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SEMIMICRO QUALITATIVE ANALYSIS

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PREFACE

The numerous advantages of using semimicro amounts of material in qualitative analysis are now generally recognized. Among these are: greatly increased sharpness of separations, since adsorption of ions is much decreased when only small precipitates are involved and filtration is replaced by centrifugation; astonishingly small amounts detectable by an average student; accomplishment of nearly twice as much work in a laboratory period; and greatly reduced cost of laboratory instruction.

Hitherto the general adoption of small-scale analysis has been retarded by lack of reliable procedures. If the average student is to remain interested and enthusiastic, he must be furnished laboratory directions which are precise and which he finds *work* in practice. This book is planned to furnish such directions and, at the same time, to teach the maximum amount of inorganic chemistry that can be absorbed in the allotted time.

The methods prescribed in the text have been gradually evolved during a period of six years. They have been thoroughly tried out on large classes and found to give exceptionally good results. Two features are, so far as we know, entirely new. These are analysis for anions by elimination, and analysis both of cation Group III without removal of arsenate and phosphate and of cation Group IV without use of the rather unsatisfactory reagent, ammonium carbonate. It has been demonstrated that, after a student has mastered the details, he can make an anion analysis with surprising accuracy in a comparatively short time. It is obvious that the time required for a cation analysis can be reduced nearly one half by elimination of the tedious special procedures for precipitation of arsenic from arsenic acid in Group II and removal of phosphate before analyzing for Group III.

Experience has shown that accurate manipulation is essential to good results. For this reason a special section is devoted to semimicro technique and all laboratory instructions are given in very full detail. The chemistry of each procedure is discussed fully in notes. Use is made of only a few organic reagents, which have been found valuable in changing possible uncertainty into relative certainty.

Recent views regarding the structure of matter have been included as far as it seems absolutely necessary to acquaint the elementary student with these views. Probably at no period since its beginning has chemistry undergone such rapid and far-reaching change as within the last decade. It is our opinion that the beginning student should acquire the modern viewpoint even if he is not yet ready to comprehend all its details.

The formulation of many compounds will be found decidedly different from that in most textbooks. For this we offer no apologies; we merely state that a careful attempt has been made to formulate chemical compounds as modern investigations show them to be.

Acknowledgments are due to many authors whose works have been consulted in the preparation of this book. Among these, special mention should be made of Feigl's *Tüpfelreactionen*, second edition, and Curtman's *Qualitative Analysis*, a model of organization of material.

Dr. D. W. Pearce has contributed generously of his time in reading the manuscript and has made many valuable suggestions. To Dr. R. F. Newton we owe certain important modifications of the chapter on redox reactions. We are deeply grateful to both these colleagues.

To Dr. W. M. Latimer, editor of this series of texts, we are also deeply indebted both for many helpful criticisms and suggestions and for permission to make free use of the values of equilibrium constants and molal potentials given in his recent book, *Oxidation Potentials.*

Arthur R. Middleton
John W. Willard

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PART I

THEORY

CHAPTER 1

THE USE OF UNITS IN CHEMICAL CALCULATIONS

The numbers dealt with in scientific calculations are nearly always *concrete* rather than *abstract*. This means that a *unit* becomes *part* of each number and must be carried algebraically through all the operations to which the number is submitted arithmetically. Nearly all chemical problems state clearly the unit of the answer. The first step in the solution should be to note and set down this unit. If an algebraic equation containing the units of the data in the problem is set up so that it gives the unit of the quantity to be found, the same operations performed on the numbers will give the correct answer.

Before one begins to use these units, their nature and origin should be understood. This is important because some of them (for example, mass and weight, cubic centimeter and milliliter) are frequently interchanged although they are not identical.

THE CENTIMETER-GRAM-SECOND SYSTEM

This is the system of units used exclusively in exact scientific work.

The centimeter is 0.01 of the *standard meter*, the distance between two marks on a bar of platinum-iridium preserved at the International Bureau of Weights and Measures near Paris. This distance was intended to be one ten-millionth of the distance from the equator to a pole of the earth. More accurate subsequent surveys have shown that it is slightly less.

The gram is 0.001 of the mass of the *standard kilogram*, a piece of platinum-iridium preserved at the International Bureau. It was intended to equal exactly the *mass* of a cube of water 10 cm on an edge at its temperature of greatest density, 4°C. Actually it weighs 0.027 g more, since the maximum absolute density (at 3.98°) of water has been found to be 0.999973 g per cm^3.

The second is $\frac{1}{86400}$ of the *siderial day*, the interval between successive arrivals of a certain fixed star at a given meridian of the earth.

In the chemical handbooks all the important physical and chemical units are tabulated together with the most probable value of each and the probable absolute exactness of the value given.

MASS, WEIGHT, DENSITY, AND SPECIFIC GRAVITY

Mass is the quantity of matter in an object and is constant.

Weight is the measure of the force (unit, dynes) by which a given mass is attracted toward the center of gravity of the earth. This force varies with location above or below the surface of the earth and also, since the earth is not a perfect sphere, with location between the equator and the poles. It varies from about 978 dynes per gram at the equator to about 983 dynes per gram at the poles. At the Bureau of Standards in Washington, D.C., it has the value 980.097 dynes per gram. (A dyne is that force which imparts to a mass of 1 g an acceleration of 1 cm per second per second.)

$$\text{Weight} = \text{mass} \times \frac{g \text{ cm}}{\text{sec}^2}, \tag{1}$$

in which g has values varying about 980.

When a mass is weighed, both it and the counterpoising weights lose weight equal to the weight of air they displace; and the weight of air varies from day to day. Determination of the *exact mass* of an object involves several corrections of its weight, although the sum of the corrections is relatively very small. It is customary, in all but work of the highest precision, to use the two terms "mass" and "weight" interchangeably, since gravity has a constant value at any particular place. Equation (1) above becomes, for that place,

$$\text{Weight} = \text{mass} \times \text{a constant}. \tag{2}$$

Density is mass per unit volume and its unit is g/cm^3. The density of water at 4° is taken as 1 in the C.G.S. system, although its absolute maximum density (3.98°) is 0.999973.

Specific gravity, or relative density, is the *ratio* of the *weights* of equal volumes of a substance and a standard substance under like conditions of temperature, pressure (barometer reading), and value of gravity. Being the ratio of two weights, it has no unit. Water at 4°C. is the usual standard of comparison for liquids and solids. Gases are compared with hydrogen, with air, or with oxygen. Since the density of water at 4°C. is taken as 1, specific gravities become practically identical with densities at that temperature.

The expression $D20°/4°$ (vac.) = 0.3448 g/cm³ for a 30% HCl solution, of which the specific gravity 1.1492 was measured, means that the specific gravity which was measured at 20°C. has been calculated to compare with the *vacuum* weight of 1 cm³ of water at 4°C., which is assumed to be 1 g. Specific gravity has thus been calculated into the *density* (weight per cm³) of the HCl in the solution. The chemical handbooks contain tables which give the relations between specific gravity, density at 4°C., and composition, for various solutions.

UNITS USED CHIEFLY IN CHEMISTRY

Chemical calculations are frequently based on the number of particles in a given volume. This is particularly true of applications of the Equilibrium Principle or Law of Mass Action. For such calculations, commonly used weight units are the following:

Gram atom, the number of grams equal to the *atomic* weight of the substance (for example, 16.00 g of oxygen, 1.0081 g of hydrogen, 107.88 g of silver, 35.46 g of chlorine). Each weight is 1 gram atom of the element.

Gram mol, or simply mol, the number of grams equal to the molecular weight of the substance (for example, 32.00 g of oxygen, 2.0162 g of hydrogen, 70.92 g of chlorine).

Gram ion, the number of grams equal to the sum of the weights of the atoms in an ion (for example, 1.0081 g of H^+, 60.00 g of $CO_3^=$, 96.06 g of $SO_4^=$).

Gram equivalent, or simply equivalent, the number of grams of an atom or an ion which will displace or react with 1.008 g of hydrogen or with 8 g of oxygen. In general it is the gram atom or the gram ion divided by the valence of the ion (for example, 26.97/3 g of Al^{+3}, 24.32/2 g of Mg^{++}, 211.888/4 g of $[Fe(CN)_6]^{-4}$). However, the number of equivalents in a mol may vary according to the reaction the molecule undergoes. Compare problem 1, page 9.

Concentration is weight per unit volume. The standard unit of volume is the *liter*, defined by the U. S. Bureau of Standards as "the volume occupied by a quantity of pure water at 4°C. having a *mass* of one kilogram". Since the liter is derived from the unit of mass instead of the unit of volume, its subdivisions are, strictly, milliliters instead of cubic centimeters. Actually 1 liter equals 1000.028 cm³ and 1 ml equals 1.000028 cm³.

A molar solution (M) is one which contains 1 gram mol of solute in a liter of solution (volume concentration).

A molal solution is one which contains 1 gram mol of solute in 1000 g of solvent (weight concentration).

If the density of a solution is known, the conversion molar $\rightleftarrows$ molal can be made.

Since a millimol is 0.001 of a mol and a milliliter is 0.001 of a liter, the unit m.mol/ml is numerically identical with the unit mol/liter. In semimicro analysis the milliunits are most convenient.

A normal solution (N) is one which contains one equivalent weight of solute in 1 liter of solution.

Solution of Problems

Consider two methods of solving the following problem. In the first method no consideration is given to units.

Problem. Three drops from a dropper which delivers 18 drops per ml will give how many mg of an ion if the solution contains 10 mg of the ion per milliliter?

Method 1. By the well known "dice method," often used by beginners in scientific calculation, seven different answers will be found.

$$(1)\ 3 \times 10 \times 18 = 540; \quad (2)\ \frac{18 \times 10}{3} = 60; \quad (3)\ \frac{3 \times 18}{10} = 5.4;$$

$$(4)\ \frac{3 \times 10}{18} = 1\frac{2}{3}; \quad (5)\ \frac{3}{10 \times 18} = \frac{1}{60}; \quad (6)\ \frac{10}{18 \times 3} = \frac{10}{54};$$

$$(7)\ \frac{18}{3 \times 10} = \frac{9}{15}.$$

Method 2. The unit of the answer is mg. 18 drops per ml, and 10 mg per ml are fractional units by *statement* of experimentally ascertained facts. Therefore, 3 drops is the single quantity which is not a fractional unit. We set down

$$\text{mg} = 3 \text{ drops}.$$

Using the fractional units to convert drops to mg,

$$\text{mg} = 3 \text{ drops} \times \frac{1 \text{ ml}}{18 \text{ drops}} \times \frac{10 \text{ mg}}{1 \text{ ml}};$$

whence mg $= 1\frac{2}{3}$. This shows at once that, of the seven solutions of method 1, only (4) is correct.

Note that method 2, the "fractional unit" method, gives a correct answer unfailingly. Method 1 gives the user one chance in seven for getting the correct answer.

THE "FRACTIONAL UNIT" METHOD

The essential steps are:

1. Set down the unit of the quantity to be calculated (the answer) followed by = (equals).
2. After =, set down, with its unit, the single quantity in the problem which is not a "fractional unit."
3. Multiply this quantity by the fractional unit, or series of fractional units, which is necessary to convert its unit to the unit of the answer.

A *fractional unit* is a unit the numerator of which equals the denominator either by definition or as a statement of an experimentally ascertained fact. Hence, a fractional unit is always equal to unity and a quantity can be multiplied by any number of fractional units without changing its value. The answer may be itself a fractional unit. By *definition* 1000 mg/1 g and 1 g/1000 mg are fractional units. By *experiment* 18 drops/1 ml and 1 ml/18 drops are "fractional units" for a dropper which has been found to deliver 18 drops per ml. Since a fractional unit is equal to unity, its *inverted form* can always be used. Some of the most frequently used fractional units are listed in Table 1.

Use of Fractional Units in Solving Problems

Problem 1. How many grams of $Al(NO_3)_3 \cdot 9H_2O$, molecular weight 375.13, must be weighed out to make 100 ml of solution which will contain 10 mg/ml of Al^{+3} (atomic weight, 26.97)?

The unit of the answer is grams. Fractional units are 375.13 g/mol, 26.97 g/g.atom and 1000 mg/g. The single quantity not a fractional unit is 100 ml. We set down:

$$\text{g (of salt)} = 100 \text{ ml} \times \frac{10 \text{ mg } Al^{+3}}{1 \text{ ml}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{375.13 \text{ g salt}}{1 \text{ mol}} \times \frac{1 \text{ mol salt}}{1 \text{ g.atom } Al^{+3}} \times \frac{1 \text{ g.atom } Al^{+3}}{26.97 \text{ g } Al^{+3}};$$

whence g = 13.91.

Observe the order in which undesired units were eliminated: (1) ml, (2) mg, (3) mol, (4) g.atom. Note that all units cancel out

except the desired unit (grams) and that this cancellation (before making any numerical computation) *proves* that the equation is

TABLE 1

FRACTIONAL UNITS

TERM	UNIT	EXAMPLE
Gram mol (mol. wt.)	$\frac{x\text{ g}}{1\text{ mol}} = \frac{x\text{ mg}}{1\text{ m.mol}}$	$\frac{98\text{ mg }H_2SO_4}{1\text{ m.mol }H_2SO_4}$
Gram atom (at. wt.)	$\frac{x\text{ g}}{1\text{ g.atom}}$	$\frac{14\text{ g N}}{1\text{ g.atom N}}$
Gram ion (ionic wt.)	$\frac{x\text{ g}}{1\text{ ion}}$	$\frac{96\text{ g }SO_4^{=}}{1\text{ g.ion }SO_4^{=}}$
Gram equivalent (eq. wt.)	$\frac{x\text{ g}}{1\text{ eq.}} = \frac{x\text{ mg}}{1\text{ milli eq.}}$	$\frac{48\text{ mg }SO_4^{=}}{1\text{ m.eq.}}$
Molar solution (M)	$\frac{x\text{ mol}}{1\text{ liter}} = \frac{x\text{ m.mol}}{1\text{ ml}}$	$2\ M\ \text{HCl} = \frac{2\text{ m.mol HCl}}{1\text{ ml soln.}}$
Normal solution (N)	$\frac{x\text{ eq.}}{\text{liter}} = \frac{x\text{ m.eq.}}{\text{ml}}$	$2\ N\ \text{HCl} = \frac{2\text{ m.eq.}}{1\text{ ml soln.}}$
Density	$\frac{x\text{ g}}{\text{ml}}$	$D\ H_2O(4°) = 1 = \frac{1\text{ g }H_2O}{1\text{ ml }H_2O}$
Specific gravity	ditto	ditto
Concentration (weight)	$\frac{x\text{ g}}{\text{liter}} = \frac{x\text{ mg}}{\text{ml}}$	$\frac{10\text{ mg }Al^{+3}}{1\text{ ml soln.}}$
Per cent (weight)	$\frac{x\text{ g pure substance}}{100\text{ g mixture}}$	(1) 28% HCl soln. $= \frac{28\text{ mg HCl}}{100\text{ mg soln.}}$
		(2) 10% Cu alloy $= \frac{10\text{ mg Cu}}{100\text{ mg alloy}}$
Per cent (volume)	$\frac{x\text{ ml}}{100\text{ ml}}$	50% alcohol $= \frac{10\text{ ml alcohol}}{20\text{ ml mixture}}$
Conversion units[a]	$\frac{1000\text{ ml}}{1\text{ liter}}$	
	$\frac{1000\text{ mg}}{\text{g}}$	
	$\frac{22.4\text{ l (S.T.P.)}}{1\text{ mol}}$	

[a] Many pages of conversion units applicable to various fields of scientific work are to be found in the chemical handbooks.

properly set up and hence that the computation indicated by the equation *must* give the correct answer, barring numerical errors.

Problem 2. Concentrated H_2SO_4 has a sp. gr. 1.84 and contains 96% by weight of H_2SO_4. Calculate its normality.

The unit of the answer is a fractional unit, m.eq./ml(N). The fractional units in the problem are (1.84 g acid)/(ml acid) and (96 g H_2SO_4)/(100 g acid). Then, since the unit of the answer is a fractional unit and all fractional units equal unity, we set down

$$\frac{\text{m.eq.}}{\text{ml}} = 1 \times \frac{1 \text{ m.eq.}}{49 \text{ mg } H_2SO_4} \times \frac{1.84 \text{ g acid}}{1 \text{ ml acid}} \times \frac{96 \text{ g } H_2SO_4}{100 \text{ g acid}} \times \frac{1000 \text{ mg}}{\text{g}};$$

whence m.eq./ml(N) = 36.03.

Again observe the order in which undesired units were eliminated.

Problem 3. How many drops of 6N NH_3 and how many drops of water should be taken to make one ml of 0.6N solution if the dropper delivers 18 drops per ml?

The two quantities to be calculated are related as x drops and $18 - x$ drops. Therefore only x(= drops of 6N NH_3) need be considered. The unit of the answer is drops. The given fractional units are 6 m.eq./ml, 0.6 m.eq./ml, and 18 drops per ml. The quantity not a fractional unit is 1 ml.

$$\text{Drops } (6N) = 1 \text{ ml} \times 0.6 \frac{\text{m.eq.}}{\text{ml}} \times \frac{1 \text{ ml}}{6 \text{ m.eq.}} \times \frac{18 \text{ drops}}{1 \text{ ml}};$$

whence drops = 1.8. Therefore, 2 drops of 6N NH_3 and 16 drops of water should be taken.

Since 1 ml of 0.6N NH_3 is desired, the latter is the first fractional unit to be placed in the equation.

Problems

1. A solution containing 100 mg of chrome alum, $KCr(SO_4)_2 \cdot 12H_2O$ (499.1) in 12 ml has what normality with respect to (*a*) K^+, (*b*) Cr^{+3}, (*c*) $SO_4^{=}$? *Ans.* (*a*) 0.0167N; (*b*) 0.05007N; (*c*) 0.06677N.

2. How many mg of K^+ (39.1) in 1 ml of 0.1N KCl solution? *Ans.* 3.9 mg.

3. How many mg of (*a*) K^+ and (*b*) $SO_4^{=}$ in 1 ml of 0.1N K_2SO_4 solution? *Ans.* (*a*) 3.9; (*b*) 4.8.

4. What is the normality of a solution containing 10 mg/ml of $SO_4^{=}$ (96)? *Ans.* 0.2083N.

5. How many grams of $MnCl_2 \cdot 4H_2O$ (197.9) should be taken to make 100 ml of a solution containing 10 mg/ml of Mn^{++}? *Ans.* 3.6 g.

Dilution Problems

The principle underlying dilution problems is that the total *amount* of solute remains unchanged by dilution. That is,

$$N_1V_1 = NV, \text{ or } M_1V_1 = MV,$$

where N_1 or M_1 are the normality or molarity of the solution after dilution from V to V_1 liters or ml. These equations reduce to m.eq. = m.eq. and m.mols = m.mols.

Example. How many ml of conc. HCl, sp. gr. 1.19, containing 37.2% by weight of HCl, should be diluted to make 100 ml of $4N$ acid?

Solution. 1 ml of concentrated acid weighs 1.19 g and contains $(1.19 \times 0.372) = 0.44268$ g of HCl. A $4N$ solution contains, in 100 ml, 36.457×4 eq/l $\times$ 0.1 l = 14.583 g. This will require 14.583 g/0.44268 g per ml which is 32.94 ml.

Proof. 100 ml of $4N$ = 32.94 ml of $12.12N$.

6. How many ml of glacial acetic acid, sp. gr. 1.048, 99.5% AcOH by weight, should be taken to make 30 ml of $6N$ acid? *Ans.* 10.4 ml.

7. How many ml of HNO_3, sp. gr. 1.415, 68.6% HNO_3 by weight, should be taken to make 30 ml of $3N$ acid? *Ans.* 5.8 ml.

8. How many ml of HCl, sp. gr. 1.19, 37.23% HCl by weight, should be taken to make 30 ml of $3N$ acid? *Ans.* 7.0 ml.

9. How many ml of H_2SO_4, sp. gr. 1.84, 95.6% H_2SO_4 by weight, should be taken to make 30 ml of $3N$ acid? *Ans.* 2.5 ml.

10. How many ml of NH_3 solution, sp. gr. 0.898, 29.01% NH_3 by weight, should be taken to make 30 ml of $6N$ solution? *Ans.* 11.8 ml.

11. How much NaOH, 10% water, should be weighed out to make 30 ml of 6 N solution? *Ans.* 8 g.

12. Using a dropper which delivers 20 drops per ml, how many drops of $3N$ HCl and how many drops of water should be taken to make 1 ml of $0.3N$ acid? *Ans.* 2 drops HCl, 18 drops water.

13. A wash liquid is to be $0.05N$ in H_2SO_4. To one drop of $3N$ H_2SO_4 how many drops of water should be added? *Ans.* 59 drops.

14. Using an 18 drops per ml dropper, how many drops of 6 *N* NaOH should be diluted to make 1 ml of 1.0 *N* solution? *Ans.* 3 drops + 15 drops of water.

15. It becomes necessary to dilute 1 ml of 3 *N* HCl so that it shall become 1.4 *N*. How many drops of water should be added from a dropper which delivers 21 drops per ml? *Ans.* 24 drops.

CHAPTER 2

LOGARITHMS

In many calculations, particularly those based upon chemical equilibrium, exceedingly small numbers are involved, such as 0.0000031. In calculations involving the number of gas molecules in a given volume, exceedingly large numbers have to be dealt with, for instance 6.06×10^{23}. Calculations involving either very small or very large quantities are greatly facilitated by use of logarithms.

A *logarithm* is the power to which an *arbitrarily chosen* number called the *base* must be raised in order to equal a given *number*.

$$\text{Base}^{\log} = \text{number}$$

The words "arbitrarily chosen" imply that *any* number whatsoever, whether integral or fractional, may be taken as the base of a *system* of logarithms. Such, indeed, is the case. For example,

$$10^2 = 100$$
$$0.9^2 = 0.81$$
$$2.5^2 = 6.25.$$

Two is the logarithm of 100 in a system in which 10 is the base. Two is also the log of 0.81 in a system in which 0.9 is the base, and it is the log of 6.25 in a system in which 2.5 is the base.

Two systems of logarithms are in common use, one having as its base the number 10, the other having as its base the quantity e, the limit of the sum of the terms of the infinite converging series

$$\left[1 + 1 + \frac{1}{1 \times 2} + \frac{1}{1 \times 2 \times 3} \cdots\right] = 2.71828 \cdots$$

The logarithmic function e^x is extremely useful in dealing with physical phenomena which obey the "compound interest law." Logarithms based on the equation, $10^{\log} = \text{number}$, are called common, or Briggs, logs. Those based on the equation, $e^{\log} = \text{number}$, are called natural, hyperbolic, or Napierian logs. Napier discovered logarithmic functions in 1614. The first "log table" was computed by Briggs a few years later.

Since

$$\log_{10} e = \log_{10} 2.718 = 0.4343,$$
$$e = 10^{0.4343}, \text{ and}$$
$$10 = e^{2.3026}.$$

Therefore,

$$\log_e a = \log_{10} a \times 2.3026, \text{ and}$$
$$\log_{10} a = \log_e a \times 0.4343.$$

CHARACTERISTIC AND MANTISSA OF LOGS

The integral part of a logarithm is called its *characteristic*, the decimal part is called its *mantissa*. It is important to remember that the mantissa is always positive. In

$$\log_{10} \text{ of } 126.4 = 2.1018,$$

2 is the characteristic and 0.1018 the mantissa of the log.

The characteristics of logs are readily obtained from the definition of a common, or Briggs, log,

$$\text{number} = 10^{\log},$$

and two principles of algebra: (1) any quantity with 0 for an exponent is equal to 1 ($10^0 = 1$), and (2) any quantity with a negative exponent equals the reciprocal of that quantity with an equal positive exponent ($10^{-1} = 1/10^1$). From these it follows that

10^2	= 100	and log	100	=	2
10^1	= 10	" "	10	=	1
10^0	= 1	" "	1	=	0
10^{-1}	= 0.1	" "	0.1	=	−1
10^{-2}	= 0.01	" "	0.01	=	−2
10^{-3}	= 0.001	" "	0.001	=	−3
10^{-4}	= 0.0001	" "	0.0001	=	−4.

Notice that

$$\log\ 10 = 1 \text{ and } \log 0.1 = -1,$$
$$\text{"}\ 100 = 2 \text{ "} \text{ "}\ 0.01 = -2, \text{ etc.}$$

Note that the *characteristic* of the log of any number between 1 and 10 is 0; that of any number between 0.1 and 1 is −1. In other words, the characteristic cannot become as large as 1 until the number is as large as 10; as large as 2 until the number is as large as 100, and so on. Similarly the characteristic of the log of any

number of tenths is -1, of any number of hundredths is -2, of any number of thousandths is -3, and so on.

Log tables give only the mantissas, or decimal parts, of logs. The characteristics are readily obtained by inspection of the number.

A 10-inch slide rule is essentially a 3-place log table; that is, it gives 3 digits with an accuracy of about one unit in the third digit.

Problems

Write down the logs of the following numbers: (1) 6871; (2) 68.71; (3) 6.871; (4) 0.6871; (5) 0.06871; (6) 0.006871; (7) 0.0006871; (8) 424,700,000,000; (9) 2.0; (10) 0.025.

