H		
18. Ac^-	SA	WH	W	W	H	W$_{Gr}$	W			WH$_{Y}$	

W = Soluble in water.
A = Soluble in cold, dilute HCl or HNO_3, insoluble in water.
I = Insoluble in cold, dilute HCl or HNO_3, insoluble in water.
WH = Soluble in water, some hydrolysis, some precipitation.