Write down the numbers of which the following are the logs: (1) 3.7128; (2) $\bar{3}.7128$; (3) 0.6990; (4) $\bar{2}.6990$; (5) 0.0086; (6) 0.9999; (7) 6.6294; (8) 0.0008; (9) 0.0033; (10) $\bar{1}.0607$.

ARITHMETICAL OPERATIONS WITH LOGS

Four operations can be performed using logs: multiplication, division, raising to powers, and extraction of roots.

1. Multiplication. The log of a product is the *sum* of the logs of the factors.

$$\log_{10} (a \times b \times c) = \log_{10} a + \log_{10} b + \log_{10} c.$$

Example.

$$\text{Log } (79 \times 642) = 1.8976 + 2.8075 = 4.7051$$
$$\therefore 79 \times 642 = 50{,}710$$

2. Division. The log of a quotient is equal to the log of the dividend minus the log of the divisor.

$$\log \frac{a}{b} = \log a - \log b$$

Example.

$$\text{Log } \frac{642}{79} = 2.8075 - 1.8976 = 0.9099$$
$$\therefore \frac{642}{79} = 8.126$$

3. Raising to powers. The log of the nth power of a number is n times the log of the number.

4. Extraction of roots. The log of the real positive nth root of a number is the log of the number divided by n, since the nth root is the $1/n$th power.

$$\log a^x = x \log a; \log a^{1/x} = \frac{(\log a)}{x}$$

Example.

$$\log \frac{ab^3}{c(d)^{0.5}} = \log a + 3 \log b - \log c - 0.5 \log d$$

Problems

Using logs, find the values of the following expressions:

1. $\left(\frac{245}{311}\right)^{\frac{1}{2}}$. *Ans.* 0.8877.

2. $\frac{5^4 \times (1.9)^{\frac{1}{2}}}{6 \times (11)^2}$. *Ans.* 1.011.

3. $\left(\frac{8999}{35.14}\right)^{\frac{1}{2}}$. *Ans.* 101.65.

4. $1{,}826{,}000 \times (0.003)^2$. .

Ans. 16.43.

5. The gram molecular volume, 22420 cm^3, of any gas at 0° and 760 mm contains 6.06×10^{23} molecules. If the molecules in 1 mm^3 could be divided equally among the inhabitants of the earth, estimated to be 2.2 billion, how many molecules would each individual receive? *Ans.* More than 12 million.

6. How long would it take an individual to count the molecules he had received if he counted 3 each second for 8 hours a day, 26 days a month? *Ans.* Nearly 5.5 months.

7. How many molecules would be in 1 mm^3 of gas at 0° if the pressure were reduced to one millionth of a mm? *Ans.* More than 35 million.

Very Large and Very Small Quantities

Many physical and chemical quantities are of dimensions beyond actual human comprehension. Moreover, such quantities are not susceptible to accurate measurement and their values can be given only very approximately. Astronomers do not venture to state the exact distance of stars from the Earth. Instead, they state such distances in the enormous unit light-years, which states roughly the number of years that light from the star, traveling at the rate of 186,000 miles per second would take to reach the

Earth. Avogadro's number (problem 5 above) is probably accurate within one unit in the second decimal place, that is, the number may be in error by as much as 10^{21} molecules which certainly is far from exact. If a census of all the inhabitants of the Earth could be made, the result would be in error by a million or more before the figures could be compiled. To give Avogadro's number as 6.063246×10^{23}, or the population of the Earth as 2,199,472,000, would obviously be meaningless, since we have no means of knowing that the figure in even the first decimal place is accurate within several units.

In the same way, when we say that the solubility product constant of Ag_2S is 4×10^{-52} $(m.mol/ml)^3$, we must be dealing with an extremely rough approximation of the numbers of Ag^+ and $S^=$ in the saturated solution of Ag_2S.

In dealing with these rough approximations, we do not write the significant figures followed by a long line of ciphers, in the case of large quantities, or with a line of ciphers between the decimal point and the first significant figure, in the case of very small quantities. Instead we write the numbers as a product of the significant figures and a power of 10, for example, 6.06×10^{23} or 4×10^{-52}.

It is important to see that numbers written as products give at once the *characteristics* of their logarithms, *provided that* the decimal point of the coefficient of $10^{\log}$ be written after the *first figure*. The reason is that the log of a product is the sum of the logs of the factors, and the characteristic of the log of any number between 10 and 1 (for example, 9.9999) is 0, that is, the characteristic cannot become 1 until the number becomes as large as 10. Hence,

$$\log 6.06 \times 10^{23} = \text{log of } 6.06\ (= 0.7825) + \log 10^{23}\ (= 23);$$
$$\therefore \text{ the log of the number is } 23.7825.$$

In the same way the log of $4 \times 10^{-52} = 0.6021 + (-52)$. Since the mantissa of a log *must* be positive, the log is $\bar{5}\bar{2}.6021$, that is, $(-52 + 0.6021)$.

In operating with logs of numbers having negative exponents, errors are avoided by making the log, both characteristic and mantissa, positive. This can be done by subtracting multiples of 10 from the log. Study the following cases to see how this is done.

Instead of writing $\bar{5}\bar{2}.6021$ as the log of 4×10^{-52}, one writes $8.6021 - 60$ since $8 - 60$ is -52. Suppose it is required to find the log of $(4 \times 10^{-52})^3$. This is $3 \times \log 4 \times 10^{-52}$.

(1)	(2)
$\overline{5}2.6021$	$8.6021 - 60$
3	3
$\overline{15}5.8063$	$25.8063 - 180$ or $5.8063 - 160$, since $20 - 20 = 0$.

In method (1) it has to be constantly remembered that the mantissa is always positive and that digits carried past the decimal point in multiplying are positive and must be subtracted from the characteristic. In method (2) the entire log, characteristic as well as mantissa, is positive, the negative value of the exponent being merely indicated each time. One then does not have to remember to make a subtraction. Study the following examples not only as illustrations of this point but also as models for setting down computations with logs.

Example 1. Evaluate $\dfrac{0.033 \times (1.92 \times 10^{-5})^2}{1 \times 10^{-4}}$.

$5.2833 - 10$	log 1.92×10^{-5}
2	
$10.5666 - 20$	" $(1.92 \times 10^{-5})^2$
$8.5185 - 10$	" 0.033
$19.0851 - 30$	
$6. \quad - 10$	" 10^{-4}
$13.0851 - 20$	" *ans.*

1.217×10^{-7} *Ans.*

Example 2. Find the fifth root of 4×10^{-52}, that is, $(4 \times 10^{-52})^{\frac{1}{5}}$.

$8.6021 - 60$	log 4×10^{-52}
$40 \quad - 40$	
$5)\overline{48.6021 - 100}$	
$9.7204 - 20$	*log ans.*

5.252×10^{-11} *Ans.*

Problems

1. Write down the logs of the following numbers:

(*a*) 3.7 trillion; (*b*) 3.7 trillionths; (*c*) 378 trillion; (*d*) 378 trillionths.

2. Write down the numbers of which the following are the logs: (*a*) $7.6846 - 30$; (*b*) 18.1615; (*c*) $8.4771 - 50$; (*d*) $9.6990 - 10$; (*e*) $7.6990 - 10$.

3. How many miles is a light-year? (The speed of light is 186,000 miles per second.) *Ans.* 5.87×10^{12} miles.

4. Find the value of x in $[.03\ (.01)^4]/x = 1.5 \times 10^{-12}$. *Ans.* 200.

5. Log $(1/C_{H^+})$ is called the pH of a solution [p from *potenz* (German) meaning power or logarithm]. Calculate, to 1 decimal place only (experimentally the second decimal digit would be uncertain by at least 2 units), the pH of solutions in which C_{H^+} has the following values: (*a*) 2×10^{-7}; (*b*) 5×10^{-10}; (*c*) 0.1365; (*d*) 0.0007; (*e*) 2.54×10^{-12}; (*f*) 8.5×10^{-2}; (*g*) 1×10^{-7}; (*h*) 0.75; (*i*) 0.3.

Answers. (*a*) 6.7; (*b*) 9.3; (*c*) 0.86; (*d*) 3.2; (*e*) 11.6; (*f*) 1.1; (*g*) 7.0; (*h*) 0.1; (*i*) 0.5.

LOGARITHMS USED AS NUMBERS

In the equations used to find the equilibrium constant of redox reactions, logs are used as if they were numbers and are multiplied and divided. For this purpose the *entire* log must be positive or negative. In the latter case the *mantissa* as well as the characteristic must be negative. To make the mantissa of a log negative: (1) simply subtract it from the negative characteristic, or (2) subtract the log from 0, that is, from 10 − 10, 20 − 20, and so on, and place a minus sign on the difference.

Examples. Method (1):

$$16.9241 - 20 = \bar{4}.9241 = -3.0759.$$

Method (2):

(*a*)	(*b*)
20 − 20	10 − 10
16.9241 − 20	3.0782 − 10
−3.0759	−6.9218

This operation is necessary whenever negative logs are to be treated as numbers.

Problems

1. Evaluate the following expressions: (*a*) 0.06 log 0.2; (*b*) 0.03 log 0.0145; (*c*) 0.15 log 0.0024; (*d*) 4.0 log $\frac{3}{8}$. *Answers:* (*a*) -4.194×10^{-2}; (*b*) −0.055; (*c*) −0.0393; (*d*) −1.704.

2. Evaluate 0.03 log 0.75 − 0.02 log 0.80. *Ans.* -1.81×10^{-3}.

3. Evaluate 2 log 0.062 + 3 log 0.45. *Ans.* −3.4556.

CHAPTER 3

THE GASEOUS STATE

In chemical analysis gaseous reagents, such as H_2S, are frequently used. Mixtures of gases, for instance H_2S and H_2, CO_2 and CO, or admixtures of one or more gases with air, are encountered.

The molar concentration of a gas depends on three variables: pressure, temperature, and volume; and the interrelations of these variables must be understood. The behavior of gases at ordinary temperatures and pressures is described with close approximation by six principles, or "laws," of which two relate to mixtures. These six "laws" are known by the names of their discoverers: Boyle (1662), Charles (1787), Dalton (1802), Henry (1803), Avogadro (1811) and Graham (1833).

THE COMBINED GAS EQUATION

Boyle's law states that at a fixed temperature the volume of a confined mass of gas varies inversely as the pressure upon it.

$$V \propto \frac{1}{p} \ (T \text{ constant}), \text{ or} \tag{1}$$

$$V_1P_1 = V_2P_2 \tag{2}$$

Charles' law states that at constant pressure the volume of a confined mass of gas increases by 1/273.1 of its volume when heated 1°C. and decreases by the same fraction when cooled 1°C. If cooled 273.1° below 0°C, its volume should become that of the molecules themselves if the gas did not pass into the liquid or solid state before that temperature were reached and thus cease to be a gas. The absolute zero of temperature is therefore fixed at −273.1°C. This is the zero of the Absolute Scale of Temperature. In this scale T is the symbol for temperature while t indicates Centigrade temperature.

Charles' law may be expressed:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}, \text{ or} \tag{3}$$

$$V \propto T \ (P \text{ constant}). \tag{4}$$

Since $V \propto 1/P$ (1) and $V \propto T$ (4),

$$V \propto \frac{T}{P}$$

or, introducing a proportionality constant K,

$$PV = KT. \tag{5}$$

Avogadro's law makes possible evaluation of K in (5) for 1 g.mol of gas. The law may be stated in the following form. The molecular weight in grams of every pure gas occupies 22.412 liters at 0°C. (273.1°A) and at a pressure of 76 cm of mercury (1 atm.).

Substituting the Avogadro values, (5) becomes

$$1 \text{ atm.} \times 22.412 \text{ l/mol} = K \times 273.1°, \text{ and} \tag{6}$$

$$K = \frac{22.412 \text{ l atm.}}{273.1° \text{ mol}} = 0.082 \text{ l atm. per degree per mol,}$$

or 82 ml atm. per mol per degree. K is known as the molar gas constant and is usually symbolized by R.

$$PV = RT \text{ for 1 mol of gas, and}$$
$$PV = nRT \text{ for } n \text{ mols.} \tag{7}$$

The gas constant R is of the dimensions of work and is expressed in work units. It expresses the work done by a mol of gas in expanding against the weight of the atmosphere from 0 volume to 22.412 liters.

Since the density of mercury is 13.59 g/cm^3, 1 atm. equals 76 cm $\times$ 13.59 g/cm^3 = 1033 g/cm^2. Then R becomes

$$82 \text{ cm}^3 \times 1033 \text{ g/cm}^2 = 86400 \text{ g.cm per mole per degree.}$$

When a gas is compressed, the work done upon the gas appears as heat. When a compressed gas expands against the weight of the atmosphere, the work done takes heat from the gas which accordingly cools. Since the mechanical equivalent of heat is

$$1 \text{ calorie} = 42720 \text{ g.cm,}$$

$$R = \frac{84700 \text{ g.cm/mol degree}}{42720 \text{ g.cm/cal.}} = 1.98 \text{ cal. per mol per degree.}$$

When a current of electricity flows through a wire, the work done in overcoming the resistance of the wire appears as heat. Joule

(1841) found this to be 0.2387 cal./ohm × amperes² × sec. From Ohm's law, amp. = volt/ohm and since coulomb = amp. × sec.,

$$R = \frac{1.98 \text{ cal./mol degree}}{0.2387 \text{ cal./(volt} \times \text{coulomb)}}$$

$$= 8.316 \text{ volt} \times \text{coulomb per mol per degree.}$$

This electrical unit of R will appear later in a discussion of equilibrium in redox reactions.

We may now summarize the preceding paragraphs in the following statements.

Summary

Combination of the gas laws of Boyle, Charles, and Avogadro gives the general equation:

$$PV = nRT$$

where n is the number of mols of gas considered. The molar gas constant R is expressible in any of the various units of work.

$$\begin{aligned} R &= 84700 \text{ g} \times \text{cm per mol per degree} \\ &= 82 \quad \text{ml} \times \text{atm.} \quad \text{“ “ “ “ “} \\ &= 0.082 \text{ l} \times \text{atm.} \quad \text{“ “ “ “ “} \\ &= 1.98 \quad \text{cal.} \quad \text{“ “ “ “ “} \\ &= 8.316 \text{ volt} \times \text{coulomb per mol per degree} \end{aligned}$$

It is to be kept in mind that the gas laws are only approximations. Hydrogen and helium behave most nearly in accordance with them. In general the higher its liquifying temperature the less exactly does a gas obey the laws. Evidently all gases should obey the laws more nearly at high temperatures. For pressures not over 2 atm. and room temperatures, the general gas equation applies with an exactness sufficient for most purposes.

MIXTURES OF GASES

Dalton's law. In a mixture of gases which do not react with one another each gas exerts the pressure that it would exert if alone in the volume occupied by the mixture. Air is a mixture of N_2 and O_2 in the approximate proportions of 4 to 1. If the total pressure is 1 atm., the partial pressures are N_2, 0.8 atm.; and O_2, 0.2 atm. If a gas mixture 40% H_2, 30% CH_4, 20% CO, 2% CO_2, and 8% N_2 is under a total pressure of 1 atm., the partial pressures are: H_2, 0.4 atm.; CH_4, 0.3 atm.; CO, 0.2 atm.; CO_2, 0.02 atm.; and N_2, 0.08 atm.

Henry's law. The solubility of a gas in water (or other liquids) is proportional to its partial pressure. If a liter of water dissolves x ml of pure N_2 and y ml of pure O_2, it will dissolve (approximately) $0.8x$ ml of N_2 and $0.2y$ ml of O_2 when saturated with air at the same temp.

Graham's law. The velocity with which a gas diffuses is inversely proportional to the square root of its density, that is, $V \propto 1/d^{0.5}$ or, if two gases are compared, $V_1 d_1^{0.5} = V_2 d_2^{0.5}$.

GAS	DENSITY (AIR = 1)	$\frac{1}{\text{DENSITY}^{0.5}}$	V (AIR = 1)
H_2	0.069	3.78	3.83
CH_4	0.559	1.34	1.34
N_2	0.971	1.015	1.014
O_2	1.1056	0.951	0.950
CO_2	1.529	0.809	0.812

Since the molecular weight of a gas is proportional to its density, $VM^{0.5} = V_1 M_1^{0.5}$. If V is the velocity of diffusion of a gas of known molecular weight M (say $O_2 = 32$), and V_1 is the measured velocity of diffusion of another gas of unknown molecular weight, the latter M_1 can be calculated. This principle has been used to effect detectable separation of isotopes (for example, ${}_{17}Cl^{35}$ and ${}_{17}Cl^{37}$ or the isotopes of Hg, ${}_{80}Hg^{196}$ to ${}_{80}Hg^{204}$). The lighter molecules of Cl_2 ($M_1 = 70$) would diffuse more rapidly and the residual gas would be more dense than the original mixture of isotopes.

APPLICATIONS OF THE GAS LAWS

The General Gas Equation is convenient for calculations of change of volume with change of pressure or temperature, of molecular weights from density, of volume of gas required to react. Since N (mol) = g/(g per mol), the equation may contain five variables. If any four of these are given, or experimentally measurable, the fifth variable can be calculated.

Example 1. What is the molecular weight of a gas 140 ml of which collected over water at 21.4°C, weighs 2.2 g; barometer, 742 mm? Aqueous tension (vapor pressure) of water at 21.4° = 19.1 mm. (Consider Dalton's law.)

$$\frac{(742 - 19.1)\text{ mm}}{760\text{ mm/atm.}} \times 140\text{ ml} = \frac{2.2\text{ g}}{M\text{ g/mol}} \times 82\frac{\text{ml atm.}}{\text{mol degree}} \times 294.4^\circ$$

$$M = 2.2\text{ g} \times 82\frac{\text{ml atm.}}{\text{mol degree}} \times 294.4^\circ \times 760\frac{\text{mm}}{\text{atm.}} \times \frac{1}{722.9\text{ mm}} \times \frac{1}{140\text{ ml}}$$

$$M = 40\text{ g/mol.}$$

Example 2. How many ml of H_2S containing 10% H_2 and 5% air, bubbled through water at 25°C, will be required to precipitate 5 mg of Cu^{++} (63.57) as $Cu(HS)_2$? (Barometer, 734 mm, aqueous tension at 25.0° = 23.7 mm.)

$$Cu^{++} + 2H_2S = Cu(HS)_2 + 2H^+$$

$$\text{Mol } Cu^{++} = \frac{0.005\text{ g}}{63.57\text{ g/mol}}$$

Since 1 mol Cu^{++} reacts with 2 mols of H_2S and since the partial pressure of the H_2S is [0.85 (734–23.7) mm]/(760 mm/atm.), we may write

$$\frac{0.85\ (734 - 23.7)\text{ mm}}{760\text{ mm/atm.}} \times y\text{ ml} = \frac{2 \times 0.005\text{ g}}{63.57\text{ g/mol}} \times \frac{82\text{ ml atm.}}{\text{mol degree}} \times 298^\circ.$$

Then

$$y = \frac{0.01 \times 82 \times 298 \times 760}{63.57 \times 0.85\ (734 - 23.7)} = 4.84\text{ ml.}$$

Problems

(Pay careful attention to units)

1. What volume should 10 mg of dry NH_3 occupy at 740 mm and 25°C? *Ans.* 14.76 ml.

2. What should be the molecular weight of a dry gas of which 1.2 g occupies 1067 ml at 738 mm and 22°C? *Ans.* 28.4 g/mol.

3. At room temperature and atmospheric pressure the solubility of H_2S in water may be taken as 0.1 mol/1. About how many ml of the dry gas should be required to saturate 10 ml of water at 23°C if the barometer is at 742 mm? *Ans.* 25 ml.

4. What would be the dry volume at S.T.P. (0°C and 760 mm) of H_2S which, collected over water, measured 102 ml at 25°C and 736 mm? (At 25° the aqueous tension = 23.7 mm.) *Ans.* 87.6 ml.

5. How many m.mols of H_2S would be the 102 ml measured? *Ans.* 3.91 m.mol.

6. With how many mg of Ag^+ would the H_2S react to form AgHS? *Ans.* 422 mg.

7. How many ml of pure H_2S stored over H_2O at 740 mm and 23°C should be required to react with 5 mg of Bi^{+3} (209) to form $Bi(HS)_3$? (Aqueous tension at 23° = 21.1 mm.) *Ans.* 1.9 ml. (*Hint.* Calculate mol fraction of Bi^{+3} in 5 mg and fraction of a mol [S.T.P.] of H_2S required to react with it. Then calculate volume occupied under given conditions by this H_2S.)

8. When 1 ml of 1.5 *M* HCO_3^- is exactly neutralized with acid, what mol fraction of CO_2 should be formed? At 25° and 760 mm 1 volume of water dissolves 0.759 volume of *dry* CO_2. If, when 1 ml of 1.5 *M* HCO_3^- was exactly neutralized its volume became 1.4 ml and its temperature 25°C, how many ml of CO_2 should remain dissolved in it? (Barometer, 736 mm; aqueous tension at 25° = 23.7 mm.) *Ans.* 1 ml.

9. If, in problem 8, the escaping CO_2 were caught, at 25°C, over water which had been previously saturated with CO_2, how many ml would be obtained? *Ans.* 38.1 ml.

TABLE 2

THE PERIODIC ARRANGEMENT OF THE ELEMENTS

PERIOD	GROUP I	II	III	IV	V	VI	VII	VIII
1 (2)							$_{1}$H	$_{2}$He
2 (8)	$_{3}$Li	$_{4}$Be	$_{5}$B	$_{6}$C	$_{7}$N	$_{8}$O	$_{9}$F	$_{10}$Ne
3 (8)	$_{11}$Na	$_{12}$Mg	$_{13}$Al	$_{14}$Si	$_{15}$P	$_{16}$S	$_{17}$Cl	$_{18}$A
	FAMILY							
	A B	A B	A B	A B	A B	A B	A B	A B
4 (18)	$_{19}$K $_{29}$Cu	$_{20}$Ca $_{30}$Zn	$_{21}$Sc $_{31}$Ga	$_{22}$Ti $_{32}$Ge	$_{23}$V $_{33}$As	$_{24}$Cr $_{34}$Se	$_{25}$Mn $_{35}$Br	$_{26}$Fe$_{27}$Co$_{28}$Ni $_{36}$Kr
5 (18)	$_{37}$Rb $_{47}$Ag	$_{38}$Sr $_{48}$Cd	$_{39}$Y $_{49}$In	$_{40}$Zr $_{50}$Sn	$_{41}$Cb $_{51}$Sb	$_{42}$Mo $_{52}$Te	$_{43}$(Ma) $_{53}$I	$_{44}$Ru$_{45}$Rh$_{46}$Pd $_{54}$Xe
6 (32)	$_{55}$Cs $_{79}$Au	$_{56}$Ba $_{80}$Hg	$_{57}$La (and $_{58-71}$ lanthanides) $_{81}$Tl	$_{72}$Hf $_{82}$Pb	$_{73}$Ta $_{83}$Bi	$_{74}$W $_{84}$Po	$_{75}$Re $_{85}$(Am)	$_{76}$Os$_{77}$Ir$_{78}$Pt $_{86}$Rn
7 (inc.)	$_{87}$(Va)	$_{88}$Ra	$_{89}$Ac	$_{90}$Th	$_{91}$Pa	$_{92}$U		

58–71 THE LANTHANIDES

Group III, Family A

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
$_{57}$La	$_{58}$Ce	$_{59}$Pr	$_{60}$Nd	$_{61}$(Il)	$_{62}$Sm	$_{63}$Eu	$_{64}$Gd
$_{64}$Gd	$_{65}$Tb	$_{66}$Dy	$_{67}$Ho	$_{68}$Er	$_{69}$Tm	$_{70}$Yb	$_{71}$Lu

THE PERIODIC TABLE

The periodic arrangement of the elements shown in Table 2 differs in some important respects from the tables in most elementary texts. It seems desirable to call attention to these departures from tradition and to state the reasons for them. Of the two most frequently used periodic arrangements, that of Bohr has the advantage of correct scientific basis and the disadvantage that analogies of chemical properties are less quickly apparent to the beginner than they are in a Mendeleef table. In Table 2 the general arrangement is that of Mendeleef but modified to accord with modern discoveries, particularly concerning location of the inert gases in the periodic arrangement.

1. The inert gases. These elements *end* periods and immediately follow the halogens of Group VII. Placing of them in a Group 0 at the left of the Mendeleef table was done before atomic structure became determinable. The sole reason for thus locating them was their chemical inertness (zero valence) which, at that time, was unexplainable. At the present time this property is understood to be the consequence of the *completion* of an extremely symmetrical and stable outermost energy level of 8 electrons, which brings them into Group VIII immediately following the halogens of Group VII. This location follows logically Paneth's rule for formation of volatile hydrides. Thus in Period 4 we have GeH_4, AsH_3, SeH_2, BrH_1 and KrH_0. Location of these elements in Group VIII with the three triads of ultrametallic elements does not imply a relation of properties. The triads of the "A" family are in the *middle* of periods which later will be completed at the inert gas.

2. Hydrogen. Contrary to common practice, H is placed only in Group VII. The hydrogen nucleus, H^+ (the proton), can have, outside of vacuum tubes, little more chance for independent existence than the electron, e^-. On the contrary, electrolysis of salt-like hydrides, such as LiH and CaH_2, leaves no doubt of the independent existence of helium-like H^-. The analogy to formation of neon-like F^- and argon-like Cl^- is obvious.

3. Atomic weights. These have no place in a periodic table. Periodicity of properties is based upon *order number* and not at all upon atomic weight as Mendeleef and Lothar Meyer assumed. Most of the elements are composed of pleiads of isotopes, presumably all of which have the same number of protons but a varying number of neutrons and differ in their atomic weights.

4. Order numbers. In accordance with present usage in writing equations for atomic transformations, these have been written as presubscripts.

5. Elements claimed but practically unknown. The symbols proposed for elements 43, 61, 85, and 87 appear in parentheses. It is to be noted that none of these elements has been obtained in amount sufficient for determination of chemical properties. Claims for elements 43 and 61 depend upon identification of X-ray spectra; those for 85 and 87 upon a "magneto-optic" method the validity of which has not been universally accepted. These two elements should be short-lived radioactive disintegration products of $_{89}Ac$.

6. The triads of Group VIII-A and the rare earth pleiad of Group III-A. In Period 4 at $_{20}Ca$ the probable distribution among the energy levels is:

Level	Electrons
1	2
2	8
3	8
4	2

Pauli's principle permits a maximum of 18 electrons in level 3. At $_{21}Sc$ the added electron has less, but only very slightly less, energy in level 3 than it would have in level 4. The same holds for the next added 8 electrons ending

with $_{29}$Cu. Since the energies in level 3 differ very slightly from those in level 4, chemical forces readily produce shifts of these electrons from one level to the other and as a result *variable valence* characterizes these "transition elements" $_{22}$Ti to $_{29}$Cu. At $_{30}$Zn the 18 electrons of level 3 have become sufficiently stabilized so that they are not thereafter disrupted by chemical forces.

The next added electrons build up level 4 from 2 at Zn to 8 at $_{36}$Kr. Considering the great ease with which electrons are shifted between levels 3 and 4, while the former is filling from 8 to 18 electrons, it is not surprising that when it is nearly filled several successive elements should possess so nearly the same atomic and ionic radii, and hence so nearly identical chemical properties, that the group as a whole fills but *one* place in the table. For this reason the triad Fe to Ni is assigned as a whole to Group VIII-A, and the triads Ru to Pd in Period 5 and Os to Pt in Period 6 are assigned *single* VIII-A positions.

At $_{56}$Ba the arrangement in the energy levels is apparently as follows:

Level	Electrons
1	2
2	8
3	18
4	18
5	8
6	2

Levels 1, 2, and 3 contain their maximum possible electrons. But Pauli's principle permits 32 electrons in level 4. Apparently the added electron for $_{57}$La has less energy in level 6 than it would have in level 4 and La has *three* valence electrons. The next added 14 electrons, however, have less energy in level 4, and this level is then filled from 18 to its maximum of 32. Here the level being completed is far below the valence electrons and scarcely affected by chemical forces. As a result these 14 rare earths show a valence of 3 and properties so nearly identical as to make them separable from each other and from La only with great difficulty. Together with La they constitute a pleiad of 15 elements occupying a single III-A space in the Mendeleef table. This occurrence of pleiads occupying single spaces in the table in Groups VIII-A and III-A is comparable to the pleiads of isotopes, having the same electron configuration but different nuclei, which characterize most of the single elements.

7. The "lanthanide contraction." In formation of the rare earths, a proton enters the nucleus for each added electron. Because the added electrons enter a level far below the valence electrons, the increased nuclear charge exerts an increased coulomb attraction upon these electrons in level 4. This results in a continuous *shrinkage* of the atomic radius. According to Goldschmidt, the atomic radii in Ångstrom units (1Å = 10^{-8} cm) decrease from La 1.22 and Ce 1.18 to Lu 0.99. As a result $_{39}$Y 1.06 and $_{67}$Ho 1.07 have nearly identical chemical properties and yttrium behaves chemically as if it were a rare earth.

This contraction, of course, affects all elements after $_{71}$Lu. As a result, $_{72}$Hf 1.66 Å and $_{40}$Zr 1.62, $_{73}$Ta 1.44 and $_{41}$Cb 1.43, and $_{79}$Au 1.441 and $_{47}$Ag 1.442 display remarkable similarity of properties.

8. Periodicity in the lanthanides.[a] Interesting evidences of a periodicity among the 14 rare earths are furnished by colors of corresponding salts, magnetism, and anomalous valences. If $_{57}$La be included, and $_{64}$Gd be placed with it in a subgroup (1) as well as in subgroup (8), the eight subgroups shown below Table 2 are distinguishable. The pairs of elements in each subgroup show resemblances to each other and progressive differences from the preceding and succeeding subgroups.

[a] Pearce and Selwood, J. Chem. Ed., 13, 224–230 (1936).

CHAPTER 4

STRUCTURE OF MATTER

Modern methods of investigation have made practically certain that all forms of matter consist of charges of electricity. The elementary units of matter appear to be *protons, neutrons, electrons,* and *positrons.*

DEFINITIONS

Electron (e^-) is the unit of negative charge, 4.77×10^{-10} electrostatic units (e.s.u.). Apparent mass is about $\frac{1}{1840}$ that of the proton.

Proton (p^+ or H^+) is a particle having a mass of 1.66×10^{-24} g and a positive charge equal to the negative charge of the electron. It is identical with the *nucleus* of the hydrogen atom, H^+, and probably formed by union of a neutron and a positron.

Atom is a neutral particle consisting of a positive nucleus surrounded by electrons.

Nucleus is an assembly of protons and neutrons condensed into an exceedingly minute volume and having practically all the mass of the atom.

Neutron (n°) is a particle having nearly the mass of the proton but carrying no charge. It was discovered by Chadwick in 1933.

Positron (e^+) is the unit charge of positive electricity, the positive electron. It was discovered by Anderson in 1932. Protons are related to neutrons by the equations:

$$n^\circ + e^+ = p^+ + \text{energy}$$
$$n^\circ = p^+ + e^- + \text{energy}.$$

Atomic number is the *order* number of the elements from ${}_1H$ to ${}_{92}U$. Each element has 1 more proton in its nucleus and one more electron than the element immediately preceding it. The atomic number is often written as a subscript to the *left* of the chemical symbol of the atom. Chemical properties are determined by order number and not by atomic weight.

Atomic weight is chiefly the sum of the masses of the protons and neutrons in the nucleus of the atom. It is written as a superscript to the chemical symbol of the element. ${}_{11}Na^{23}$ is read: "Sodium, atomic number 11, atomic weight 23." Since atoms are electrically neutral, they must have as many protons in the nucleus as electrons outside the nucleus.

$$ {}_{11}Na^{23} = 11p^+ + 12n^\circ + 11e^- $$

Isotopes are atoms of the *same element* having the same number of protons in the nucleus but different numbers of neutrons. For example:

$${}_8O^{16} = 8p^+ + 8n^\circ; \qquad {}_8O^{17} = 8p^+ + 9n^\circ; \qquad {}_8O^{18} = 8p^+ + 10n^\circ.$$

The majority of the 92 elements are mixtures of isotopes. Tin has at least 11 isotopes, cadmium and mercury at least 9 each, Pb at least 8. Since all the isotopes of an element have the same number and same arrangement of electrons, they all have identical chemical properties and are inseparable by chemical reactions.

ENERGY LEVELS OF ELECTRONS

Electrons in the atom must be considered as in motion with a speed approximating that of light. By virtue of this motion they possess energy. Modern atomic physics has shown that as many as five components may make up the total energy of an electron. Chief of these is the charge of the nucleus and the distance of the electron from it. Electrons formerly were pictured as moving in various paths about the nucleus. One component of their energies would depend on the circular or elliptical shape of the orbits. These "orbits" are now generally referred to as *eigenfunctions*, since the position of the electron is not determined by ordinary laws of mechanics as are the motions of the planets. The "orbit" is the most probable position of the electron in a rather wide path. A moving charge acts as a magnet. Electrons have to be considered as spinning on their axes. When all these components are taken into account, it appears that in an atom *no two* electrons can have *all five* of their energy components identical. They may have four identical but the fifth component must be different. This deduction, known as Pauli's principle, fixes the maximum number of electrons that can be in various principal *energy levels*. Roughly this may be thought of as the maximum number of electrons that can be at the same average distance from the nucleus.

Principal energy levels are designated by numbers 1, 2, 3—but more commonly by letters, *K*, *L*, *M*—first employed by X-ray spectrographers. The maximum number of electrons permitted by Pauli's principle in each principal level is as follows:

Level (Spectroscopic designation)	1	2	3	4	5	6
" (X-ray ")	*K*	*L*	*M*	*N*	*O*	*P*
Maximum number of electrons	2	8	18	32	50	72

Relation of chemical properties to energy levels. The numbers of electrons in the various energy levels of the inert gases are:

	K	*L*	*M*	*N*	*O*	*P*
$_{2}$He	2					
$_{10}$Ne	2	8				
$_{18}$A	2	8	8			
$_{36}$Kr	2	8	18	8		
$_{54}$Xe	2	8	18	18	8	
$_{86}$Rn	2	8	18	32	18	8

When an energy level has once acquired its maximum number of electrons, the total energy of these electrons is at its *minimum* and hence the stability of the group is at its *maximum*. Such maximal stability cannot be disrupted by chemical forces. When level *K* has acquired at He its maximum of 2 electrons, this level persists unchanged and forms part of each succeeding atom. The same is true for the levels *L*, *M*, *N*. Levels *O* and *P* are far from being completely filled at the last element, $_{92}$U.

The highly symmetrical group of 8 electrons which in the inert gases appears in the incomplete level *M* at A, *N* at Kr, *O* at Xe, and *P* at Rn is also too stable to be disrupted by chemical forces, and as a result these elements form no chemical compounds.

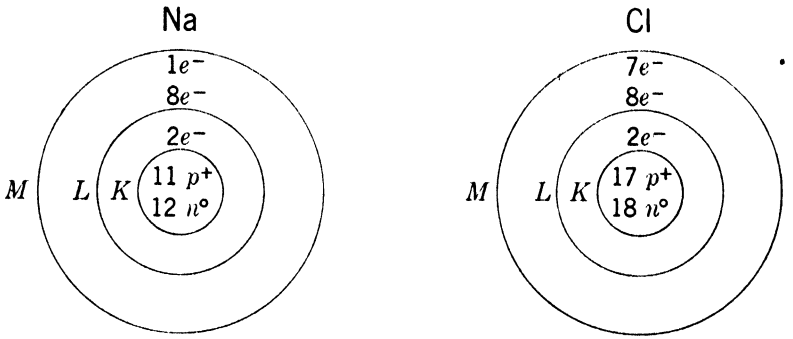
The incomplete group of 18 electrons in level *N* first becomes stable at $_{48}$Cd but later begins at $_{58}$Ce to fill up to 32.

FORMATION OF IONS

Electrons tend to locate themselves where their energy is least. Since their energy is greater in incompleted levels, they will wherever possible tend to form completely filled, and therefore stable, outer levels. This can be accomplished in two ways. (1) An atom which has only a few electrons outside of a complete level may give up these electrons to another atom which has a nearly completed level. (2) An atom, by acquiring a *share* in electrons of another atom, can complete or more nearly complete its incomplete level and thus

become more stable. Method (1) leads to formation of *ions* consisting of a *single* atom, such as Na^+, Mg^{++}, Cl^-, $S^=$. Method (2) leads to formation of *ions* containing more than one element, such as $SO_4^=$ or $Cu(NH_3)_4^{++}$, and to molecules.

Monatomic ions. If an atom which has a single electron in its outermost level, for example $_{11}Na^{23}$, approaches closely enough to an atom, such as $_{17}Cl^{35}$, which needs only one electron to complete its stable group of 8 (octet), the stronger positive charge of the Cl^- nucleus, 17 units as compared with 11 units, might pull away the



electron from Na and absorb it. In the completed *M* level of Cl^- this electron would have less energy than it did in the incomplete *M* level of Na. The coulomb force of attraction of unlike charges and repulsion of like charges is equal to the product of the magnitudes of the charges divided by the square of the distance between them.

$$F = \frac{e \times e_1}{d^2}$$

Evidently the force with which the Na nucleus with its 11 protons attracts this eleventh electron will depend mostly upon the distance between them, although it will be weakened by the electrons in levels *K* and *L*, which exert a repulsive force on the outer eleventh electron. To remove the eleventh electron of Na will *require* work (expenditure of energy). The entrance of this electron into the Cl atom will *liberate* energy. If the liberated energy (together with the energy liberated by another reaction, such as attraction of the ions into a molecule or hydration of the ions in solution) exceeds that required to remove the electron, the transfer can be accomplished. In fact, the reaction

$$\underset{(gas)}{Na^\circ} + \underset{(gas)}{Cl^\circ} = \underset{(gas)}{NaCl}$$

does take place. Apparently an atom will lose an outer electron more easily the larger and heavier it is, and will gain an electron more readily the smaller it is. Cs > Rb > K > Na > Li and I > Br > Cl > F. In spite of the greater charge of the Cs nucleus, its single outermost electron is much more distant and the attraction of the nucleus is "screened off" by more interposed electrons. Likewise, the electron entering F will approach much closer to the nucleus than if it entered Cl or Br and hence will lose much more energy. The energy relations permit any of the four halogens (periodic Group VII) to take electrons from any of the five alkali metals (Group I).

The work required to remove *two* outer electrons is much greater than twice that required to remove one. For example, in Mg

NUCLEUS	ENERGY LEVELS		
	K	L	M
$12p^+$	$2e^-$	$8e^-$	$2e^-$
$12n^\circ$			

if the first electron of level M has been removed, Mg^+ results; and the removal of the second requires additional work against the attractive force of the positive charge on the Mg^+. If the receiving element requires two electrons to complete its octet, as in O or S (Group VI),

NUCLEUS			NUCLEUS			
$8p^+$	K	L	$16p^+$	K	L	M
$8n^\circ$	2	6	$16n^\circ$	2	8	6,

the second electron entering ${}_8O^-$ or ${}_{16}S^-$ is repelled by the charge already acquired by taking up the first electron of Mg, and its entrance liberates much less energy than did the first. X rays show that crystals of MgO and MgS actually consist of Mg^{++} and O^- or S^-. These can be formed only in the absence of water because the reactions

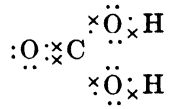
$$H_2O + O^- = 2OH^- \text{ and}$$
$$H_2O + S^- = 2SH^-$$

liberate more energy and hence give more stable compounds than does the formation of O^- and S^-.

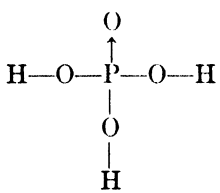
Elements of Group III. These elements appear to form compounds usually by sharing. The independent existence of tervalent

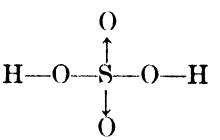
ions, such as B^{+3}, Al^{+3}, and the like, is at present a disputed matter.

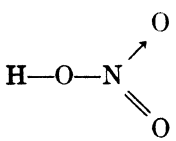
Elements of Groups IV to VII. These elements combine by sharing electrons with oxygen or water to form acids or anions, such as

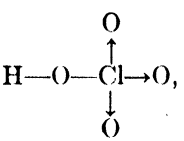


in which each H has a *share* in two electrons and carbon and oxygen atoms have completed their octets. Similarly are formed









in which the H—O oxygen atoms complete their octets by sharing one hydrogen electron and one electron of the central atom.[1] In HNO_3, one oxygen is bound to nitrogen by a single electron pair, the other by a double pair. In aqueous solution, water molecules,



which, because of the two unshared pairs of electrons in the oxygen atom, act like a magnetized rod and have a positive and a negative end, can pull away the proton from H ⁘ O - to form H_3O^+, hydronium ion. There remains in the solution NO_3^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-.

[1] In the above structural formulas, a single line denotes a normal covalent bond, that is, a shared pair of electrons (⁘) each of which is contributed by a different one of the bonded atoms; a double line denotes two such shared pairs (⁘); an arrow directed toward the acceptor atom denotes a dative covalent bond, both electrons of which are donated by the atom away from which the arrow points. This convention will be used hereafter in such formulas.

THE STRUCTURE OF SOLID COMPOUNDS: ELECTROVALENCY AND COVALENCY

It has been shown that loss of electrons can produce monatomic cations and that gain of electrons can produce monatomic anions. Sharing of electrons (formation of oppositely spinning pairs) can lead to formation of polyatomic ions and of molecules.

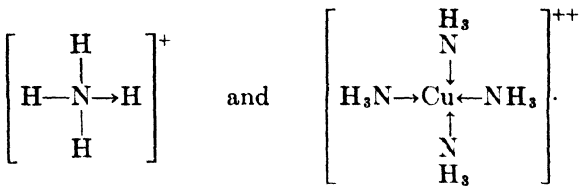
Modern investigation of solid substances by X rays reveals that, in general, two kinds of arrangement of the building units are distinguishable. The orderly arrangement of the components of a crystal is called a lattice; some substances have *ionic* lattices, others *molecular* lattices. The physical properties of the two lattices are very different, as will be shown presently. We have seen that in ions the atoms generally have completed outer levels of electrons. As a result these ions possess more or less the stability and inertness of the inert gases and can have independent existence. They differ from the inert atoms, however, in having one or more units of electrical charge *diffused uniformly* over the surface of the ion. If oppositely charged ions, for example Na^+ and Cl^-, are in solution in water, they are *relatively* too far apart for the diffused charges to attract each other effectively. As a result the ions exist independently and show little tendency to combine. If the water is evaporated off, the oppositely charged particles approach so nearly that the charges can draw the ions into approximate contact. Since the charge is uniformly diffused about the ions and not concentrated at a point, as many anions as space permits will gather about each cation.

In general, anions are considerably larger than cations. For instance, in a crystal of Na^+Cl^- each sodium ion is surrounded by six equidistant chloride ions, and each chloride ion is surrounded by six equidistant sodium ions. In the lattice of Cs^+Cl^- there is room for eight chloride ions around the considerably larger Cs^+ ion. X rays show that polyatomic cations and anions enter these ionic lattices as units. For instance, in a crystal of $Ca^{++}CO_3^=$ or one of $Na^+NO_3^-$, $CO_3^=$ and NO_3^- are arranged as *groups* about the central ion just as if they were single atoms. These ionic lattices are characteristic of the *true salts*.

Covalency. Sidgwick[2] distinguished between *normal* covalency in which each atom contributed one electron to the bond and *coordinate*, now frequently called *dative*, covalency in which one

[2] *The Electronic Theory of Valency*, Oxford University Press, 1927. *The Covalent Link in Chemistry*, Cornell University Press, 1933.

of the bonded atoms furnished *both* electrons for the bond as in



He pointed out that complex-forming molecules and ions, such as NH_3, H_2O, CN^-, and CO, invariably had pairs of free electrons which might be shared with other atoms. He called such atoms or ions *donors*. Atoms or ions which could share electron pairs donated by other ions were called *acceptors*. Sidgwick saw a cause for this sharing of electron pairs in a probable tendency of atoms with unfilled energy levels to complete these levels and so acquire the stable conformation of the next following inert gas. The stability of complex ions and molecules in many cases does lend plausibility to this view. For example, in $[Fe(CN)_6]^{-4}$ and $[Co(CN)_6]^{-3}$ the ions $_{24}Fe^{++}$ and $_{24}Co^{+3}$, by gaining a share in 12 electrons donated by 6 CN^-, complete their energy levels to the stable conformation of $_{36}Kr$. $[Fe(CN)_6]^{-3}$ and $[Co(CN)_6]^{-4}$ with $_{23}Fe^{+3}$ and $_{25}Co^{++}$ are far less stable complexes. $_{26}Fe(CO)_5$ and $_{28}Ni(CO)_4$ are stable, but carbonyls of $_{27}Co$ contain two or more Co atoms.

L. Pauling,[3] by application of wave mechanics, derived for these and other complex ions structures having the octahedral and tetrahedral or planar spatial arrangements of the 6 or 4 coordinated groups about the central ion or atom which Werner had deduced from their chemical and optical behavior. No hypotheses as to the exact nature of the bonding forces are involved.

Sidgwick's theory has been useful in that it permits visualization of the structure of complex ions and molecules. The weight of recent evidence seems to be against its validity at least as far as the mechanics of valence bond formation is concerned. It is by no means certain that atoms are actually held together by electron pairs. It may be that only coulombic fields of force are involved. The details of atomic bonding are far from finally settled, and frequent shifts of viewpoint are to be expected for many years. Whatever the actual mechanism of bond formation may be, it is often convenient in writing formulas to use Sidgwick's symbol for dative covalency.

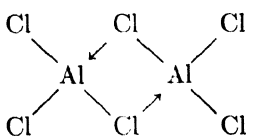
[3] J. Am. Chem. Soc., **53**, 1367, 3225 (1931).

Since in the covalent bond the bonding force is concentrated nearly to a point, atoms are drawn much nearer together so that their electron levels actually interpenetrate. Covalent compounds are shown by X rays to have *molecular* lattices in which the structural units are *molecules*, held together in three dimensions by shared pairs of electrons. Compounds having molecular lattices are likely to be insoluble in water. It is now certain that a large proportion of the compounds formerly considered to be salts are actually pure covalent compounds, for example, As_4S_6.

The following tabulation shows some of the characteristic differences of properties between electrovalent and covalent compounds.

ELECTROVALENT	NORMAL COVALENT
True salts.	Molecular compounds.
High melting and boiling point.	Low melting and boiling point; frequently liquids or gases at 25°.
Good conductors of electricity when fused or dissolved.	Nonconductors.
Usually hard.	Usually soft in solid state.
Ionic lattices.	Molecular lattices.

An interesting example of the above differences is shown by aluminum chloride, which sublimes at 183° and does not conduct an electric current when fused. In contrast, $Mg^{++}Cl_2^-$, a true salt, melts at 712°, boils at 1412°, and in fused condition conducts a current. Both the molecular weight of the vapor and X rays show that anhydrous $AlCl_3$ has a doubled formula. Sidgwick suggested that a structure such as



would be in accord with these properties. In this formulation each Al atom forms covalent (shared pair) bonds with three Cl atoms and acquires a share in a pair of electrons *donated* by a fourth Cl atom. All eight of the atoms have acquired, by sharing, complete octets (inert gas configuration). When dissolved in water, Al_2Cl_6 conducts readily, but this is because the Al^{+3} ion acquires a share in six electron pairs donated by water molecules so that the cation is now

$[Al(H_2O)_6]^{+3}$. The six Cl atoms retain the electrons that, in the solid, were shared with the two Al atoms and become ions. When crystallized from water, the salt $[Al(H_2O)_6]^{+3}Cl_3^-$ is formed. Like Al_2Cl_6, the fused anhydrous chlorides of +3 chromium and iron, Fe_2Cl_6 and Cr_2Cl_6, are nonconducting and must be covalent. In water they form conducting solutions, resulting from formation of $[Cr(H_2O)_6]^{+3}$ and $[Fe(H_2O)_6]^{+3}$.

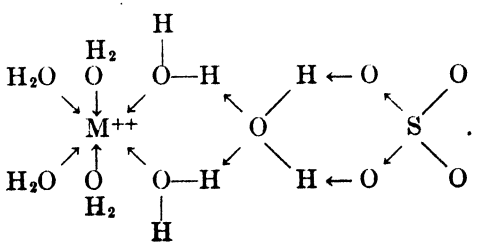
In the following table

	(1)				(2)	
Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
K	Ca	Sc	Ge	As	Se	Br
Rb	Sr		Sn	Sb	Te	I
Cs	Ba		Pb	Bi		

elements to the left of line (1) form monatomic cations; elements to the right of line (2) can form monatomic anions. Elements between the two lines tend strongly to form covalent compounds.

Hydrated ions. Except halides of alkali metal ions, most true salts have water of crystallization (for example, $Ca(NO_3)_2 \cdot 4H_2O$, $MgBr_2 \cdot 6H_2O$, $MnSiF_6 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$. X-ray examination of the crystals shows that water is coordinated to the cation with which it forms a complex ion, which enters the crystal lattice as a unit.

Vitriols and alums. Two particularly interesting classes of hydrated ions are known as vitriols and alums. Vitriols are heptahydrated monoclinic sulfates which are formed by the bivalent ions of Cr, Mn, Fe, Co, and Ni and also by Mg and Zn. The general formula is $M''SO_4 \cdot 7H_2O$. Although commonly called "blue vitriol," $CuSO_4 \cdot 5H_2O$ is not a true vitriol. Cadmium sulfate crystallizes ordinarily as $3CdSO_4 \cdot 8H_2O$. If a crystal of a less soluble vitriol is placed in a saturated solution of either $CuSO_4$ or $CdSO_4$, $CuSO_4 \cdot 7H_2O$ or $CdSO_4 \cdot 7H_2O$ will grow on the crystal as true vitriols. X rays show that the structure of the vitriols corresponds to $M''(H_2O)_6 \cdot H_2O \cdot SO_4$, linked as follows:



The H ← O bonds of the seventh H_2O are rather weak. In consequence, when the vitriol crystal is dissolved in water, they are further weakened by the approach of the positive dipole end (H) of solvent water molecules, and the bonds are easily ruptured. The solution will contain $Fe(H_2O)_6^{++}$ and $SO_4^{=}$, the latter associated more or less with water molecules.

The term alum is applied to double sulfates of a univalent and a tervalent cation with 12 molecules of water of crystallization. The general formula is $M'M'''(SO_4)_2 \cdot 12H_2O$. These salts crystallize very readily in octahedrons. M' can be Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Cu^+, Ag^+, and Tl^+. M''' can be Al^{+3}, Ti^{+3}, V^{+3}, Cr^{+3}, Mn^{+3}, Fe^{+3}, Co^{+3}, Ga^{+3}, In^{+3}, Tl^{+3}, Rh^{+3}, or Ir^{+3}. The class name comes from the best known member of the series, potassium aluminum alum, $KAl(SO_4)_2 \cdot 12H_2O$.

The structure of the alums has only recently been determined with any great probability. Results for $KAl(SO_4)_2 \cdot 12H_2O$ make certain a central ion, $Al(H_2O)_6^{+3}$, in which the water molecules are located at the corners of a regular octahedron having Al at its center. The remaining six waters are outside this core, possibly very loosely bonded to K^+, their distance from which, 2.46 Å, is rather large.[4] Four of them may be loosely bonded to the two $SO_4^{=}$ as in vitriol above.

COMPLEX IONS

In general, any ion which is composed of more than one element is complex. This term, however, is usually applied to ions which consist of a metal ion to which are bound covalently neutral molecules such as H_2O, NH_3, CO, NO or anions such as NO_2^-, halides, CN^-, NCS^-, $CO_3^{=}$, $C_2O_4^{=}$ and some others. Hundreds of compounds containing such complex cations and anions have been long known. They were completely unexplainable by the old ideas of valence. The nature of such compounds was first made clear by Alfred Werner (1866–1919). Werner observed that cations most frequently add either four or six molecules of water and, if they add NH_3, either four or six molecules of this substance. After many years of experimental work he was able to prove convincingly that in such complex ions, four added molecules must be thought of as situated usually at the corners of a regular tetrahedron[5] and six

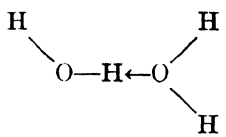
[4] Å is the symbol for the Ångstrom unit, 10^{-8} cm. Atomic distances are expressed as multiples of this unit.

[5] X rays show a planar structure for $[Cu(NH_3)_4]^{++}$, $[Ni(CN)_4]^{=}$, $Cl_2Pt(NH_3)_2$, and a few other complexes.

added molecules as located at the corners of a regular octahedron. He was the first to introduce the term *coordination number* as a property of atoms. By this term was meant the number of molecules or ions that could be linked by covalent bonds to a central atom or ion. At the present time the coordination number of an atom is considered one of its most important properties.

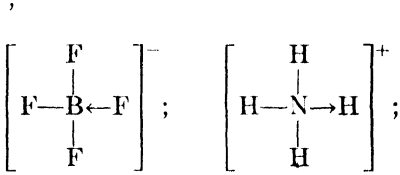
The presently accepted *maximum coordination numbers* of atoms and ions are as follows:

Two. Hydrogen only. Examples: $[F—H\leftarrow F]^-$;



which shows how bicovalent hydrogen binds water molecules in ice.

Four. Elements of the first period of eight, ${}_3Li$ to ${}_{10}Ne$. Examples: $Be(H_2O)_4^{++}$;



and $[OBe_4(AcO)_6]$. The latter is an easily sublimed, completely covalent molecule in which the four Be atoms are at the corners of a tetrahedron having the oxygen atom at its center. The six acetate ions are along the edges of the tetrahedron, each Be being attached to three acetate ions.

Six. Elements of the second short period, ${}_{11}Na$ to ${}_{18}A$, and of the first long period, ${}_{19}K$ to ${}_{36}Kr$. Examples: $Mg(H_2O)_6^{++}$, $[AlF_6]^{-3}$, $[Fe(CN)_6]^{-4}$, $[Co(NH_3)_6]^{++}$, $[Co(NH_3)_6]^{+3}$, and many others.

Eight. The remaining elements, ${}_{37}Rb$ to ${}_{92}U$. Examples: OsF_8, $[Mo(CN)_8]^{-4}$, $[W(CN)_8]^{-4}$.

It is important to bear in mind that the above numbers are *maxima* and that coordination numbers less than the maximum possible are shown by many atoms. The coordination number of Ni^{++}, Pd^{++}, and Pt^{++} as well as Cu^{++} and Zn^{++} appears to be usually 4, as in $Ni(CO)_4$, $(NH_3)_2PdCl_2$, $[Ni(NH_3)_4]^{++}$, $[Ni(CN)_4]^{=}$. The sizes of the central atom or ion as well as the size of the coordinated molecules or atoms will limit the number of the latter. Fluoride ion, because of its small size, appears always to bring out

the maximum coordination possible to an atom. For example, AsF_5 and SF_6 are known but not $AsCl_5$ or SCl_6.

Valency of complex ions. At the present time complex compounds are so numerous and form such a great part of modern inorganic chemistry that students should early become thoroughly familiar with correct methods of writing and naming them. For this purpose a considerable selection of such ions or compounds is given below. The valency of complex ions is sometimes puzzling, but it is quite systematic and can be readily learned, as the following rules will show.

1. *Neutral molecules* such as NH_3 and H_2O when coordinated to a central cation do not change the electrovalence of the latter. The resulting complex ion has the same charge that the central ion had before coordination.

2. Substitution of *anions* for neutral molecules as donors in complex *cations decreases* the electrovalence of the complex by one for each univalent ion, two for each bivalent ion, etc.

3. Substitution of anions for neutral molecules in complex *anions increases* the negative valence of the anion by one for each univalent ion, two for each bivalent ion, and so on.

$[Co(NH_3)_6]^{+3}$	hexammonocobaltic ion
$[NO_2Co(NH_3)_5]^{++}$	nitropentammonocobaltic ion
$[(NO_2)_2Co(NH_3)_4]^{+}$	dinitrotetrammonocobaltic ion
$[(NO_2)_3Co(NH_3)_3]$ (nonelectrolyte)	trinitrotriammono cobalt
$[(NH_3)_2Co(NO_2)_4]^{-}$	diammonotetranitrocobaltiate ion
$[Co(NO_2)_6]^{-3}$	hexanitrocobaltiate ion

Nomenclature of Complex Compounds

The names of complex compounds should indicate clearly their composition, and their formulas should suggest accurately descriptive names. To achieve this, Werner recommended the following rules, which are now becoming standard, although their general adoption has been tardy.

1. Mention the parts of a complex ion in the following order:

(*a*) anions: hydroxo-, OH^-; fluoro-, F^-; chloro-, Cl^-; bromo-, Br^-; iodo-, I^-; nitro-, NO_2^-; nitrato-, NO_3^-; cyano-, CN^-; thiocyanato-, NCS^-; sulfato-, $SO_4^=$; carbonato-, $CO_3^=$; oxalato-, $C_2O_4^=$; and so on.

(*b*) neutral molecules: aquo-, H_2O; ammono-, NH_3; and so on.

(*c*) the central ion.

2. Indicate the number, if more than one, of each kind of coordinated particle by prefixes di-, tri-, tetra-, penta-, hexa-.

3. Cations take the name of the central ion and indicate its valence.

4. Anions end in *-ate* (for example, argentate, cadmate, zincate) if the central atom forms only one ion; otherwise in *-o*ate for the lower-valent ion, in *-i*ate for the higher-valent ion (for example, ferr*o*ate; ferr*i*ate).

5. Nonelectrolytes take the name of the central ion as *element* (for example, pentacarbonylo iron, $Fe(CO)_5$; dichlorodiammono platinum, $[Cl_2Pt(NH_3)_2]$; trichlorotriammono chromium, $[Cl_3Cr(NH_3)_3]$).

To illustrate the application of Werner's rules, the names and formulas of a few typical complex salts and ions are listed below.

FORMULA	NAME
$[Cr(H_2O)_6]Cl_3$ (violet)	Hexaquochromic chloride
$[ClCr(H_2O)_5]Cl_2 \cdot H_2O$ (blue green)	Chloropentaquochromic chloride
$[Cl_2Cr(H_2O)_4]Cl \cdot 2H_2O$ (emerald green)	Dichlorotetraquochromic chloride
$[Co(NH_3)_6][Cr(NCS)_6]$	Hexammonocobaltic hexathiocyanatochromiate
$(NH_4)_3[Fe(C_2O_4)_3]$	Ammonium trioxalatoferriate
$[C_2O_4Co(NH_3)_4]Cl$	Oxalatotetrammonocobaltic chloride
$[NO_2Co(NH_3)_5](NO_3)_2$	Nitropentammonocobaltic nitrate[6]
$[(NO_2)_2Co(NH_3)_4]Br$	Dinitrotetrammonocobaltic bromide[6]
$K_4Fe(CN)_6$	Potassium hexacyanoferroate
$K_3Fe(CN)_6$	Potassium hexacyanoferriate
$K_2Fe(CN)_5NO$	Potassium pentacyanonitrosyloferroate[7]

[6] The *nitrito-* group (nitrite ion), $\overset{\circ}{\underset{\times}{\cdot}}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\overset{\times}{\underset{\times\times}{\cdot}}\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}\overset{\times}{\underset{\times}{\cdot}}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:$, changes rapidly, even in solids, into the *nitro-* group, $\overset{\circ}{\underset{\times}{\cdot}}N\begin{matrix}\overset{\times}{\underset{\times}{\cdot}}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}: \\ \overset{\times}{\underset{\times}{\cdot}}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\end{matrix}$. Red nitrito complexes soon change to the yellow of nitro- complexes.

[7] The *nitrosyl-* group, according to Sidgwick, is $\overset{\times}{\underset{\times}{\cdot}}\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}\overset{\times}{\underset{\times}{\cdot}}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:$. The lone electron of N probably reduces Fe^{+3} in $K_4Fe(CN)_6$ to Fe^{++}, thereby making NO an ion, NO^+, which neutralizes the charge of one CN^-. As a result the complex ion becomes bivalent.

$[CO_3Cr(NH_3)_4]_2SO_4$	Carbonatotetrammonochromic sulfate
$[OH\ H_2OCr(NH_3)_4]SO_4$	Hydroxoaquotetrammonochromic sulfate
$[Cu(NH_3)_2]^+$	Diammonocuprous ion
$[Cu(CN)_3]^-$	Tricyanocuproate ion
$[Cu(NH_3)_4]^{++}$	Tetrammonocupric ion
$[Cu(CN)_4]^-$	Tetracyanocupriate ion
$[(SCN)_3Cr(NH_3)_3]$	Trithiocyanatotriammono chromium
$[(OH)_3Cr(NH_3)_2H_2O]$	Trihydroxodiammonoaquo chromium

Stability of complex compounds. Complex compounds show extreme variations of stability, ranging from those which are scarcely affected by chemical reagents to those which are completely decomposed in dilute aqueous solution. At one end of the range stand ions like $[Co(CN)_6]^{-3}$ and $[Fe(CN)_6]^{-4}$ which are scarcely affected by concentrated aqueous acids, in spite of the slight ionization of HCN. When $[Co(NH_3)_6]I_3$ is heated with concentrated HNO_3, $[Co(NH_3)_6](NO_3)_3$ is formed, but no NH_3 is removed from the cation. At the other end of the range is the large class formerly called "double salts," such as the alums, $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$ and K_2MnCl_4 (aq.), solutions of which differ in no respect from equivalent mixtures of the separate components. The ion $[Co(NH_3)_6]^{++}$ has little stability and loses all its NH_3 on gentle warming. In the presence of water, Mn^{++}, Fe^{++}, and Fe^{+3} do not form complexes with NH_3, the aquo- complexes apparently being the more stable.

CHAPTER 5

WRITING AND READING CHEMICAL EQUATIONS

Qualitative inorganic analysis can and should be a discipline of the greatest permanent value to the student of chemistry. This *permanent* value resides not in expertness in analyzing materials but in the systematized first-hand knowledge which laboratory practice gives the student regarding the characteristic reactions of the commercially important chemical elements. This stock of knowledge constitutes the working equipment, in inorganic chemistry, of the chemist and the chemical engineer. It should include:

1. Both the formulas and the names of common compounds.
2. The relative solubilities in water of such compounds.
3. The relative degrees of ionization of the so-called "weak" electrolytes, a class which includes many acids, NH_3, and a few covalent compounds.
4. The distinction between electrovalent and covalent compounds.
5. A thorough understanding of which elements form only cations, which form only anions, and which form both.
6. The various valencies of the transition elements and the nature of their compounds in each valence.
7. Familiarity with and ability to use the periodic table (Table 2, page 25) as the great systematizer of inorganic chemistry. Families of elements form similar compounds having more or less similar properties. Knowing the family to which an unfamiliar element belongs enables one to write the formulas of its common compounds and to predict their properties with considerable accuracy.

This essential knowledge is acquired most readily by constant practice of writing equations accurately and reading them with full comprehension of their significance.

Chemical equations constitute the chemist's system of shorthand. To preserve for later reference and study the essential results of a simple test tube experiment, such as those made in a study of the characteristic reactions of elements and their compounds, might require writing a hundred words. The saving of

time is obvious, if this information can be conveyed by one or two equations. But one must learn not only to *write* shorthand but also to *read* it. No part of elementary training in chemistry is more important than writing equations and learning to transpose into words all the information that an equation can convey. Experience has shown that students, when reading equations in textbooks, frequently miss as much as half the important information contained in them.

A properly written equation should show:

1. The correct formulas of the reactants and products. The electrical charge of an ion is an essential part of its formula.
2. Whether any of these are solids or gases. This is shown most clearly by underscoring solids and overscoring gases.
3. Whether molecules or ions react or are formed.
4. Whether electrolytes are completely or only partially ionized. It is customary to write very weak electrolytes, such as $HAsO_2$, HCN, as molecules.
5. The *proportions* in which the reactants react or in which the products are formed. This is essential if the law of equilibrium is to be applied to a reversible reaction. This means that the equation must be *balanced* not only chemically but electrically. The same number of atoms of each element must appear on each side and, in ionic equations, the total net charges must be the same on both sides.

THE SIGNIFICANCE AND LIMITATIONS OF "EQUATIONS"

While the writing of chemical "equations" is both a time-saving method of recording experiments and the best means of acquiring a necessary stock of knowledge, it should be kept in mind that frequently such expressions do not convey "the truth, the whole truth, and nothing but the truth." The word *equation* implies mathematical equality. A chemical equation as an equality implies that no other product than those contained in the equation has been formed. Furthermore, it implies that the reactants have been transformed completely into the products. Modern investigations show that few reactions are absolutely complete, not even those reactions which are used for purposes of quantitative determination and calculation.

For example, let us consider the precipitation of Ag^+ by a small excess of Cl^-. This reaction is used in quantitative analysis and

may be taken as a typical "complete" reaction. If, at the end of the reaction, C_{Cl^-} is 0.01 M in the solution, since in a saturated solution of AgCl

$$C_{Ag^+} \times C_{Cl^-} = 1.7 \times 10^{-10},$$

$C_{Ag^+} = 1.7 \times 10^{-8} M$. Since there are 6.06×10^{23} silver ions in a gram-ionic weight (107.88), there would remain in a liter of solution $1.7 \times 10^{-8} \times 6.06 \times 10^{23}$, or 10^{16} ions and, in 1 ml of solution, 10^{13} ions. Actually the weight of 10^{13} ions would be about 2×10^{-6} mg, far less than an analytical balance can detect.

In the second place, X-ray examination demonstrates that many of the formulas assigned to chemical compounds are incorrect. For example, the compounds long written as As_2S_3, Sb_2S_3, and P_2O_5 actually have the molecular composition As_4S_6, Sb_4S_6, and P_4O_{10}. The gels for which definite formulas used to be written, such as $Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$, H_4SiO_4, and the like, are now known to be huge aggregates of covalently bonded metal atoms, water, and OH^- of variable and constantly changing composition. It is obvious that no chemical formula can truthfully represent the variable composition of such aggregates.

In the third place, it is now known that frequently, perhaps as a rule, one or several side reactions accompany a principal reaction. For example, in reactions where HNO_3 is used as an oxidant it has been shown that compounds of nitrogen in all valencies can be detected. Such compounds would be NO_2, HNO_2, NO, N_2O, N_2, $(OHNH_3)^+$, $(N_2H_5)^+$, and NH_4^+. Unless a chemical reaction is known to have been investigated thoroughly for completeness and absence of side reactions, no strictly quantitative equation can be written to describe it. Under carefully controlled conditions many reactions can be brought nearly enough to completeness to be usable for quantitative purposes.

Equations are convenient and useful shorthand descriptions of the *general tendencies* of reactants toward compound formation. A certain degree of skepticism about their strictly quantitative truth is always advisable until this is known to have been thoroughly investigated. Many, perhaps most, of the "equations" written in qualitative analysis should be regarded as convenient but incomplete or partial statements, serving to call attention to the principal one, of possibly several reactions which take place simultaneously.

In the writing of chemical equations, compounds should be formulated in accordance with established facts. The student

should bear in mind that modern tools of investigation, particularly X rays, give far more exact information about chemical compounds than ever before was available; and that, as a result, chemistry is undergoing more rapid revision than at any period of its history. The present-day student must be prepared to adjust himself to frequent revisions of chemical formulas.

INTELLIGENT READING OF EQUATIONS

When shorthand is read, it has to be turned into words. Chemical shorthand—that is, equations—should always be read in words. Practice in exact reading of equations is no less important than ability to write them. Solids, gases, and substances in solution should be distinguished from each other clearly in writing and in reading. Molecules should be distinguished from ions. If it is made a rule to underscore solids, overscore gases, and indicate the number of positive or negative charges belonging to each ion, these important properties are emphasized. The formula $\underline{BaSO_4}$ should be read *solid barium sulfate;* $\overline{CO_2}$ should be read *carbon dioxide gas.*

Inability to write formulas when the names of compounds are given is due largely to failure to read equations in words and to acquire the habit of doing this.

Examples of Correct Reading

The equation

$$\underline{CaCO_3}(\text{heated}) \rightleftarrows \overline{CO_2} + \underline{CaO}$$

should be read:

"When solid calcium carbonate is decomposed by heat, each gram-molecular weight (mol) decomposed forms *one* gram-molecular weight (or 22.4 liters S.T.P.) of carbon dioxide gas and *one* gram-molecular weight of solid calcium oxide, but these products recombine to form calcium carbonate unless the gas is removed as fast as it is formed."

The equation

$$\underset{\text{(yellow)}}{2SrCrO_4} + 2AcOH \rightleftarrows \underset{\text{(orange)}}{Cr_2O_7^{=}} + 2Sr^{++} + 2AcO^{-} + H_2O$$

should be read:

"If *two* mols of yellow solid strontium chromate reacted with exactly *two* mols of little ionized acetic acid, *one* mol of orange-

colored bivalent dichromate anion would be formed, together with *two* mols of bivalent strontium cation, *two* mols of univalent acetate anion, and *one* mol of water. However, since the sign of reversibility is used, the products can react to reform the reactants unless an excess (more than two mols) of acid is used."

The equation

$$H_2AsO_4^- + 2I^- + 3H^+ \rightleftarrows HAsO_2 + I_2 + 2H_2O$$

should be read:

"In acid solution *one* gram ion of univalent primary arsenate anion, *two* gram ions of univalent iodide anion, and *three* gram ions of hydronium ion[1] (acid) form 'quantitatively' *one* mol of little ionized arsenious acid, *one* mol of solid iodine, and *two* mols of water."

The quantitative information contained in a balanced equation. When we write $3H_2 + N_2 \rightleftarrows 2NH_3$, the equation states that 3 gram-molecular weights of hydrogen react with one gram-molecular weight of nitrogen to form reversibly two gram-molecular weights of ammonia. Since the gram-molecular weights of all gases (S.T.P.) occupy 22.4 liters, the equation also tells us that 3 volumes of H_2 react with 1 volume of nitrogen to form 2 volumes of NH_3. In other words, whether gram-molecular weights (mols) or volumes are considered, the proportions of reactants and product are *always* 3:1:2.

It follows then that the equation

$$3H_2 + N_2 \rightleftarrows 2NH_3$$

can be read in terms of various units.

1. 3 g.mols + 1 g.mol form 2 g.mols.
2. 3 mols + 1 mol " 2 mols.
3. 6.048 g + 28 g " 34.048 g.
4. 3 vol. + 1 vol. " 2 vols. (all at the *same* temperature and pressure)
5. 67.2 l + 22.4 l " 44.8 l (*all at S.T.P.*)

The student should practice reading equations in terms of various units until he becomes familiar with the quantitative information that can be derived from a *balanced* equation.

[1] The proton H^+ in aqueous solution exists largely as hydronium ion H_3O^+. To save time in writing laboratory notes, it is permissible to write H^+, but it should invariably be thought of and read as "hydronium ion."

WRITING AND BALANCING CHEMICAL EQUATIONS

Chemical reactions may be divided into two classes:

1. Those in which no element changes valency.
2. Those in which changes of valency take place (redox reactions).

Before any attempt is made to balance a chemical reaction, it should be determined which type of reaction is taking place. This is best done by writing the reactants and the products and checking the "apparent valency" (page 53) of each element in reactants and products to determine whether there is a change of valency. For example, in the reaction

$$2CrO_4^{=} + 2H^+ \rightleftarrows Cr_2O_7^{=} + H_2O$$

one might think that change of valency was involved. But the "apparent valency" of Cr is +6, both in $CrO_4^{=}$ and in $Cr_2O_7^{=}$. Therefore, change of valency is not involved.

If no change of valency occurs, the following rules apply. If there are valency changes, follow the rules on page 56.

Since most inorganic salts and the *strong* acids and bases are to be considered completely ionized in aqueous solution, their reactions in this solvent should be written as *ionic equations*. In the old system of writing equations, metathetical reactions were considered to involve a "trading of partners" between molecules. For example:

$$BaCl_2 + Na_2SO_4 = \underline{BaSO_4} + 2NaCl$$

In the modern system of writing equations for reactions in aqueous solution, only those ions are considered which change their concentrations as a result of the reaction. For example:

$$Ba^{++} + SO_4^{=} = \underline{BaSO_4},$$

since the reaction would be identical between $BaCl_2$ and Na_2SO_4 and between $Ba(NO_3)_2$ and K_2SO_4, all four substances being completely ionized even in crystal form.

Rules for Balancing Equations Not Involving Valency Changes

1. Set down the *correct* formulas of the reactants and those of the products (skeleton equation), remembering that correct electrical charge on an ion is as essential a part of its formula as are the atoms themselves.

2. Starting at the extreme left, make the number of atoms of each element except H and O the same on the product side as it is on the reactant side. (The peroxo group —O ⁘ O— is to be considered a bivalent unit.)

3. Balance the equation electrically using H^+ or OH^-, depending upon whether the solution is acid or basic, so that the sum of the charges on the reactant side equals the sum of the charges on the product side.

4. Balance the equation chemically using H_2O as reactant or product to balance the H and O atoms that were not balanced in step 2.

5. Consider the completeness of the reaction and determine which of the signs ($\rightarrow$, $\rightleftarrows$, $=$) conveys the intended meaning.

Examples

A. To write an equation for the reaction of hydrogen peroxide on dichromate ion in a very dilute, slightly acid solution to form blue diperoxochromic oxide. No change of valency.

Rule 1. $Cr_2O_7^= + H_2O_2 \rightarrow OCr(O_2)_2$

Rule 2. By observation of skeleton equation

(*a*) it is evident that there are 2 Cr atoms on the reactant side and one on the product side. Therefore, to make them equal we write

(*b*) $Cr_2O_7^= + H_2O_2 \rightarrow 2OCr(O_2)_2.$

We now note that there are four $(O_2)^=$ groups on the product side and only one on the reactant side. Therefore, we write:

$$Cr_2O_7^= + 4H_2O_2 \rightarrow 2OCr(O_2)_2.$$

Rule 2 is now completed, as we do not balance H or O in this step.

Rule 3. The sum of the charges on the reactant side equals -2, that of those on the product side equals 0; therefore (because the solution was acid) we must add $2H^+$ to the reactant side to balance the equation electrically. The equation then becomes

$$Cr_2O_7^= + 4H_2O_2 + 2H^+ \rightarrow 2OCr(O_2)_2.$$

Rule 4. As there are now 10 hydrogen atoms on the reactant side and none on the product side, we balance the equation chemically by adding $5H_2O$ to the right.

$$Cr_2O_7^= + 4H_2O_2 + 2H^+ \rightarrow 2OCr(O_2)_2 + 5H_2O$$

Rule 5. Choice of sign is difficult in this case. The reaction is not known to be quantitative. It is not reversible, for in water the blue compound is rapidly reduced to $Cr(H_2O)_6^{+3}$. "Tends to form" appears as near the truth as any statement based on present knowledge. The final balanced equation is, therefore,

$$Cr_2O_7^{=} + 4H_2O_2 + 2H^+ \rightarrow 2OCr(O_2)_2 + 5H_2O.$$

B. To write a balanced ionic equation for dissolution of arsenious sulfide in a mixture of sodium hydroxide and sodium hydrosulfide to form thioarsenite ion.

Rule 1. $As_4S_6 + HS^- + OH^- \rightarrow [AsS_3]^{-3}$ (as stated)

" *2a.* $As_4S_6 + HS^- + OH^- \rightarrow 4[AsS_3]^{-3}$

" *2b.* $As_4S_6 + 6HS^- + OH^- \rightarrow 4[AsS_3]^{-3}$

" *3.* $As_4S_6 + 6HS^- + 6OH^- \rightarrow 4[AsS_3]^{-3}$ (balanced electrically)

" *4.* $As_4S_6 + 6HS^- + 6OH^- \rightarrow 4[AsS_3]^{-3} + 6H_2O$ (balanced chemically)

" *5.* $As_4S_6 + 6HS^- + 6OH^- \rightleftarrows 4[AsS_3]^{-3} + 6H_2O$

Rules for Reactions Involving the Dissolution of Bases in NH_4^+

Ammonium ion, NH_4^+, is a weak acid with the following ionization:

$$NH_4^+ \rightleftarrows H^+ + NH_3, \qquad K_{ion} = 5.56 \times 10^{-10}.$$

The dissolution in NH_4^+ is therefore an acid-base reaction.

1. $Mg(OH)_2 + 2H^+ \rightleftarrows Mg^{++} + 2H_2O$

2. We then write the equation for the ionization of NH_4^+ as an acid so that the same number of H^+ are furnished by ionization as were used in the dissolution reaction.

$$2NH_4^+ \rightleftarrows 2NH_3 + 2H^+$$

3. Upon adding the two equations algebraically, canceling wherever possible, the final equation

$$Mg(OH)_2 + 2NH_4^+ \rightleftarrows Mg^{++} + 2H_2O + 2NH_3$$

is obtained.

If the cation formed can react with the NH_3 present to form a complex ion, this reaction can be written as a complement of the second equation.

Example

$Cd(OH)_2$ dissolves in NH_3 and NH_4^+ to form $Cd(NH_3)_4^{++}$.

Rule 1. Applying our rules for dissolution of bases in NH_4^+, we would first consider the $Cd(OH)_2$ to be dissolved in H^+ ion.

$$\underline{Cd(OH)_2} + 2H^+ \rightleftarrows Cd^{++} + 2H_2O$$

Rule 2a. Then, writing the equation for the ionization of NH_4^+ as an acid,

$$2NH_4^+ \rightleftarrows 2NH_3 + 2H^+.$$

Rule 2b. The equation for formation of the complex ion is

$$Cd^{++} + 4NH_3 \rightleftarrows Cd(NH_3)_4^{++}.$$

Rule 3. Adding equations (1), (2*a*), and (2*b*) algebraically, we obtain

$$\underline{Cd(OH)_2} + 2NH_4^+ + 2NH_3 \rightleftarrows Cd(NH_3)_4^{++} + 2H_2O.$$

REACTIONS INVOLVING VALENCY CHANGE (REDOX REACTIONS)

Redox reactions differ from nonredox only in that, in the former, electrons are both reactants and products although they do not appear in the final equation.

In the balancing of valency changes of ions or within ions, the following should be kept in mind:

1. All redox reactions take the sign of reversibility ($\rightleftarrows$).

2. Oxidation is loss of electrons. Electrons are *products* of the reaction. Example: $Fe^{++} \rightleftarrows Fe^{+3} + e^-$.

3. Reduction is *gain* of electrons. Electrons are *reactants*. Example: $Fe^{+3} + e^- \rightleftarrows Fe^{++}$.

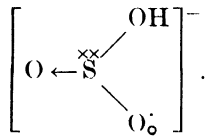
4. In a *balanced* equation the number of electrons given off by the oxidant *must equal* the number of electrons taken up by the reductant. Since the solution always remains electrically neutral, this is the *fundamental consideration* in balancing valency change equations. In order to find the number of electrons gained and lost, it is necessary to write partial equations showing the number of electrons lost by the *reductant* (oxidation of reductant) and the number gained by the *oxidant* (reduction of oxidant). These numbers are readily determined, even in complicated cases, by

considering the "apparent" valency, in its ions, of the element undergoing valency change.

The "apparent valency" (valence number) of the central atom in complex ions. By complex ion we here mean any ion which contains more than one atom. We have already seen that Be, B, Al, and elements of periodic Groups IV, V, and VI (except as $S^{=}$, $Se^{=}$, $Te^{=}$) exist only in complex ions. In such complexes we have seen that both normal and dative covalencies may be present. How shall we find the "apparent" valency of the central atom—for example, sulfur—in the following valency change?

$$HSO_3^- + H_2O \rightleftarrows SO_4^{=} + 3H^+ + 2e^-$$

In $SO_4^{=}$ the two negative charges on the ion show that two electrons have been acquired from an external source, such as H. Since each atom in the ion possesses or shares an octet of electrons, and both S and O *atoms* had six electrons in their incomplete levels, the four oxygen atoms, in order to complete their octets, must have acquired a share in eight more electrons. Since two came from outside, six must have come from S. We may then *think* of the valence of S in $SO_4^{=}$ as +6, although we know that no ion S^{+6} can have *independent* existence.

In HSO_3^- we may think that three oxygen atoms have acquired six electrons, one from outside, one from H, and, consequently, only four from the S atom which must in this ion have two *unshared* electrons  . S has shared four electrons and we may *think* of its valence as +4. In formation of $SO_4^{=}$ the two unshared electrons of S in HSO_3^- are shared with a fourth oxygen. This must come from a molecule of the solvent with release of two protons which immediately attach themselves to other molecules of solvent to form hydronium ions. The important point in this reasoning is that, in thinking of S^{+6} and S^{+4}, we by no means postulate the *independent existence* of such ions.

Valency changes of H_2O_2. H—O—O—H can act as either oxidant or reductant. It is, like water, a very weak acid. Alkaline solutions contain HO_2^-. In alkaline solutions, reduction of HO_2^- proceeds according to

$$HO_2^- + H_2O + 2e^- \rightleftarrows 3OH^- \qquad (1)$$

TABLE 3

APPARENT VALENCE OF COMMON ELEMENTS IN COMPLEX IONS OR COMPOUNDS

Element	Ions or Compounds	Apparent Valence from Electrons Shared
Al	$[Al(H_2O)_6]^{+3}$, $[AlCl_6]^{-3}$, $[Al(OH)_6]^{-3}$, $[(H_2O)_3Al(OH)_3]$	+3
Sb	$[SbCl_4]^-$, Sb_4S_6, $[SbS_3]^{-3}$, $[SbOS_2]^{-3}$, SbOCl	+3
Sb	$[SbCl_6]^-$, Sb_2S_5, $[SbS_4]^{-3}$, $[SbO_2S_2]^{-3}$, $HSb(OH)_6$	+5
As	$HAsO_2$, As_4O_6, As_4S_6, $[AsS_2]^-$, $[AsS_3]^{-3}$, $[AsCl_4]^-$, $[As(OH)_4]^-$	+3
As	AsF_5, H_3AsO_4, As_2S_5, $As(HS)_5$, $[AsCl_6]^-$, $[AsS_4]^{-3}$	+5
Bi	$[BiCl_4]^-$, BiOCl, BiO^+, Bi_2S_3	+3
Bi	BiO_3^-	+5
Br	BrO_3^-	+5
C	$C_2O_4^-$ (C:C)[a]	+3
Cl	HCl, Cl^-	−1
Cl	HClO, Cl_2O	+1
Cl	$HClO_2$	+3
Cl	ClO_2	+4
Cl	Cl_2O_5, $HClO_3$, ClO_3^-	+5
Cl	Cl_2O_7, $HClO_4$, ClO_4^-	+7
Cr	$[Cr(H_2O)_6]^{+3}$, $[Cr(NH_3)_5H_2O]^{+3}$, $[Cr(OH)_6]^{-3}$, $[(H_2O)_3Cr(OH)_3]$	+3
Cr	CrO_4^-, $Cr_2O_7^-$, $Cr_3O_{10}^-$, $HCrO_4^-$, $OCr(O_2)_2$	+6
Co	$[Co(NH_3)_6]^{++}$, $CoCl_4^-$	+2
Co	$[Co(NH_3)_6]^{+3}$, $[CoCl_6]^{-3}$, $[Co(NO_2)_6]^{-3}$	+3

[a] The shared pair of electrons in $[O:O]^-$, $[O_2S:SO_3]^-$, $[O_2C:CO_2]^-$, and $[Hg:Hg]^{++}$ lowers the usual valency to an "apparent" valency of one less.

TABLE 3.—(*Continued*)

APPARENT VALENCE OF COMMON ELEMENTS IN COMPLEX IONS OR COMPOUNDS

Element	Ions or Compounds	Apparent Valence from Electrons Shared
Co	CoO_2	+4
Cu	Cu^+, $[Cu(NH_3)_3]^+$, $[CuCl_3]^{-3}$, $[Cu(CN)_3]^-$	+1
Cu	$[Cu(NH_3)_4]^{++}$, $[Cu(CO_3)_2]^-$, $[CuCl_4]^-$, $Cu(HS)_2$	+2
I	IO_3^-	+5
Fe	$[Fe(CN)_6]^{-4}$, $[Fe(CN)_5NO]^-$	+2
Fe	$[Fe(H_2O)_6]^{+3}$, $[FeCl_6]^{-3}$, $[Fe(NCS)_6]^{-3}$, $[Fe(CN)_6]^{-3}$, $[FeF_6]^{-3}$	+3
Pb	$[HPb(OH)_4]^-$, $[PbCl_4]^-$	+2
Pb	$[Pb(OH)_6]^-$, $[PbCl_6]^-$	+4
Mn	$[MnCl_4]^-$	+2
Mn	$[MnCl_6]^{-3}$, $[Mn(PO_4)_2]^{-3}$	+3
Mn	$MnO_2 \cdot H_2O$	+4
Mn	MnO_4^-	+6
Mn	MnO_4^-	+7
Hg	Hg_2Cl_2	+1
Hg	$[HgCl_4]^-$, $[Hg(NCS)_4]^-$, $[HgI_4]^-$, $HgNH_2Cl$	+2
N	NH_3, NH_4^+, NH_2^-, Ca_3N_2, AlN, Li_3N	−3
N	N_2O	+1
N	NO	+2
N	N_2O_3, HNO_2, NO_2^-	+3
N	NO_2, N_2O_4	+4
N	N_2O_5, HNO_3, NO_3^-	+5

TABLE 3.—(*Continued*)

APPARENT VALENCE OF COMMON ELEMENTS IN COMPLEX IONS OR COMPOUNDS

Element	Ions or Compounds	Apparent Valence from Electrons Shared
O	H_2O_2, HO_2^-, O_2^-, Na_2O_2, $OCr(O_2)_2$ (see p. 59)	−1
S	H_2S, HS^-, $S^=$	−2
S	SO_2, H_2SO_3, HSO_3^-, $SO_3^=$	+4
S	SO_3, H_2SO_4, HSO_4^-, $SO_4^=$	+6
S	$S_2O_3^=$ (S^{+6}, S^{-2})[b] (average)	+2
S	$S_2O_6^=$ ($S^{+5}S$)[b] (average)	+5
S	$S_3O_6^=$ ($2S^{+6} + S^{-2}$)[b] (average)	+3½
S	$S_4O_6^=$ ($2S^{+6}$, S^0, S^{-2})[b] (average)	+2½
Sn	$[HSn(OH)_4]^-$, $[Sn(OH)_4]^=$, $[SnCl_4]^=$, SnS	+2
Sn	$[Sn(OH)_6]^=$, $[SnCl_6]^=$, $[SnS]^=$, SnS_2	+4

[b] In thiosulfuric acid and the thionic acids $H_2S_3O_6$, $H_2S_4O_6$, all the sulfur atoms do not have the same valency. However, for balancing redox reactions, it is permissible to assume the *average* "apparent" valency listed. For probable structures see Morgan and Burstall, *Inorganic Chemistry*, page 165.

In acid solution H_2O_2 acts as either oxidant or reductant. As oxidant it is reduced according to

$$H_2O_2 + 2H^+ + 2e^- \rightleftarrows 2H_2O \qquad (2)$$

By very powerful oxidants, such as MnO_4^- and $OCr(O_2)_2$, it is oxidized to O_2.

$$H_2O_2 \rightleftarrows O_2 + 2H^+ + 2e^-.$$

Note that two electrons are involved in both oxidation and reduction of H_2O_2.

Sodium peroxide, if added *slowly* to water containing much ice to absorb heat of reaction, forms HO_2^-. The reaction is one of hydrolysis.

$$Na_2O_2 + H_2O \rightleftarrows HO_2^- + OH^- + 2Na^+.$$

HO_2^- reacts as oxidant as in (1) above.

Rules for Balancing Redox Equations

1. Set down the formulas of the substances that change valencies. for example:

$$MnO_4^- + H_2S \rightleftarrows Mn^{++} + HSO_4^-.$$

2. Set down the skeletons of the two partial equations.

a Oxidant + e^- $\rightleftarrows$ reduction product.

$$MnO_4^- + e^- \rightleftarrows Mn^{++}$$

b Reductant $\rightleftarrows$ oxidation product + e^-.

$$H_2S \rightleftarrows HSO_4^- + e^-$$

3. Determine the difference between the "apparent" valency of the central atom in the oxidant and its reduction product and that between the "apparent" valency of the central atom in the reductant and its oxidation product. Consult, if necessary, Table 3, page 53. For example, Mn in MnO_4^- is +7; in Mn^{++} it is +2; difference, 5. S in H_2S is −2; in HSO_4^- is +6; difference, 8. Make the number of electrons in the partial equations equal to these differences.

$$MnO_4^- + 5e^- \rightleftarrows Mn^{++} \qquad (Mn^{+7} \text{ to } Mn^{+2})$$
$$H_2S \rightleftarrows HSO_4^- + 8e^- \qquad (S^{-2} \text{ to } S^{+6})$$

4. Consider whether the reaction takes place in acid or in basic solution.[2] Balance the partial equations *electrically* by adding H^+ if the solution is acid or OH^- if the solution is basic.

$$MnO_4^- + 5e^- + 8H^+ \rightleftarrows Mn^{++}$$
$$H_2S \rightleftarrows HSO_4^- + 8e^- + 9H^+$$

5. Balance the partial equations *chemically*, using H_2O as product or as reactant.

$$MnO_4^- + 5e^- + 8H^+ \rightleftarrows Mn^{++} + 4H_2O$$
(reduction of oxidant)
$$H_2S + 4H_2O \rightleftarrows HSO_4^- + 8e^- + 9H^+$$
(oxidation of reductant)

6. Multiply one or both partial equations by such factors as will make the number of electrons gained by the oxidant equal to the number of electrons lost by the reductant.

$$8MnO_4^- + 40e^- + 64H^+ \rightleftarrows 8Mn^{++} + 32H_2O$$
$$5H_2S + 20H_2O \rightleftarrows 5HSO_4^- + 40e^- + 45H^+$$

7. Add these multiplied partial equations, canceling equal numbers of the same ion or molecule on opposite sides.

$$8MnO_4^- + 5H_2S + 19H^+ \rightleftarrows 8Mn^{++} + 5HSO_4^- + 12H_2O$$

[2] Experimental directions for laboratory work usually indicate this. In practice exercises, if it is not specifically stated, the acidity or basicity of the solution can usually be inferred by observing the formulas of certain compounds. Anions of weak acids exist only in basic solutions, the acids in unionized form only in acid solution. Moderately stable ammono and cyano complex ions exist only in basic solutions. MnO_4^- in acid solution is reduced usually to Mn^{++}; in basic or nearly neutral solution to hydrated MnO_2.

Acid Solution	Basic Solution	Acid Solution	Basic Solution
$HAsO_2$	AsO_2^-	H_2S	HS^-, S^-
$H_2AsO_4^-$	$HAsO_4^-$	decomposed	MnO_4^-
BiO^+	$BiOOH$	NH_4^+	NH_3
$Cr_2O_7^-$	CrO_4^-	HNO_2	NO_2^-
$[Cr(H_2O)_6]^{+3}$	$[Cr(OH)_6]^{-3}$	HSO_3^-	SO_3^-
$HClO$	ClO^-	HSO_4^-	SO_4^-
HCN	CN^-	$[SnCl_6]^{-4}$	$[HSn(OH)_4]^-$
H_2O_2	HO_2^-	$[Zn(H_2O)_4]^{++}$	$[Zn(NH_3)_4]^{++}$ or $[HZn(OH)_4]^-$

Note that this *final equation* is balanced both *electrically* and *chemically*.

Examples

A. Aluminum metal reduces nitrate ion to ammonia in sodium hydroxide solution.

Rule 1. $NO_3^- + Al^\circ \rightleftarrows NH_3 + [Al(OH)_6]^{-3}$

" *2.* $NO_3^- + e^- \rightleftarrows NH_3$

$Al^\circ \rightleftarrows [Al(OH)_6]^{-3} + e^-$

" *3.* $NO_3^- + 8e^- \rightleftarrows NH_3$ (N^{+5} to N^{-3})

$Al^\circ \rightleftarrows [Al(OH)_6]^{-3} + 3e^-$ (Al° to Al^{+3})

" *4.* $NO_3^- + 8e^- \rightleftarrows NH_3 + 9OH^-$

$Al^\circ + 6OH^- \rightleftarrows [Al(OH)_6]^{-3} + 3e^-$

" *5.* $NO_3^- + 8e^- + 6H_2O \rightleftarrows NH_3 + 9OH^-$

(reduction of oxidant)

$Al^\circ + 6OH^- \rightleftarrows [Al(OH)_6]^{-3} + 3e^-$

(oxidation of reductant)

" *6.* $3NO_3^- + 24e^- + 18H_2O \rightleftarrows 3NH_3 + 27OH^-$

$8Al^\circ + 48OH^- \rightleftarrows 8[Al(OH)_6]^{-3} + 24e^-$

" *7.* $3NO_3^- + 8Al^\circ + 21OH^- + 18H_2O \rightleftarrows 3NH_3 + 8[Al(OH)_6]^{-3}$

B. Air oxidizes ferrous hydroxide to "ferric hydroxide" gel.

Rule 1. $Fe(OH)_2 + O_2 \rightleftarrows Fe(OH)_3$

" *2.* $O_2 + e^- \rightleftarrows OH^-$

$Fe(OH)_2 \rightleftarrows Fe(OH)_3 + e^-$

" *3.* $O_2 + 4e^- \rightleftarrows OH^-$ (O° to O^{-2})

$Fe(OH)_2 \rightleftarrows Fe(OH)_3 + e^-$

(Fe^{++} to Fe^{+3})

" *4.* $O_2 + 4e^- \rightleftarrows 4OH^-$

$Fe(OH)_2 + OH^- \rightleftarrows Fe(OH)_3 + e^-$

" *5.* $O_2 + 4e^- + 2H_2O \rightleftarrows 4OH^-$

(reduction of oxidant)

$Fe(OH)_2 + OH^- \rightleftarrows Fe(OH)_3 + e^-$

(oxidation of reductant)

" *6.* $O_2 + 4e^- + 2H_2O \rightleftarrows 4OH^-$

$4Fe(OH)_2 + 4OH^- \rightleftarrows 4Fe(OH)_3 + 4e^-$

" *7.* $4Fe(OH)_2 + O_2 + 2H_2O \rightleftarrows 4Fe(OH)_3$

C. When *fused* in excess of Na_2CO_3 with an oxidant such as $NaNO_3$, manganese compounds of valency lower than +6 form green manganate. Assume that NO_3^- is reduced to NO_2^-.

Rule 1. $\underline{MnO_2} + NO_3^- \rightleftarrows MnO_4^- + NO_2^-$

" *2.* $\underline{NO_3^-} + e^- \rightleftarrows NO_2^-$

$\underline{MnO_2} \rightleftarrows MnO_4^- + e^-$

" *3.* $\underline{NO_3^-} + 2e^- \rightleftarrows NO_2^-$ (N^{+5} to N^{+3})

$\underline{MnO_2} \rightleftarrows MnO_4^- + 2e^-$ (Mn^{+4} to Mn^{+6})

" *4.* Here Na_2CO_3 replaces H_2O *as solvent;* that is, $CO_3^=$ $\rightleftarrows \overline{CO_2}$ replaces $H_2O \rightleftarrows H^+ + OH^-$.

$NO_3^- + 2e^- \rightleftarrows NO_2^- + CO_3^=$

$\underline{MnO_2} + 2CO_3^= \rightleftarrows MnO_4^- + 2e^-$

" *5.* $NO_3^- + 2e^- + \overline{CO_2} \rightleftarrows NO_2^- + CO_3^=$ (reduction of oxidant)

$\underline{MnO_2} + 2CO_3^= \rightleftarrows MnO_4^- + 2e^- + 2\overline{CO_2}$ (oxidation of reductant)

" *6.* Unnecessary, since electrons balance.

" *7.* $\underline{MnO_2} + NO_3^- + CO_3^= \rightleftarrows MnO_4^- + NO_2^- + \overline{CO_2}$

D. In acid solution excess of H_2O_2 rapidly reduces the blue diperoxochromic oxide to $[Cr(H_2O)_6]^{+3}$ with liberation of O_2.

Rule 1. $OCr(O_2)_2 + H_2O_2 \rightleftarrows [Cr(H_2O)_6]^{+3} + \overline{O_2}$

" *2.* $OCr(O_2)_2 + e^- \rightleftarrows [Cr(H_2O)_6]^{+3}$

$H_2O_2 \rightleftarrows \overline{O_2} + e^-$

" *3.*[3] $OCr(O_2)_2 + 7e^- \rightleftarrows [Cr(H_2O)_6]^{+3}$

$H_2O_2 \rightleftarrows \overline{O_2} + 2e^-$ [$(O_2)^=$ to O_2°]

" *4.* $OCr(O_2)_2 + 7e^- + 10H^+ \rightleftarrows [Cr(H_2O)_6]^{+3}$

$H_2O_2 \rightleftarrows \overline{O_2} + 2e^- + 2H^+$

" *5.* $OCr(O_2)_2 + 7e^- + 10H^+ + H_2O \rightleftarrows [Cr(H_2O)_6]^{+3}$ (reduction of oxidant)

$H_2O_2 \rightleftarrows \overline{O_2} + 2e^- + 2H^+$ (oxidation of reductant)

" *6.* $2OCr(O_2)_2 + 14e^- + 20H^+ + 2H_2O \rightleftarrows 2[Cr(H_2O)_6]^{+3}$

$7H_2O_2 \rightleftarrows 7\overline{O_2} + 14e^- + 14H^+$

" *7.* $2OCr(O_2)_2 + 7H_2O_2 + 6H^+ + 2H_2O \rightleftarrows 2[Cr(H_2O)_6]^{+3} + 7\overline{O_2}$

[3] According to Schwarz [Ber., 65, 871 (1932)], $Cr^{+6} + 3e^- \rightarrow Cr^{+3}$ and $2(O_2)^= + 4e^- + 8H^+ \rightarrow 4H_2O$.

The method for balancing redox equations outlined in the preceding pages differs from the so-called "ion-electron" method in that the partial equations are balanced *first* electrically and *then* chemically. The use of "apparent" valencies of the central atom of complex ions makes this method readily applicable. It has three important advantages.

1. The emphasis on the importance of electron transfers prepares the student to comprehend electrode potentials (Chapter 11) as the driving force of redox reactions and readily to calculate the equilibrium constants of these reactions.
2. It gives a rapid and sure method for balancing equations for many redox reactions which are extremely difficult, if not impossible, to balance first chemically and then electrically.
3. It forces the student to learn the various valencies of the elements which show variable valency in their compounds.

Until the method is thoroughly understood, the beginner is advised to follow *in exact order* the seven rules. After that, and when the common redox reactions and the valency changes occurring in them have become familiar, the student will write only the balanced electron partials (rule 5), multiply them by necessary factors (rule 6), and add them.

QUESTIONS

1. Write balanced ionic equations for:

(*a*) Reaction of sodium peroxide (Na_2O_2) and water.

(*b*) Reaction of hot 3 *N* nitric acid on silver sulfide to form sulfur, nitric oxide, and so on.

(*c*) Reaction of iodine to oxidize thiosulfate ($S_2O_3^=$) to tetrathionate ($S_4O_6^=$).

(*d*) Reduction of hydroperoxide ion (HO_2^-) (electron partial).

(*e*) Oxidation of hydrogen peroxide (H_2O_2) (electron partial).

(*f*) Oxidation of manganous ion in alkaline solution by oxygen of air.

(*g*) Ferric sulfide dissolving in hydrochloric acid.

(*h*) Zinc metal dissolving in NaOH to form $HZn(OH)_4^- + H_2$.

2. Read aloud the following equations in *words*.

(*a*) $\underline{FePO_4} + 2H^+ + 6H_2O \rightleftarrows Fe(H_2O)_6^{+3} + H_2PO_4^-$

(*b*) $\underline{Co^{++}} + 2H^+ + 4NCS^- \rightleftarrows H_2Co(NCS)_4$ (blue)

(*c*) $2Mn^{++} + 4OH^- + O_2 \rightleftarrows \underline{2MnO_2 \cdot H_2O}$

(*d*) $\underline{Na_2CO_3} + 2H^+ = 2Na^+ + H_2CO_3 \rightleftarrows H_2O + \overline{CO_2}$

3. State the proportions of reactants and products in the equations of question 2 in terms of (*a*) mols; (*b*) grams.

4. Complete and balance the following equations, writing under each equation the quantitative information that can be derived from the balanced equation.

(*a*) $CN^- + NH_4^+ \rightleftarrows NH_3 + HCN$

(*b*) $NH_3 \rightleftarrows N_2 + H_2$

(*c*) $Mg^{++} + 2NH_3 + 2H_2O \rightleftarrows \underline{Mg(OH)_2} + 2NH_4^+$

(*d*) $NO + O_2 \rightleftarrows NO_2$

(*e*) $NO_2 \rightleftarrows N_2O_4$

5. Assuming that x mols ionize, how many gram ions of each product should be formed in each of the following cases?

$$AcOH \rightleftarrows H^+ + AcO^-$$

$$Cu(NH_3)_4^{++} \rightleftarrows Cu^{++} + 4NH_3$$

$$\underline{Ag_3AsO_4} \rightleftarrows 3Ag^+ + AsO_4^{-3}$$

CHAPTER 6

CONTROL OF REACTIONS: THE LAW OF EQUILIBRIUM

In the carrying out of chemical reactions on a commercial scale, the completeness of the reaction (that is, the *yield* of the product desired) and the *time required* (that is, the *speed* of the reaction) are matters of primary importance. In this chapter we shall consider the factors which control the speeds and completeness of reactions.

FACTORS CONTROLLING REACTIONS

Four factors are of major importance in controlling reactions. These are temperature, pressure, concentration, and catalyst.

Temperature. If a mixture of H_2 and Br_2 is enclosed in a sealed tube, we may expect HBr to be formed.

$$H_2 + Br_2 \rightarrow 2HBr \qquad (1)$$

According to the kinetic theory of gases the molecules of H_2 and Br_2 are in violent motion and constantly colliding with the walls of the container and with each other. Each collision adds to the energy of the molecules, that is, it makes each a *little* more unstable. If the gases are at about atmospheric pressure, millions of such collisions occur each second. We may suppose that after a sufficient number of collisions a H_2 molecule and a Br_2 molecule, both having acquired practically the full amount of energy needed to cause reaction, collide with each other and that as a result of that final collision, two molecules of a new substance HBr result. The effect of increasing the temperature of the gas mixture is to increase the velocity of the molecules and more collisions must take place each second. As a result HBr should form faster at the higher temperature. It is a rough and ready rule based on observation that a rise of 10° approximately doubles the rate of a large number of reactions.

Pressure. The effect of pressure is to bring gas molecules closer together, that is, to increase the *concentration* of the gas. At pres-

sures of 1 to 2 atmospheres or less, the concentration of a gas is proportional to its pressure. In gas mixtures the partial pressure (in atmospheres) of each gas may be taken instead of its concentration (in mols per liter).

Concentration. The more molecules there are in unit volume of a gas the more frequently they must collide with the container walls and with each other and so the rate of reaction must increase. For example in equation (1) above, if the gases were under a pressure of two atmospheres, the concentration of H_2 molecules would be doubled and a Br_2 molecule would collide twice as often with a H_2 molecule. But the concentration of the Br_2 molecules would also be doubled and a H_2 molecule would collide twice as often with a Br_2 molecule. The net result should then be that formation of HBr should proceed four times as rapidly as when the gases were under a pressure of one atmosphere.

The Law of Mass Action. The effect of concentration on reaction rate was first studied experimentally by Guldberg and Waage (1864–1867). They stated their results as the Law of Mass Action. The velocity (speed) of a reaction *at any moment* is proportional to the *molecular* concentrations of the reacting substances present at that moment, each concentration being raised to the power corresponding to the number of particles of that substance that enters into the balanced equation for the reaction. If two molecules of a substance, designated as A, react with one molecule of a substance, designated as B,

$$2A + B \rightarrow A_2B,$$

the speed at any moment of the reaction is proportional to the *second* power of the molar concentration of A and to the *first* power of the molar concentration of B present at that moment. Expressed mathematically,

$$v \propto C^2_A \times C_B, \qquad (2)$$

since a quantity that is proportional to each of several quantities is proportional to their product.

The molar concentration of A is *squared* because the speed of the reaction at any moment is proportional to $C_A \times C_A \times C_B$. If we imagine that collision of B with *one* molecule of A first forms a particle AB which then collides with another molecule of A to form A_2B, we see that the speed of formation of AB is proportional to

$C_A \times C_B$ and that of formation of A_2B is proportional to $C_{AB} \times C_A$. Thus, the rate of formation of A_2B is proportional to $C_B \times C_A \times C_A$ or $C^2_A \times C_B$.

Possibly a more readily comprehended illustration of this point is the ionic reaction

$$2H^+ + CO_3^= \rightarrow H_2CO_3,$$

the speed of which at any instant is proportional to $C^2_{H^+} \times C_{CO_3^=}$. Formation of HCO_3^- by collision of $CO_3^=$ with a H^+ is proportional to $C_{H^+} \times C_{CO_3^=}$. To form H_2CO_3, the HCO_3^- must collide with another H^+. This reaction is also proportional to C_{H^+}. The speed of formation of H_2CO_3 must then be proportional to

$$C_{H^+} \times C_{H^+} \times C_{CO_3^=}.$$

We can change the proportionality, (2) above, to an equation by introducing a *proportionality constant.* Proportionality (2) then becomes

$$v = C^2_A \times C_B \times k. \qquad (3)$$

The value of k, the proportionality constant or *speed constant*, must be determined by *experiment* for each reaction. Note that the Law of Mass Action says nothing about the *products* of the reaction. The velocity of the reaction depends in no way on them but on the concentrations (or partial pressures) of the reactants and upon the temperature.

Catalyst. A catalyst is a substance which changes the speed of a reaction but remains unchanged at the end of the reaction. A catalyst cannot initiate a reaction which does not take place spontaneously, even if at an imperceptible rate. It frequently permits working at temperatures at which the rate of formation of the product exceeds that of its decomposition.

THE LAW OF EQUILIBRIUM

Reversible reactions. By a reversible reaction is meant a reaction in which the products can react with each other to reform the reactants. The following are reversible:

$$2NO_2 \rightleftarrows N_2O_4$$
$$3H_2 + N_2 \rightleftarrows 2NH_3$$
$$H_2 + I_2 \rightleftarrows 2HI$$

Reversible reactions can be forced to completion only if one or more of the products is removed as fast as formed. Otherwise a stage is reached at which the products are reforming the reactants at the same rate as the reactants are forming the products. The reacting system reaches a state of *equilibrium*. If we consider the reaction

$$2A + B \rightleftarrows C + 2D$$

(read "two molecules of substance A react with one molecule of substance B to form one molecule of substance C and two molecules of substance D, and two molecules of substance D react with one molecule of substance C to form one molecule of substance B and two molecules of substance A") the speed at any instant of the forward reaction, $2A + B$, at a fixed temperature is given by

$$v_1 = k_1 \times C^2{}_A \times C_B. \tag{4}$$

The speed of the reverse reaction, $2D + C$, is given by

$$v_2 = k_2 \times C^2{}_D \times C_C. \tag{5}$$

Speeds and speed constants must be distinguished by subscript figures because it is not to be expected that the same number of collisions of molecules C and D are required to cause them to interact as are required to cause molecules A and B to interact. Hence, the speed constants k_1 and k_2 will probably have different numerical values at a fixed temperature. The speeds of the two reactions are both constantly changing. If the molecules A and B are enclosed in a sealed tube and heated to a temperature $t°$ at which they react at a measurable speed, equation (4) shows that the speed v_1 will be greatest at the beginning of the reaction and then will decrease because A and B are being used up and C_A and C_B become less at each successive instant. Similarly at the first instant v_2 must have the value zero since no C and D have yet been formed. After that instant C and D will be present and will react with an increasing speed as their concentrations continue to increase. Since v_1 steadily decreases and v_2 steadily increases, a time must be reached when they become equal.

At equilibrium,

$$v_1 = v_2.$$

Then

$$k_1 \times C^2{}_A \times C_B = k_2 \times C_C \times C^2{}_D. \tag{6}$$

Rearranging,

$$\frac{C_C \times C^2_D}{C^2_A \times C_B} = \frac{k_1}{k_2} = K_{\text{equil.}} \tag{7}$$

Equation (7) is a mathematical statement of the *Law of Equilibrium.* In words, "If the products of a reaction can react with each other to reform the reactants, the reaction must reach a state of equilibrium at which point the *product* of the molar concentrations of the products has (at any fixed temperature) a *definite fixed ratio* to the *product* of the molar concentrations of the reactants, each concentration being raised to the power corresponding to the number of particles (molecule, ion) in the *balanced* equation for the reaction." In its most generalized form, if

$$aA + bB + dD \rightleftarrows mM + nN + pP,$$

then at equilibrium

$$\frac{C^m_M \times C^n_N \times C^p_P}{C^a_A \times C^b_B \times C^d_D} = K_{\text{equil.}}$$

That the equilibrium constant, $K_{\text{equil.}}$ (equation 7), is actually equal to the ratio of the opposing speed constants (k_1, k_2) has been proved repeatedly by experiment.

The difference between the speed of a reaction and its equilibrium condition is well illustrated by the case of

$$2H_2 + O_2 \rightleftarrows 2H_2O, \text{ or}$$
$$H_2 + \frac{1}{2}O_2 \rightleftarrows H_2O.$$

The value of the equilibrium constant at 25°C. indicates that the forward reaction should be very nearly complete, but at 25° the forward reaction proceeds so slowly that a mixture of H_2 and O_2 can be maintained for years without a detectable amount of H_2O being formed. At 500° the reaction proceeds at a measurable speed. If, however, a spark is passed through the mixture at 25°, combination takes place instantly and with explosive violence. This is because the spark raises the temperature of a small portion of the gas to a point at which reaction takes place. The heat evolved is so great that the temperature of the whole mass is raised to a point at which the speed of the forward reaction becomes enormously rapid.

Effect of changing concentrations. The Law of Equilibrium is concerned only with the *ratio* of the *products* of the molar concentrations of reactants and of products when a state of equilibrium is reached. From equation (7) it is evident that if, after this state has been reached, more of *any one* of the reactants or products is added to the system, the concentrations of *all* the other substances present will change spontaneously so that equilibrium may again be reached.

This is well illustrated by the reversible reaction

$$H_2 + I_2 \rightleftarrows 2HI,$$

which takes place at temperatures high enough to maintain iodine in the gaseous state.

If a sealed tube containing 1 mol per liter each of H_2 and I_2 is kept at 400° until equilibrium is reached,

$$\frac{C^2_{HI}}{C_{H_2} \times C_{I_2}} = K_{equil.}$$

By experiment the value of $K_{equil.}$ at 400° has been found to be 50. If $x = C_{HI}$ at equilibrium, $1 - 0.5x$ must then be the C_{H_2} and also the C_{I_2} that remains unchanged.

$$\frac{x^2}{(1 - 0.5x)^2} = 50$$

Whence $x = 1.5591\,M$. The molar concentrations at equilibrium then are

H_2	I_2	HI
$0.2205\,M$	$0.2205\,M$	$1.5591\,M$

If enough H_2 were now brought into the tube to double the concentration of this molecule, more HI would have to form. When equilibrium was again reached,

$$\frac{(1.5591 + 2x)^2}{(0.4410 - x)(0.2205 - x)} = 50$$

Whence $x = 0.0672\,M$. At the new equilibrium the molar concentrations would be

H_2	I_2	HI
$0.3738\,M$	$0.1533\,M$	$1.6937\,M$

Doubling C_{H_2} has caused more HI to form, until nearly one-third of the I_2 present at the first equilibrium has been used up.

Effect of temperature. The effect of temperature on equilibria depends on whether the reaction read from left to right evolves or absorbs heat energy. Evolution of heat increases the stability of the system. Absorption of heat makes the system more unstable. Explosives are substances which absorb large quantities of heat energy during formation. The effect of temperature upon a reversible action can be inferred by applying the *Rule of Le Chatelier*. "Any change in the factors which affect an equilibrium will cause a system already in equilibrium to shift in such a way as to neutralize the effect of the change." For example in the reaction $3H_2 + N_2 \rightleftarrows 2NH_3 +$ heat, rise of temperature will cause NH_3 to decompose since heat opposes the left-to-right reaction and favors the right-to-left reaction. The effect of changing temperature is to change the value of the $K_{equil.}$. If a reaction evolves heat, rise of temperature *decreases* the value of $K_{equil.}$ (compare data below for synthetic ammonia).

Effect of pressure. If the products of a gas reaction occupy less space than did the reactants, increase of pressure will promote the reaction. If the products occupy more space than did the reactants, increase of pressure will oppose the reaction.

Effect of a catalyst. A catalyst increases the speed of *both* the forward and the reverse reactions. It causes equilibrium to be reached more rapidly but it has *no effect* on the value of the equilibrium constant.

The effect of pressure, temperature, and catalyst are well illustrated by the Haber process for making NH_3. The reaction

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \underset{\text{heat}}{\overset{\text{pressure}}{\rightleftharpoons}} NH_3 + 10.95 \text{ Cal.}$$

has been made commercially profitable only through careful application of the principle of equilibrium. At 25°C. the speed of the forward reaction is practically zero. By raising the temperature, the rate of the forward reaction is increased but the rate of the reaction from right to left is still more increased. Since the product occupies less volume than does the reactants, high pressure will favor the forward reaction. The equilibrium condition is given by

$$\frac{p_{NH_3}}{p^{\frac{1}{2}}_{N_2} \times p^{\frac{3}{2}}_{H_2}} = K_{equil.}$$

The following table shows (1) the dependence of $K_{equil.}$ on temperature and (2) the volume per cent of NH_3 in the equilibrium mixture at various temperatures and pressures.

		VOLUME PER CENT OF NH_3 AT EQUILIBRIUM			
t	$K_{equil.}$	1 atm.	30 atm.	100 atm.	200 atm.
200°C	0.660	15.3	67.6	80.6	85.8
400°	0.0138	0.44	10.7	25.1	36.3
500°	0.0040	0.129	0.362	10.4	17.6
1000°	0.000136	0.0044	0.13	0.44	0.87

The table shows that the maximum volume per cent of NH_3 in the equilibrium mixture is at the lowest temperature and highest pressure but at 200° the union of N_2 and H_2 takes place with such extreme slowness that the equilibrium concentration of NH_3 would be obtained only after years. If the temperature were raised to a point at which the gases combine at an appreciable rate, NH_3 would decompose as fast as formed. The only possible solution lay in finding a catalyst which would cause the reactions to proceed at a profitable rate at a much lower temperature. The commercial feasibility of the process depends solely on a suitable catalyst. It should be carefully noted that the catalyst in no way changes the equilibrium relations or alters the value of $K_{equil.}$. The sole effect is to greatly increase the *speeds* of the reactions. By passing the equilibrium mixture through a cooling coil, the NH_3 is liquefied before much has decomposed. In the Claude modification of the Haber process the pressure is 1000 atm. and the temperature 400–500°. At 400° the yield of NH_3 should be about 80%.

Heterogeneous and homogeneous equilibria. A *heterogeneous* equilibrium is an equilibrium between two or more *phases* of the same substance, as, for example, ice $\rightleftarrows$ water $\rightleftarrows$ vapor. A *phase* must have a definite bounding surface. In the example just given, water, vapor, and ice constitute three phases of H_2O because each is separated by a definite boundary surface. A mixture of water and alcohol or a mixture of O_2, N_2, CO_2 are each single phases because there is no definite boundary between the components of the mixture. On the other hand a solution of Br_2 in water and a solution of Br_2 in CS_2 after being shaken together form a heterogeneous equilibrium $Br_2(CS_2) \rightleftarrows Br_2(H_2O)$ because the two solvents, being nearly insoluble in each other, separate into two layers with a defi-

nite boundary surface between them. A solid in contact with its saturated solution constitutes a heterogeneous equilibrium. Mixtures of salts in solution and mixtures of molecules and their component ions constitute *homogeneous* equilibria.

In analytical chemistry two especially important cases of heterogeneous equilibrium are the precipitation and dissolution of solid compounds and the partition of a solute between two immiscible solvents. Especially important cases of homogeneous equilibria are those between slightly ionized molecules and their ions and between complex ions and their component parts. All these will be discussed in later chapters.

SUMMARY

The velocity (rate, speed) of a reaction is the number of mols changed per unit time. The speed of a reaction is increased by increasing the concentrations of the reactants. The speed constant changes with temperature and is (normally) increased by presence of a catalyst. Pressure or concentration appears to have little effect on the *time* required to reach equilibrium.

In reversible reactions the value of $K_{equil.}$ *decreases* with rising temperature when heat is evolved by the reaction and *increases* when heat is absorbed. Catalysts do not change the value of $K_{equil.}$. They merely accelerate the forward and reverse reaction and decrease the *time required* to reach equilibrium.

Increased pressure on the entire system causes a shift of the equilibrium in the direction attended by decrease of volume. If the products occupy less volume than the reactants, increased pressure will increase the *yield*. If no change of volume takes place, pressure will have no effect on the equilibrium.

PROBLEMS

1. Assuming that the speed of a certain reaction doubles for every 10° rise of temperature, how many times as fast will it proceed at 60° as at 10°?

2. In the following reactions, assume that the speed of the forward reaction is *one* when the partial pressure of each reactant is one atm. What should be the speed of each reaction when the partial pressures of each of its reactants are (*a*) 2 atm.; (*b*) 0.5 atm.?

(*a*) $H_2 + I_2 \rightleftarrows 2HI$

(*b*) $CO_2 + H_2 \rightleftarrows CO + H_2O$ (steam)

(*c*) $2NO_2 \rightleftarrows 2NO + O_2$

(*d*) $3H_2 + N_2 \rightleftarrows 2NH_3$

3. For the equation

$$\frac{a^2 \times b}{c \times d^2} = K$$

calculate the value of K if $a = 2$, $b = 3$, $c = 0.5$, $d = 4$.

From the value of K and the given values of a, b, c, or d calculate the value of x required to make the ratio a^2b/cd^2 equal to the calculated value of K.

	a	b	c	d
(*a*)	1	3	x	2
(*b*)	4	x	2	2
(*c*)	4	3	10	x
(*d*)	2.5	6	1	x
(*e*)	x	5	3	7

4. For the reaction $H_2 + I_2 \rightleftarrows 2HI$ at 450° when equilibrium was reached, the following molar concentrations of the components were found in various experimental tubes.

Tube	C_{H_2}	C_{I_2}	C_{HI}	$K_{equil.}$
1	0.0268	0.0002	0.0177	
2	0.0099	0.002	0.0328	
3	0.00321	0.0078	0.0337	
4	0.0017	0.0114	0.0315	
5	0.0003	0.0242	0.0202	

Calculate the value at 450° of $K_{equil.}$ for each tube and its *average* value for the *five* experiments.

5. Using the average value of $K_{equil.}$ found in problem 4, what should be the C_{HI} at equilibrium if 0.01 mol per liter each of H_2 and I_2 is heated at 450°?

6. In the reaction

$$2SO_2 + O_2 \rightleftarrows 2SO_3 + 44.4 \text{ Cal.}$$

(*a*) What will be the effect upon *time of reaching equilibrium* of: (1) raising the temperature, (2) increasing the pressure, (3) introducing finely divided platinum?

(*b*) How will the value of the *equilibrium constant* be affected by each of the changes in (*a*)?

(*c*) How will the *per cent* of SO_3 present at equilibrium (yield) be affected by each of the changes in (*a*)?

7. Write the equilibrium expressions (ratio of molar concentrations of products to product of molar concentrations of reactants) for the reversible gas reactions in problem 2 and also for the following ionic reactions in aqueous solution.

$$10Br^- + 2MnO_4^- + 16H^+ \rightleftarrows 5Br_2 + 2Mn^{++} + 8H_2O^1$$

$$\underline{HgS}^2 + OH^- + SH^- \rightleftarrows HgS_2^= + H_2O$$

$$\underline{As_2S_3}^2 + 2S_2^= + S^= \rightleftarrows 2AsS_4^{-3}.$$

[1] *Water* is not written in equilibrium equations in aqueous solution because its molar concentration, $\frac{1000\ g/l}{18\ g/mol} = 55.55\ \frac{mol}{l}$, is not changed as a result of the reaction, since the amount of solvent water is enormous compared to that of the solute. Since C_{H_2O} does not change, it need not appear in the equilibrium equation.

[2] *Solids* are not written in equilibrium equations. Their molar concentrations (densities) are constant and hence need not be considered.

CHAPTER 7

HOMOGENEOUS EQUILIBRIUM IN AQUEOUS SOLUTION

INTRODUCTION

Modern tools of investigation have revealed many unsuspected properties of water. As a result present-day views regarding the mechanism by which water acts as a solvent, and particularly as an ionizing solvent, differ greatly from those formerly held.

Only in recent years have the properties of the proton, the hydrogen nucleus, come to be appreciated. As a positively charged particle having less than 2000 times the mass of the electron, its behavior should resemble that of the electron more nearly than formerly was realized.

This resemblance appears particularly in the hydrogen bond which differs markedly from the ordinary covalent bond. Thus, in crystals of $NaHF_2$ the distance of the fluorine atoms from each other in $[F : H{\leftarrow}F]^-$ appears to be 2.36 Å, actually less than twice the radius of the fluorine atom. The proton belongs no more to one F atom than to the other and the ion acts as if it were in a state of resonance between the two forms HF and F^-, that is, the distribution of electron density appears to be the average of that for HF and for F^-. The extraordinary mobility of H^+ and the far less but still great mobility of OH^- must depend on resonance of protons between oxygen atoms of neighboring water molecules.

$$\begin{array}{l} H \qquad\quad H \\ | \qquad\quad | \\ O \leftarrow H \rightarrow O - H \rightleftarrows OH^- + H_3O^+ \end{array}$$

Historical Review

That views regarding the mechanism of ionization have undergone radical changes is shown by the following brief review.

The Arrhenius-van't Hoff theory. Faraday in the 1850's studied electric current transmission through salt solutions and reached the conclusion that the current broke down the salt molecules into oppositely charged particles which he called *ions.*

In the 1880's Arrhenius, restudying this field, was forced by his experimental data to the conclusion that the water itself, and not the current, effected this breaking down of salt molecules into ions. During the same decade van't Hoff devised methods for determining molecular weights of solutes from observation of the lowering of the freezing point or the elevation of the boiling point of the solvent caused by a known weight of solute. These data supported the ideas of Arrhenius even quantitatively. The investigations of these two scientists led to what came to be known as "The Electrolytic Dissociation Theory of Arrhenius and van't Hoff." Although at first violently opposed by the majority of chemists, who regarded "physical" chemists as irresponsible "reds," the theory had won general acceptance by 1915. Briefly summarized, its main features were as follows:

1. Solutes in solution were believed to exert an osmotic pressure[1] (tendency to become more dilute) which obeyed the gas laws. The osmotic pressure depended only on the *number* of solute particles and not at all on their size or weight. The solute behaved as if it were a gas confined in the volume occupied by the solvent. Van't Hoff's methods of measuring molecular weights in solution depended on this principle.

2. Chemical substances in general were classified as either electrolytes or nonelectrolytes.

Nonelectrolytes dissolved in water did not increase the electrical conductivity of the water. They caused a "normal" lowering of the freezing point of the water or rise of its boiling point, corresponding to the fraction of a mol of solute which had been dissolved in a given volume of solvent. Examples of such substances are cane sugar, benzene, and many other compounds now known to be covalent.

Electrolytes dissolved in water more or less increased the conductivity of water even when themselves nonconducting in pure anhydrous state. Electrolytes were found to exert abnormally great osmotic pressure in solution, that is, the number of solute particles indicated as present was always greater than the number of molecules dissolved.

[1] Modern treatment of solutions replaces osmotic pressure by free energy of dilution. The solute lowers the fugacity (escaping tendency) of the solvent in proportion to its concentration. At infinite dilution the fugacity becomes that of the pure solvent. In other words the osmotic pressure of the solute becomes zero.

3. This abnormally large number of particles in solutions of electrolytes was assumed to be due to water having broken down more or less the solute molecules into oppositely charged *ions* which then conducted the current through the solution. The extent of this ionization of the solute molecules was found to vary greatly in different electrolytes, but all electrolytes were assumed to be ionized completely in a solution infinitely dilute.

4. According to the extent of their ionization at finite dilutions electrolytes were classed as strong or weak, although one class merged gradually into the other. The electrolytes classified as *strong* included most inorganic salts, the common acids HCl, HNO_3, and H_2SO_4, the bases NaOH, KOH, and $Ba(OH)_2$. *Weak* electrolytes included a very few salts (notably $HgCl_2$, $Hg(CN)_2$, and $(AcO)_2Pb$), NH_3 solution, and very many acids.

5. The conductivity of an electrolyte depends on the *speeds* at which its cation and anion move through the solution when an electric current is applied. The speed of the cation is not in general the same as that of the anion. Kohlrausch had devised methods for measuring or computing the speeds of ions in infinitely dilute solutions and, from these, the individual "conductance" of each species of ion. Arrhenius assumed the conductivity at infinite dilution, Λ_0, to be the sum of the conductances of cation and anion. The measured conductivity, Λ_v, of a solution containing v equivalents per liter, when divided by Λ_0 was assumed to give the fraction of the electrolyte ionized at that concentration.

$$\alpha = \frac{\Lambda_v}{\Lambda_0}$$

Ionization was clearly a reversible process, for when the solvent was removed the ions reunited into molecules. Taking acetic acid as an example,

$$AcOH \rightleftarrows H^+ + AcO^-,$$

the law of equilibrium should apply; and, at any concentration of the acid,

$$\frac{C_{H^+} \times C_{AcO^-}}{C_{AcOH}} = K_{equil.}$$

should hold true.

It quickly became apparent that the ratio of the product of the ion concentrations to the concentration of the unionized solute was

not exactly constant even for weak electrolytes except in moderately dilute solutions. In the case of strong electrolytes the ratio was quite different at different concentrations. Furthermore, it became apparent that the ionization of the strong electrolytes was not an independent process, since it was considerably decreased by presence of other electrolytes in the solution, even though these had no ion in common with the solute under consideration.

The final status of the Arrhenius-van't Hoff theory was that it could be considered a law of limited application as are the gas laws. A *weak* electrolyte came to signify one for which the law of equilibrium held nearly exactly over a considerable range of concentration. A *strong* electrolyte was one for which the law of equilibrium did not hold at all.

Modern Views

By 1918 X rays had revealed that the crystals of salts consist of *ions* held together by their opposite charges. When the salt was dissolved in water, the solvent, as a dielectric (compare page 79), weakened the attraction of the opposite charges, and so the oppositely charged ions separated and diffused out through the solution. Water did not *cause* them to ionize. As a consequence, it had to be assumed that crystals of true salts (ionic lattices) already consisted of ions, and that as such they must be *completely* ionized in solution. Conductivity measurements had indicated that in $0.1\,M$ solution salts of the type of NaCl (uni-univalent) were about 85% ionized. Those like Na_2SO_4 or $BaCl_2$ (uni-bivalent or bi-univalent) were indicated to be about 70%, and those like $MgSO_4$ (bi-bivalent) about 40% ionized. Only in extremely dilute solutions did all these salts appear to be completely ionized.

The Debye-Hückel theory. In 1923 a theory was proposed by Debye and Hückel to account for the partial ionization of strong electrolytes indicated by conductivity measurements. They assumed that the indicated steady decrease in the ionization of strong electrolytes as their concentration increased was due not to actual decrease in the number of ions in the solution but to decreases of their *speeds*. At higher concentrations the ions, being closer together, would attract each a shell of oppositely charged ions about itself and thus as a larger body meet more resistance to its motion and so move more slowly through the solution in conducting current. This would result in apparent decrease of the fraction of the

electrolyte indicated by conductivity measurements to be ionized at that concentration. In a mixture of electrolytes any cation would attract any anion regardless of its nature and dependent only on the size of its electrical charge, that is upon its valence; and similarly any anion would attract indifferently all species of cations in the solution. Thus, the apparent ionization would depend on the *total* ionic strength of the solution and also considerably upon the valencies of the various ions in the solution.[2]

In order to apply the law of equilibrium to solutions of strong electrolytes, Debye and Hückel introduced a new term called the *activity coefficient.* This is usually indicated by γ and is the ratio of the "activity," the *effective* concentration of the ion, to the total concentration of the solution.

$$\gamma = \frac{a}{c} \text{ or } a = \gamma c$$

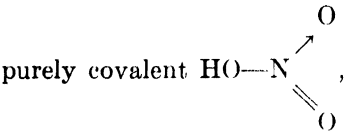
The activity coefficient may be thought of as showing what fraction of the total concentration is effective in producing equilibrium. It is usually far from being identical with α, the fraction indicated by conductivity measurements as being ionized.

Substitution of activities for concentrations has permitted the application of the law of equilibrium to strong electrolytes in concentrations up to $0.1\,M$ and in some cases up to $1.0\,M$. In the solutions used in qualitative analysis, which are frequently much more concentrated than $1\,M$, the introduction of activity coefficients, which themselves vary with the total concentration of all electrolytes present in the solution, does not render equilibrium calculations very much more accurate. In consequence of this we shall assume for purposes of equilibrium computations that the strong electrolytes are completely ionized in all solutions. It should be kept in mind, however, that computations based on this assumption, while of value qualitatively as indicating general tendencies, would not be in very close agreement with experimentally determined data.

The Hantzsch theory. Hantzsch and Wolf (1925) suggested that the strength of acids is to be measured not by their ability to furnish protons but by their tendency to form salts. They were able to isolate from nearly anhydrous mixtures of nitric and perchloric

[2] To what extent the behavior of salt solutions depends on the nature of the solvent has been shown by Kraus and Fuoss, J. Am. Chem. Soc., **55**, 21 (1933). In a mixed nonaqueous solvent the dissociation of a salt could be gradually increased from zero to 100% by varying the proportions of the two components of the solvent mixture.

acids *nitronium perchlorates* $(OH)_3N(ClO_4)_2$ and $(OH)_2NOClO_4$, substances of salt-like appearance which could be recrystallized, the former in perchloric acid, the latter in nitric acid. They concluded that nearly anhydrous nitric acid is an equilibrium mixture of

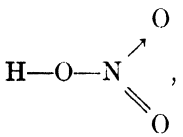


purely covalent , a minute amount of $H_3O^+NO_3^-$, and salt-like nitronium nitrate $(HO)_3N(NO_3)_2$. Upon progressive dilution of the acid, reactions such as

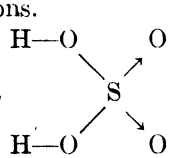
$$\begin{array}{cccccc} A_1 & & B_2 & & B_2 & & A_1 \\ (HO)_3N^{++} & + H_2O & \rightleftarrows & (HO)_2NO^+ & + H_3O^+ \\ (HO)_2NO^+ & + H_2O & \rightleftarrows & HONO_2 & + H_3O^+ \\ HONO_2 & + H_2O & \rightleftarrows & NO_3^- & + H_3O^+ \end{array}$$

take place until at sufficient dilution only ions of the *salt*, hydronium nitrate, are in the "acid."

Extension of the Hantzsch theory to other acids. Like



anhydrous liquid HCl is a covalent compound, H : Cl, unable to conduct a current when dissolved in anhydrous benzene. When dissolved in water, ions of the *salt*, hydronium chloride, $H_3O^+ + Cl^-$, are in the water because, compared with water, Cl^- has practically no tendency to add protons.

When purely covalent  is progressively diluted with water, ions of the salt hydronium bisulfate $H_3O^+HSO_4^-$ are formed and at large dilution $SO_4^=$ is formed in amount increasing with dilution, since water can take protons even from HSO_4^- to a certain extent.

Even in water itself salt formation, hydronium hydroxide, $H_3O^+OH^-$, takes place to a minute extent since the small conductivity of even the purest water shows the presence of ions in it. Likewise in anhydrous liquid NH_3 the slight conductivity shows the

presence of ions of a salt, ammonium amide, $NH_4^+NH_2^-$, in very minute concentrations.

Effect on ionization of dipolarity of the solvent. If one considers the dipolarity of H_2O, it would seem not unlikely that the negative ends of the dipoles might on sufficiently close approach to the positive ends of other molecules occasionally detach protons *temporarily* from them, thus forming ions H_3O^+ and OH^-. Considering the violent motion of molecules even in liquids, it would not be probable that an instant later the protons would remain part of these H_3O^+ ions. More probably they would have departed to attach themselves to OH^- or even to other molecules of H_2O. We have to imagine a *continuous* motion of protons from particle to particle in the liquid. The net result would be that *at any instant* a certain number of protons would be attached to molecules, leaving an equal number of OH^- anions present. Thus, when a current was passed through the water, the presence of a few ions in the liquid would be revealed by a very slight conductivity.

An exactly similar process in anhydrous liquid NH_3 would cause the presence *at any instant* of a few ions NH_4^+ and NH_2^- as protons darted about from molecule to molecule.

Water and anhydrous liquid NH_3 thus would appear to owe their ability to cause ionization to the dipolarity of their molecules which enables the negative end of one molecule to detach a proton from another molecule. Closely related to the dipolarity of molecules is their *dielectric constant*, their effectiveness as insulators. Molecules appear to be better ionizing solvents the stronger their dipole moment and, in consequence, the larger their dielectric constants.

Below are given the experimentally found values of some ionizing solvents. In accordance with its small dielectric constant, benzene has practically no ionizing power.

SUBSTANCE	DIELECTRIC CONSTANT
Liquid HCN	96.0
Water	80.0
Formic acid	62.0
Ethyl alcohol	25.0
Acetic acid	21.3
Liquid NH_3	16.0
Benzene	2.3
Low vacuum	1.0

The statement that water has a dielectric constant of 80 implies that the work required to separate by unit distance two oppositely charged bodies is $\frac{1}{80}$ as great when the bodies are immersed in water as when they are in a vacuum. In other words, a solvent tends to insulate the charges. It is this high insulating power of water that separates the oppositely charged ions of salts when they dissolve. Having existed only as ions in the solid, they naturally are "strong" electrolytes in the water where the attractive force of their opposite charges is screened off by the insulating film of water about each ion.

Energy changes and ionization. The "strong" acids, although purely covalent molecules in their anhydrous state, "ionize" completely in aqueous solution to form hydronium salts. Their protons lose energy in passing from the covalent bond, H : O, H : Cl, to the more stable H_3O^+. Since the anions of these "strong" acids have almost no ability to take protons from H_3O^+, practically all the protons will be attached to H_2O and not to the anion of the "acid."

If the proton possesses little more energy when covalent, H : O, than in H_3O^+, water will detach fewer protons from the covalent acid molecule and so the "acid" will form little hydronium salt, that is, in the terminology of Arrhenius it will be a "weak" acid.

Summary

OLD VIEW	MODERN VIEW
1. In reactions in aqueous solution, water acted as an *inert* medium.	1. Water, as both a weak acid and a weak base or as a strongly dipolar molecule, takes *some* part in all reactions in aqueous solution.
2. Salts in crystals consisted of *molecules*.	2. Salts in crystals are built up of ions held together by their opposite charges.
3. Water *ionized* salts.	3. Water insulates the ions of salts so that in *dilute* solution their opposite charges exert little attraction upon each other.
4. Salts were ionized by water to varying extents dependent on the valency of their ions.	4. *All* salts are ionized completely in water. In concentrated solutions close approach makes the charges effective and the "activities" of the ions decrease.

5. Acids were compounds of H^+ more or less firmly bound.	5. All substances which are neutralized by bases are acids. An acid need not contain hydrogen just as an oxidant need not contain oxygen. Acids[3] correspond to Sidgwick's *acceptors* of electron pairs. SO_3, SO_2, CO_2, BCl_3, Al^{+3}, Be^{++}, Ag^+ as well as H^+ would be acids.
6. H^+ had independent existence like Na^+ and other ions.	6. The proton (hydrogen nucleus) like the electron attaches itself to other particles. H^- has independent existence as in LiH and CaH_2 which are true salts.
7. Bases were substances which in solution formed OH^-.	7. Bases[3] are ions or molecules which have electron pairs to share with other ions or molecules. They correspond to Sidgwick's *donor* molecules and ions. H_2O, NH_3, acetone, and ether are bases, as are CN^-, SO_4^-, and Cl^-.
8. Measurement of the equivalent conductivity of solutions of salts, acids, and bases permitted calculation of the fraction of the solute ionized at that concentration.	8. Conductivity measurements give reliable information about the fraction ionized only for "weak" electrolytes and for many of these only over a moderate range of concentration.

IONIZATION OF SALTS, ACIDS, AND BASES

To understand all the implications of the modern theory of acids and bases requires a knowledge of organic and physical chemistry. For the elementary student we shall limit the discussion to *hydrogen compounds in water solution.* It must be kept in mind that these constitute a very restricted portion of acids, bases, and salts. If acceptors of electron pairs are considered to be acids and donors

[3] G. N. Lewis, J. Frank. Inst., **226**, 293 (1938). Lewis points out that, excepting combination of odd molecules with each other, neutralization appears to be the only type of chemical reaction that does not require added heat of activation.

of electron pairs to be bases, as Lewis proposes, all complex formation becomes neutralization.

Our consideration of ionization in water will be based on the following restrictions.

Acid is any substance which can give up protons.

Base is any substance which can take up protons.

Salt is any substance which in water is completely ionized and in solid form has an ionic lattice. Notice that (1) according to this definition Na^+OH^- is a salt and $HgCl_2$, $Hg(CN)_2$, As_4S_6 are *not* salts but chiefly covalent compounds; (2) in so far as they are ionized, acids exist in solution as hydronium *salts*.

The terms "acid" and "base" are related to protons just as the terms "oxidant" and "reductant" are related to electrons.

$$\text{H atom} \rightleftarrows \text{proton} + \text{electron}.$$
$$\text{Reductant} \rightleftarrows \text{oxidant} + \text{electron}.$$
$$\text{Acid} \rightleftarrows \text{base} + \text{proton}.$$

Just as reductants vary widely in their tendency to lose electrons and oxidants vary widely in their tendency to take up electrons (electrode potentials), so acids vary widely in their tendency to lose protons and bases vary widely in their tendency to gain protons. One may think of acids and bases as possessing proton potentials (ionization constants). Like electrons, protons tend to attach themselves instantly to molecules or ions. In water the proton forms H_3O^+; in liquid NH_3 it forms NH_4^+.

In the following applications of the equilibrium principle to ionization we shall distinguish between "strong" and "weak" acids.

As a *strong* acid we shall understand one which exists in solution practically entirely as the ions of its hydronium salt. In other words, its anion has little or no affinity for protons. Examples of such acids are HCl, HNO_3, $HClO_4$, $HClO_3$, and H_2SO_4 in its *primary* ionization,

$$H_2SO_4 + H_2O \rightleftarrows H_3O^+ + HSO_4^-,$$

but *not* in its *secondary* ionization,

$$HSO_4^- + H_2O \rightleftarrows H_3O^+ + SO_4^=,$$

since HSO_4^- has a considerable tendency to retain protons.

As a *weak* acid we shall understand one the anion of which has an affinity for protons (covalently bound) comparable in general to that of water. For example, in a solution of HCN in water,

$$\underset{\text{ACID}_1}{HCN} + \underset{\text{BASE}_2}{H_2O} \rightleftarrows \underset{\text{BASE}_1}{CN^-} + \underset{\text{ACID}_2}{H_3O^+},$$

not many ions of the salt, hydronium cyanide, are formed because CN^- is nearly as strong a base as water is. Hence, the water will remove protons from $H\times\dot{C}:\overset{\times}{\underset{\times}{\ddot{\text{N}}}}\times$ to only a slight extent. These are the acids for which the law of equilibrium applies with fair approximation over a considerable range of concentration, provided other electrolytes are absent.

In Table 4 are assembled the values of the ionization constants of some 40 weak acids. In order that the student quickly may acquire an idea of the relative tendencies of the various acids to give up protons, they have been arranged in *increasing* order of this tendency.

That ionizing solvents must be amphoteric has been implied in discussing the slight ionizations of H_2O and of anhydrous liquid NH_3.

$$\begin{array}{cccccc} A_1 & & B_2 & & B_1 & A_2 \\ H_2O & + & H_2O & \rightleftarrows & OH^- & + H_3O^+ \\ NH_3 & + & NH_3 & \rightleftarrows & NH_2^- & + NH_4^+ \end{array}$$

To these may be added anhydrous liquid SO_2 now being studied by Gerhard Jander[4] and his co-workers. In this solvent, according to Jander, proton exchange is replaced by *oxide exchange.*

$$\begin{array}{cccccc} A_1 & & B_2 & & B_1 & A_2 \\ SO_2 & + & SO_2 & \rightleftarrows & (O{\cdot}SO_2)^= & + SO^{++} \\ H_2O & + & H_2O & \rightleftarrows & OH^- & + (H{\cdot}H_2O)^+ \end{array}$$

Consider the complete analogy of the following "neutralization" reactions, all of which are "quantitative." According to obsolete ideas these would be:

	BASE	+ ACID	= SALT	+ SOLVENT
(in water)	$AgOH$	+ H_3OCl	= $\underline{AgCl}$	+ $2H_2O$
(in liquid NH_3)	$NaNH_2$	+ NH_4Cl	= $\underline{NaCl}$	+ $2NH_3$
(in liquid SO_2)	Cs_2SO_3	+ $SOCl_2$ (thionyl chloride)	= $2\underline{CsCl}$	+ $2SO_2$

According to modern ideas they would be only:

[4] Z. anorg. Chem., **230** (1937), *et seq.*

TABLE 4

WEAK ACIDS IN ORDER OF INCREASING STRENGTH TOGETHER WITH SOME WEAK BASES

	Acid	Reaction					Ionization Constant (25°)
	A_1		B_2		A_2	B_1	
1.	$(H_2O)_4Sn(OH)_2$	+	H_2O	$\rightleftarrows$	H_3O^+	+ $[(H_2O)_3Sn(OH)_3]^-$	6×10^{-13}
2.	$(H_2O)_3Cr(OH)_3$	+	"	$\rightleftarrows$	"	+ $[(H_2O)_2Cr(OH)_4]^-$	9×10^{-17}
3.	H_2O	+	"	$\rightleftarrows$	"	+ OH^-	1.8×10^{-16}
4.	$(H_2O)_2Zn(OH)_2$	+	"	$\rightleftarrows$	"	+ $[(H_2O)Zn(OH)_3]^-$	2×10^{-16}
5.	$(H_2O)_4Pb(OH)_2$	+	"	$\rightleftarrows$	"	+ $[(H_2O)_3Pb(OH)_3]^-$	2.1×10^{-16}
6.	HS^-	+	"	$\rightleftarrows$	"	+ $S^=$	1×10^{-15}
7.	$HAsO_4^-$	+	"	$\rightleftarrows$	"	+ AsO_4^{-3}	1×10^{-13}
8.	$(H_2O)_3Al(OH)_3$	+	"	$\rightleftarrows$	"	+ $[(H_2O)_2Al(OH)_4]^-$	4×10^{-13}
9.	$HPO_4^=$	+	"	$\rightleftarrows$	"	+ PO_4^{-3}	1×10^{-12}
10.	$HSiO_3^-$	+	"	$\rightleftarrows$	"	+ $SiO_3^=$	ca. 10^{-12}
11.	H_2O_2	+	"	$\rightleftarrows$	"	+ HO_2^-	2.4×10^{-12}
12.	$(H_2O)_3Sb(OH)_3$	+	"	$\rightleftarrows$	"	+ $[(H_2O)_2Sb(OH)_4]^-$	ca. 10^{-11}
13.	HIO	+	"	$\rightleftarrows$	"	+ IO^-	ca. 10^{-11}
14.	HCO_3^-	+	"	$\rightleftarrows$	"	+ $CO_3^=$	4.7×10^{-11}
15.	H_2SiO_3	+	"	$\rightleftarrows$	"	+ $HSiO_3^-$	ca. 10^{-10}
16.	HCN	+	"	$\rightleftarrows$	"	+ CN^-	4×10^{-10}
17.	NH_4^+	+	"	$\rightleftarrows$	"	+ NH_3	5.56×10^{-10}
18.	H_3BO_3	+	"	$\rightleftarrows$	"	+ $H_2BO_3^-$	5.8×10^{-10}
19.	H_3AsO_3	+	"	$\rightleftarrows$	"	+ $H_2AsO_3^-$	6×10^{-10}
20.	$HBrO$	+	"	$\rightleftarrows$	"	+ BrO^-	2×10^{-9}
21.	$HClO$	+	"	$\rightleftarrows$	"	+ ClO^-	5.6×10^{-8}
22.	$H_2PO_4^-$	+	"	$\rightleftarrows$	"	+ $HPO_4^=$	6.2×10^{-8}
23.	$H_3AsO_4^-$	+	"	$\rightleftarrows$	"	+ $HAsO_4^=$	10^{-7}
24.	HSO_3^-	+	"	$\rightleftarrows$	"	+ $SO_3^=$	1×10^{-7}
25.	H_2S	+	"	$\rightleftarrows$	"	+ HS^-	1.15×10^{-7}
26.	$HCrO_4^-$	+	"	$\rightleftarrows$	"	+ $CrO_4^=$	3.2×10^{-7}
27.	CO_2	+	"	$\rightleftarrows$	"	+ HCO_3^-	4.3×10^{-7}
28.	$H_2PO_3^-$	+	"	$\rightleftarrows$	"	+ $HPO_3^=$	7×10^{-7}
29.	$HC_2H_3O_2$	+	"	$\rightleftarrows$	"	+ $C_2H_3O_2^-$	1.85×10^{-5}
30.	$HC_2O_4^-$	+	"	$\rightleftarrows$	"	+ $C_2O_4^=$	6.4×10^{-5}
31.	$Al(H_2O)_6^{+3}$	+	"	$\rightleftarrows$	"	+ $[Al(H_2O)_5OH]^{++}$	1.4×10^{-5}
32.	$HCNS$	+	"	$\rightleftarrows$	"	+ CNS^-	ca. 10^{-4}
33.	$HCNO$	+	"	$\rightleftarrows$	"	+ CNO^-	1.2×10^{-4}
34.	$HCOOH$	+	"	$\rightleftarrows$	"	+ HCO_2^-	1.8×10^{-4}
35.	HNO_2	+	"	$\rightleftarrows$	"	+ NO_2^-	4.5×10^{-4}
36.	HF	+	"	$\rightleftarrows$	"	+ F^-	7.2×10^{-4}
37.	H_3AsO_4	+	"	$\rightleftarrows$	"	+ $H_2AsO_4^-$	4.8×10^{-3}
38.	H_3PO_4	+	"	$\rightleftarrows$	"	+ $H_2PO_4^-$	7.5×10^{-3}
39.	HSO_4^-	+	"	$\rightleftarrows$	"	+ $SO_4^=$	1.2×10^{-2}
40.	SO_2	+	"	$\rightleftarrows$	"	+ HSO_3^-	1.2×10^{-2}
41.	H_3PO_3	+	"	$\rightleftarrows$	"	+ $H_2PO_3^-$	1.6×10^{-2}
42.	$Cr_2O_7^=$	+	"	$\rightleftarrows$	"	+ $2HCrO_4^-$	2.3×10^{-2}
43.	$H_2C_2O_4$	+	"	$\rightleftarrows$	"	+ $HC_2O_4^-$	5.9×10^{-2}

WEAK BASES

	B_1		A_2		A_1		B_2	
1.	H_2O	+	H_2O	$\rightleftarrows$	H_3O^+	+	OH^-	1.8×10^{-16}
2.	$AsOOH$	+	"	$\rightleftarrows$	AsO^+	+	OH^-	5×10^{-15}
3.	NH_3	+	"	$\rightleftarrows$	NH_4^+	+	OH^-	1.8×10^{-5}

$$\begin{array}{cccccc} \text{BASE}_2 & \text{ACID}_1 & & \text{ACID}_2 & & \text{BASE}_1 \\ OH^- & + H_3O^+ & \rightleftarrows & H_2O & + & H_2O \\ NH_2^- & + NH_4^+ & \rightleftarrows & NH_3 & + & NH_3 \\ SO_3^= & + SO^{++} & \rightleftarrows & SO_2 & + & SO_2 \end{array}$$

That in each case a *salt* is precipitated depends only on its small solubility in the particular solvent: AgCl in water, NaCl in liquid NH_3, CsCl in liquid SO_2.

CALCULATION OF EQUILIBRIUM RELATIONS IN WEAK ELECTROLYTES

The ion product of water. It has been pointed out that water molecules take protons from other water molecules to a slight extent.

$$\begin{array}{cccccc} A_1 & & B_2 & & A_2 & B_1 \\ H_2O & + & H_2O & \rightleftarrows & H_3O^+ & + OH^- \end{array}$$

Applying the law of equilibrium to this reaction, we obtain

$$\frac{C_{H_3O^+} \times C_{OH^-}}{C^2_{H_2O}} = K_{equil.}$$

The molar concentration of water is $\frac{1000 \text{ g/liter}}{18 \text{ g/mol}} = 55.55 \text{ mol/l}$ approximately. (At 25° a liter of water does not weigh exactly 1000 g and at this temperature the water contains molecules of greater weight such as $(H_2O)_2$ and $(H_2O)_3$.) Since chemical reactions do not change the *molar concentration* of the solvent water, it is customary to write

$$C_{H_3O^+} \times C_{OH^-} = K.$$

By at least seven different experimental methods the concentration of H_3O^+ in pure water has been found to be very nearly $1 \times 10^{-7} M$ at 25° and since pure water is electrically neutral, C_{OH^-} must have the same value. We may then write

$$C_{H_3O^+} \times C_{OH^-} = 1 \times 10^{-14}.$$

Since the ion product always equals 1×10^{-14}, in any solution

$$C_{H_3O^+} = \frac{1 \times 10^{-14}}{C_{OH^-}}$$

and, conversely, in any solution

$$C_{OH^-} = \frac{1 \times 10^{-14}}{C_{H_3O^+}}.$$

This constancy of the ion product in aqueous solution is one of the most important relations of chemistry.

The ionization of water increases considerably with rise of temperature so that at 100° the ion product is considerably larger.

Constancy of the ionization constant. If acetic acid, AcOH, is dissolved in water, some of the acid should give up protons,

$$\underset{A_1}{AcOH} + \underset{B_2}{H_2O} \rightleftarrows \underset{A_2}{H_3O^+} + \underset{B_1}{AcO^-},$$

because H_2O is a somewhat stronger base than is AcO^-. Applying the law of equilibrium to this reversible reaction,

$$\frac{C_{H_3O^+} \times C_{AcO^-}}{C_{AcOH}} = K_{equil.}$$

For this particular kind of equilibrium the equilibrium constant is usually called the ionization constant and is written K_{ion}. Concentrations of ions and molecules must be expressed in mols per liter, or its equivalent, millimols per milliliter. That the ratio of the ion product to the molar concentration of the unionized acid remains substantially constant over a considerable range of concentrations is shown by the following data which concern the pure acid in absence of strong electrolytes.

MOLARITY	PER CENT IONIZED	$C_{H_3O^+}$	C_{AcOH}	K_{ion}
0.1	1.34	0.00134	0.09866	1.82×10^{-5}
.08	1.50	.0012	.0788	1.83×10^{-5}
.03	2.45	.000735	.02927	1.85×10^{-5}
.01	4.15	.000415	.009585	1.796×10^{-5}

The approximate constancy of K_{ion} over a considerable range of concentrations has been found experimentally to hold equally true for other weak electrolytes in absence of large concentrations of strong electrolytes. The K_{ion} of weak electrolytes varies, however, with the total ionic strength of the solution.

Solution of Problems Involving Chemical Equilibrium

The following types of calculations, all based on the constancy of the ratio ion product to unionized solute, frequently have to be made:

1. Given the molarity or normality of the solution of a weak acid and the per cent ionized at this concentration, to find the concentration of hydronium ion, of the anion of the acid, and of the unionized acid.

2. Given, or having calculated as in 1, the concentrations of the ions and of the unionized acid, to calculate the K_{ion} of the weak acid.

3. Given the molarity or normality of a weak acid and its K_{ion}, to calculate the concentrations of the ions and of the unionized acid.

Example 1. In $1\,M$ solution, acetic acid is 0.43% ionized. Calculate $C_{H_3O^+}$, C_{AcO^-}, and C_{AcOH} in the solution.

$$\underset{A_1}{\text{AcOH}} + \underset{B_2}{\text{H}_2\text{O}} \rightleftarrows \underset{B_1}{\text{AcO}^-} + \underset{A_2}{\text{H}_3\text{O}^+}$$

The equation shows that each mol of AcOH ionized gives 1 mol of H_3O^+ and 1 mol of AcO^-. Since 0.0043 mol of acid is ionized, (1 − 0.0043) mol remains unionized.

$$C_{H_3O^+} = C_{AcO^-} = 1\,M \times 0.0043 = 0.0043\,M.$$
$$C_{AcOH} = 1 - 0.0043 = 0.9957\,M.$$

Example 2. From the concentrations calculated in example 1, calculate the K_{ion} of acetic acid.

$$\frac{C_{H_3O^+} \times C_{AcO^-}}{C_{AcOH}} = K_{ion} \text{ and } \frac{0.0043 \times 0.0043}{0.9957} = 1.86 \times 10^{-5}.$$

Example 3. Taking the K_{ion} of acetic acid to be 1.85×10^{-5}, calculate the $C_{H_3O^+}$ in $0.75\,M$, in $0.5\,M$, and in $0.25\,M$ solutions of the acid. Calculate the per cent of the acid ionized at each concentration.

Let x mol/liter $= C_{H_3O^+} = C_{AcO^-}$. Then the concentration of the unionized acid is $(0.75 - x)$ mol/liter. Substituting in

$$\frac{C_{H_3O^+} \times C_{AcO^-}}{C_{AcOH}} = K_{ion},$$
$$\frac{x^2}{(0.75 - x)} = 1.85 \times 10^{-5}.$$

The small value of K_{ion} indicates that the ratio $x^2/(0.75 - x)$ is very small and that x will be small. Since x^2 is very much smaller than x, its quotient when divided by $0.75 - x$ will not differ appreciably

from that by 0.75. Hence, we may write as a close approximation

$$\frac{x^2}{0.75} = 1.85 \times 10^{-5}$$

whence $x = 3.726 \times 10^{-3} M$.

By solving the quadratic $x^2/(0.75 - x) = 1.85 \times 10^{-5}$, $x = 3.716 \times 10^{-3}$. It is clear that the exact value of x differs by a negligible amount from that found by approximation.

In $0.75 M$ solution, the acid is $0.003726 M/0.75 M \times 100 = 0.496\%$ ionized.

Similarly, for the $0.5 M$ and $0.25 M$ solutions, $x^2/0.5 = 1.85 \times 10^{-5}$, whence $x = 3.042 \times 10^{-3} M$; and $x^2/0.25 = 1.85 \times 10^{-5}$, whence $x = 2.151 \times 10^{-3} M$. In the $0.5 M$ solution the acid is about 0.61% ionized; in the $0.25 M$ solution it is about 0.86% ionized.

Ionization of ammonia solution. When NH_3 gas is dissolved in water, the solution is distinctly basic.

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^- \qquad (1)$$

It was long assumed that the solution contained a *weak* base NH_4OH, since the C_{OH^-} in $0.1 M$ NH_3 solution is far smaller than that in $0.1 M$ NaOH or KOH. But ammonium salts of strong acids are little more hydrolyzed in solution than are the corresponding K^+ or Na^+ salts. This shows that NH_4OH, if it exists, must be a rather *strong* base. The relatively low C_{OH^-} in NH_3 solutions is evidently due to very little of the NH_3 combining with H_2O, as is evidenced by the strong odor of even very dilute solutions. NH_4OH, like NH_4Cl, should be odorless.

As a base comparable to OH^- although much weaker, NH_3 will take some protons from H_2O, leaving some OH^- in the solution. Thus, it is unnecessary to assume NH_4OH as the source of OH^-. In NH_3 solutions the equilibrium constant for reaction (1) above is

$$\frac{C_{NH_4^+} \times C_{OH^-}}{C_{NH_3}} = K_b = 1.8 \times 10^{-5}. \qquad (2)$$

For the reaction

$$NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+, \qquad (3)$$

the equilibrium constant is,

$$\frac{C_{NH_3} \times C_{H_3O^+}}{C_{NH_4^+}} = K_a = 5.56 \times 10^{-10}. \qquad (4)$$

In an NH_3 solution NH_4^+ and OH^- will form until C_{OH^-} increases enough so that equation (4) and

$$C_{H_3O^+} \times C_{OH^-} = 1 \times 10^{-14}$$

become simultaneously satisfied by a much decreased $C_{H_3O^+}$.

Example. Calculate $C_{NH_4^+}$ and C_{NH_3} in 1 M NH_3 solution.

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

By approximation, if $x = C_{NH_4^+} = C_{OH^-}$, then x in $1 - x = C_{NH_3}$ is negligible and

$$\frac{x^2}{1} = K_b = 1.8 \times 10^{-5}.$$

Whence $x = C_{NH_4^+} = C_{OH^-} = 4.24 \times 10^{-3} M$, and $C_{NH_3} = (1 - 0.00424) = 0.996 M$.

Since $C_{H_3O^+}$ in the solution equals $\frac{10^{-14}}{4.24 \times 10^{-3}} = 2.36 \times 10^{-12}$, substituting values in

$$\frac{C_{NH_3} \times C_{H_3O^+}}{C_{NH_4^+}} = K_a,$$

we have

$$\frac{0.996 \times 2.36 \times 10^{-12}}{4.24 \times 10^{-3}} = 5.533 \times 10^{-10}$$

in close agreement with the given value of K_a. This shows that in an NH_3 solution *both* K_b of NH_3 and K_a of NH_4^+ are simultaneously satisfied.

Ionization of Polybasic Acids

A polybasic acid is one which can furnish more than one proton per molecule, as H_2SO_4, H_3PO_4, H_2CO_3, H_2S, and the like. The *first* proton of a polybasic acid is always more readily removed by a base than is the second and the second more readily than the third. Determine from Table 4 the values of the first, second, and third ionization constants of H_3PO_4 and of H_3AsO_4.

In a solution of a *weak* dibasic acid only the *first* ionization,

$$H_2A + H_2O \rightleftarrows H_3O^+ + HA^-,$$

takes place and even that to only a small extent. In such a solution

$C_{H_3O^+}$ practically equals C_{HA^-} and, as a result, in

$$\frac{C_{H_3O^+} \times C_{A^-}}{C_{HA^-}} = K_{II}$$

C_{A^-} equals K_{II} practically.

It can be shown, similarly, that in a solution of a tribasic acid, such as H_3PO_4 or H_3AsO_4, C_{HPO_4} or C_{HAsO_4} equals K_{II}, but $C_{PO_4^{-3}}$ or $C_{AsO_4^{-3}}$ is practically zero.

These relations do not hold for *strong* polybasic acids, such as H_2SO_4 or H_2CrO_4. The equilibria in solutions of these acids are discussed below.

For example, in water saturated with CO_2 at 25° and atmospheric pressure, the solubility of the gas is 1.449 g per liter or 1.45 (g/l)/44 (g/mol) = 0.033 mol/l. A small, but not definitely known, fraction of the CO_2 is combined with water as H_2CO_3. This fraction will be proportional to the pressure of the CO_2 and therefore to its concentration.

$$C_{H_2CO_3} = k \times C_{CO_2}$$

The ion concentrations will then be proportional to the *total* CO_2 present, whether as dissolved gas or combined with water.

$$CO_2 + 2H_2O \rightleftarrows H_3O^+ + HCO_3^-$$

Putting $x = C_{H_3O^+} = C_{HCO_3^-}$, and $C_{CO_2} = (0.033 - x)$ in

$$\frac{C_{H_3O^+} \times C_{HCO_3^-}}{C_{CO_2}} = 4.3 \times 10^{-7}, \tag{5}$$

by approximation

$$\frac{x^2}{0.033} = 4.3 \times 10^{-7},$$

whence $C_{HCO_3^-}$ = about $1.2 \times 10^{-4} M$.

But in this solution K_{II} must simultaneously be satisfied.

$$\frac{1.2 \times 10^{-4}(C_{H_3O^+}) \times C_{CO_3^-}}{1.2 \times 10^{-4}(C_{HCO_3^-})} = 4.7 \times 10^{-11}, \tag{6}$$

whence $C_{CO_3^-} = 4.7 \times 10^{-11}$, the value of K_{II}. Multiplying (5) by (6)

$$\frac{C^2_{H_3O^+} \times C_{CO_3^-}}{C_{CO_2}} \text{ should equal } 2.02 \times 10^{-17}. \tag{7}$$

Substituting concentrations in (7),

$$\frac{(1.2 \times 10^{-4})^2 \times 4.7 \times 10^{-11}}{0.033} = 2.05 \times 10^{-17},$$

which shows that $C_{CO_3^-} = K_{II}$ satisfies the $K_{equil.}$ of (7).

Equilibrium in H_2S solution. A saturated solution of H_2S in water at 25° and 1 atm. is very nearly $0.1\,M$. In this solution practically the only reaction is

$$H_2S + H_2O \rightleftarrows H_3O^+ + HS^-.$$

Then

$$\frac{C_{H_3O^+} \times C_{HS^-}}{0.1(C_{H_2S})} = 1.15 \times 10^{-7}, \text{ and} \qquad (8)$$
$$C_{H_3O^+} = C_{HS^-} = 1.07 \times 10^{-4} M.$$

Since in any solution *all* possible equilibria must be satisfied simultaneously,

$$\frac{C_{H_3O^+} \times C_{S^-}}{C_{HS^-}} = 1 \times 10^{-15}. \qquad (9)$$

Substituting in (9) values of $C_{H_3O^+}$ and C_{HS^-},

$$\frac{1.07 \times 10^{-4} \times C_{S^-}}{1.07 \times 10^{-4}} = 1 \times 10^{-15}.$$

In water saturated at room temperature with H_2S, the C_{S^-} is about $1 \times 10^{-15} M$. Multiplying (8) by (9),

$$\frac{C^2_{H_3O^+} \times C_{S^-}}{0.1} = 1.15 \times 10^{-22},$$

or $C^2_{H_3O^+} \times C_{S^-} = 1.15 \times 10^{-23}$, which shows that in any solution *saturated* with H_2S the C_{S^-} varies inversely as the *square* of $C_{H_3O^+}$. This ion product at 25° for saturated H_2S water is comparable to the ion product of water at 25°.

$$C_{H_3O^+} \times C_{OH^-} = 1 \times 10^{-14}$$

In the saturated H_2S water, since $C_{H_3O^+} = 1.07 \times 10^{-4} M$, $C_{OH^-} = 9.34 \times 10^{-11} M$, or about 90,000 times the C_{S^-}. From such a solution, hydroxides, rather than sulfides, might be expected to precipitate. This would indicate that *hydrosulfides* rather than

sulfides are precipitated by H_2S. Repeated experimental indications that this is the fact will be found in the laboratory work.

Concentration of sulfate ion in dilute sulfuric acid. Because HSO_4^- ($K_{ion} = 1.2 \times 10^{-2}$) is not a very weak acid, the $C_{SO_4^=}$ in a dilute solution of H_2SO_4 is *not* equal to K_{II} as the following calculations show.

Example. Calculate $C_{SO_4^=}$ in (*a*) 1 *M*, (*b*) 0.1 *M* solution of H_2SO_4.

In dilute solution water removes the first proton completely, giving $C_{H_3O^+} = 1\,M$. But ionization of HSO_4^- will increase this $C_{H_3O^+}$ by an amount equal to the $C_{SO_4^=}$ formed and will decrease by the same amount the $C_{HSO_4^-}$ formed by removal of the first proton. In

$$HSO_4^- + H_2O \rightleftarrows H_3O^+ + SO_4^=,$$

setting $x = C_{SO_4^=}$, $C_{HSO_4^-}$ at equilibrium will be $1 - x$, and $C_{H_3O^+}$ will be $1 + x$. Then at equilibrium in the equation

$$\frac{C_{H_3O^+} \times C_{SO_4^=}}{C_{HSO_4^-}} = 0.012$$

we shall have for the 1 *M* solution

$$\frac{(1 + x)x}{1 - x} = 0.012, \text{ or}$$

$$x^2 + 1.012x - 0.012 = 0,$$

whence $x = 0.0117\ M$. In the 1 *M* acid $C_{H_3O^+} = 1.0117\,M$, $C_{HSO_4^-} = 0.09883\,M$, and $C_{SO_4^=} = 0.0117\,M$. The $C_{HSO_4^-}$ is about 9 times that of the $SO_4^=$.

In 0.1 *M* solution

$$\frac{(0.1 + x)x}{0.1 - x} = 0.012, \text{ or } x^2 + 0.112x - 0.0012 = 0,$$

whence $x = 0.009848$. The 0.1 *M* acid is then $0.10985\,M$ in H_3O^+, $0.09015\,M$ in HSO_4^-, and $0.00985\,M$ in $SO_4^=$. $C_{HSO_4^-}$ is about 9.15 times $C_{SO_4^=}$.

Since in H_2SO_4 solutions the $C_{H_3O^+}$ from ionization of HSO_4^- is *not* neglibly small in comparison with that from the first ionization, a quadratic equation must *always* be solved for this case.

Behavior of chromic acid. In acid solution chromate ion as a proton acceptor changes largely into dichromate ion.

$$\underset{\text{yellow}}{2CrO_4^-} + 2H_3O^+ \rightleftarrows 2HCrO_4^- \rightleftarrows \underset{\text{orange}}{Cr_2O_7^-} + 2H_2O$$

The equilibrium constants involved are

$$\frac{C_{H_3O^+} \times C_{CrO_4^-}}{C_{HCrO_4^-}} = 3.2 \times 10^{-7} \text{ and} \tag{10}$$

$$\frac{C^2_{HCrO_4^-}}{C_{Cr_2O_7^-}} = 0.023. \tag{11}$$

In any chromate solution the ratio $C_{CrO_4^-}/C_{Cr_2O_7^-}$ is extraordinarily dependent on $C_{H_3O^+}$, as the following calculated data show for a solution 1 M in total Cr.

The ion concentrations are calculated as follows. Let

$$x = C_{CrO_4^-}; \quad y = C_{HCrO_4^-}; \quad z = C_{Cr_2O_7^-}.$$

Then

$$x + y + 2z = 1. \tag{12}$$

(Because $Cr_2O_7^-$ contains 2Cr, z is multiplied by 2.) *Assuming* $C_{H_3O^+} = 10^{-6}$, (10) becomes

$$10^{-6}x = 3.2 \times 10^{-7}y, \tag{13}$$

whence $x = 0.32y$. Similarly, (11) becomes

$$z = \frac{y^2}{0.023}. \tag{14}$$

Substituting in (12)

$$0.32y + y + \frac{2y^2}{0.023} = 1, \text{ and}$$

$$2y^2 + 0.03036y - 0.023 = 0,$$

whence $y = 0.09991\,M$, $x = 0.03197\,M$, and $z = 0.43406\,M$.

At other *assumed* concentrations of H_3O^+, combination of equations (10), (11), and (12) gave the ion concentrations tabulated below.

$C_{H_3O^+}$	$C_{CrO_4^-}$	$C_{HCrO_4^-}$	$C_{Cr_2O_7^-}$
10^{-4}	0.000325	0.1016	0.44903
10^{-6}	0.03197	0.09991	0.43406
10^{-7}	0.27456	0.0858	0.3198
10^{-8}	0.9024	0.0282	0.0347
10^{-9}	0.9960	0.003113	0.00042

Notice that in a very mildly acid solution ($C_{H_3O^+} = 10^{-4}$) nearly 90% of the total Cr is in the form of $Cr_2O_7^=$. In a very mildly basic solution ($C_{H_3O^+} = 10^{-9}$) 99% of the total Cr is in the form of $CrO_4^=$ while $Cr_2O_7^=$ has practically vanished.

The Common Ion Effect

If to a solution of a weak acid one of its soluble salts be added, the $C_{H_3O^+}$ will be correspondingly decreased. For example, 0.5 M AcOH is about 0.61% ionized. As shown in Example 1, page 87, the expression

$$\frac{0.00305\ (C_{H_3O^+}) \times 0.00305\ (C_{AcO^-})}{0.49695\ (C_{AcOH})} = 1.875 \times 10^{-5}$$

can be written. If to a liter of this solution 0.5 mol of solid AcONa is added, the new C_{AcO^-} becomes 0.50305 M;

$$\frac{0.00305 \times 0.50305}{0.49695} > 1.875 \times 10^{-5},$$

and the equilibrium

$$AcOH + H_2O \rightleftarrows H_3O^+ + AcO^-$$

will shift toward the left until

$$\frac{(0.00305 - x) \times (0.50305 - x)}{0.49695 + x} = 1.875 \times 10^{-5}. \qquad (15)$$

If all the H_3O^+ in the solution united with AcO^- to form AcOH, the concentration of the latter could not exceed 0.5. The C_{AcO^-} would then be that coming from the added acetate. As a close approximation to (15) we may write

$$\frac{x \times 0.5}{0.5} = 1.875 \times 10^{-5}, \qquad (16)$$

in which x, equal to $C_{H_3O^+}$, becomes 1.875×10^{-5}.

The common ion effect may be considered from the following slightly different viewpoint. Since in

$$\frac{0.00305 \times 0.50305}{0.49695} = 1.875 \times 10^{-5}$$

the denominator C_{AcOH} is practically constant at 0.5 M before and after adding the salt, $C_{H_3O^+}$ varies inversely as C_{AcO^-}. We shall have then

$$\frac{\text{(old) } C_{AcO^-}\ 0.00305}{\text{(new) } C_{AcO^-}\ 0.50305} = \frac{\text{(new) } C_{H_3O^+}}{\text{(old) } C_{H_3O^+}\ 0.00305}.$$

Then new

$$C_{H_3O^+} = \frac{(0.00305)^2}{0.50305} = 1.85 \times 10^{-5} M,$$

in substantial agreement with that previously calculated. The addition of an acetate has caused the $C_{H_3O^+}$ to decrease to $\frac{1}{183}$ of its former value. This addition of one of its soluble salts to a solution of a weak acid is known as *buffering* the acid solution. The properties of buffered solutions will be considered in the chapter on hydrolysis.

Example. If a weak acid, such as H_2S, is in the presence of a strong acid, such as HCl, its ionization must be greatly decreased and the concentrations of HS^- and $S^=$, which can be in the solution, must be correspondingly decreased. In 0.3 M HCl saturated with H_2S at 25°, the $C_{H_3O^+}$ will be 0.3.

$$\frac{0.3 \times C_{HS^-}}{0.1} = 1.15 \times 10^{-7},$$

whence $C_{HS^-} = 3.83 \times 10^{-8} M$; and

$$\frac{0.3 \times C_{S^=}}{3.83 \times 10^{-8}} = 1 \times 10^{-15},$$

whence $C_{S^=} = 1.28 \times 10^{-22} M$.

In water saturated with H_2S we have found $C_{S^=}$ to be $1 \times 10^{-15} M$. Since for a solution *saturated* at 25° with H_2S

$$C^2_{H_3O^+} \times C_{S^=} = 1.15 \times 10^{-23},$$

it is evident that $C_{S^=}$ varies *inversely* as the *square* of the $C_{H_3O^+}$ and that the presence of completely ionized acids must greatly decrease the effectiveness of H_2S as a precipitating agent. This will become apparent in connection with the *solubility products* of sulfides.

Hydronium Ion Concentration as pH

Biochemists introduced the use of the term *p*H for hydronium ion concentration, and the term is now in general use by all chemists. *p*H is defined as the negative log of $C_{H_3O^+}$. That is,

$$p\text{H} = \log \frac{1}{C_{H_3O^+}}$$

Similarly, the term pOH is used to indicate $\log (1/C_{OH^-})$. p is abbreviated from *potenz*, German for "power" or "logarithm." Notice the following relations:

$C_{H_3O^+}$	10^{-13}	10^{-12}	10^{-11}	10^{-10}	10^{-9}	10^{-8}	10^{-7}
pH	13	12	11	10	9	8	7

$C_{H_3O^+}$	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}
pH	6	5	4	3	2	1

Since in pure water $C_{H_3O^+}$ at 25° equals $10^{-7}M$, an exactly neutral solution has a pH of 7. Basic solutions have pH greater than 7, acid solutions have pH less than 7.

Deriving pH from C_{OH^-}. Since $C_{H_3O^+} \times C_{OH^-} = 10^{-14}$,

$$C_{H_3O^+} = \frac{10^{-14}}{C_{OH^-}}.$$

Inverting,

$$\frac{1}{C_{H_3O^+}} = \frac{C_{OH^-}}{10^{-14}}.$$

Taking logs,

$$p\text{H} = \log \frac{1}{C_{H_3O^+}} = \log C_{OH^-} - (-14)$$

therefore

$$p\text{H} = \log C_{OH^-} + 14.$$

Example 1. The $C_{H_3O^+}$ in a solution is 1.85×10^{-5}. What is the pH of the solution?

$$\begin{aligned} p\text{H} = \log \frac{1}{C_{H_3O^+}} &= \log 1 - \log 1.85 \times 10^{-5} \\ &= 0.0000 - (5.2672 - 10) \\ &= 4.7328 \end{aligned}$$

Since pH values are written only to the *second* decimal figure *at most*, usually only to the first decimal figure, the pH would be stated as 4.7, or 4.73.

Example 2. (*a*) Calculate the $C_{H_3O^+}$ in a solution of which the pH is 6.8. (*b*) Calculate also the pOH of the solution.

(*a*)
$$\begin{aligned} 6.8 &= \log 1 - \log C_{H_3O^+} \\ \log C_{H_3O^+} &= \log 1 - 6.8 = 3.2 - 10 \\ C_{H_3O^+} &= 1.585 \times 10^{-7} \end{aligned}$$

$$(b)\quad C_{OH^-} = \frac{10^{-14}}{1.587 \times 10^{-7}} = 6.31 \times 10^{-8}$$

$$pOH = \log \frac{1}{C_{OH^-}} = 0.0000 - 2.8000 - 10 = 7.2.$$

The pH of the solution is 6.8; its pOH is 7.2.

Example 3. Calculate the pH of a solution in which $C_{OH^-} = 0.05\,M$.

$$pH = \log C_{OH^-} + 14$$
$$= 8.6990 - 10 + 14 = 12.7$$

Example 4. Calculate the pH of $0.05\,M$ HCl.

$$pH = \log 1 - \log 0.05 = 1.3$$

PROBLEMS

(For values of K_{ion} consult Table 4, page 84. Use approximation methods unless otherwise directed.)

1. Calculate the $C_{H_3O^+}$ and the per cent of acetic acid ionized in the following solutions: (*a*) $0.05\,M$, (*b*) $0.15\,M$, (*c*) $0.2\,M$. *Ans.* (*a*) $9.62 \times 10^{-4}\,M$, 1.92%; (*b*) $1.66 \times 10^{-3}\,M$, 1.11%; (*c*) $1.93 \times 10^{-3}\,M$, 0.96%.

2. Calculate: (*a*) $C_{H_3O^+}$, and (*b*) the per cent ionized in $0.04\,M$ solution of HCN. *Ans.* (*a*) $4 \times 10^{-6}\,M$; (*b*) 10^{-2}%.

3. Calculate the ionization constants of the following acids:

HA	1.3% ionized in $0.1\,M$ solution	*Ans.* 1.69×10^{-5}
HB	0.05% ionized in $0.1\,M$ solution	2.5×10^{-8}
HC	0.021% ionized in $0.25\,M$ solution	1.1×10^{-8}

4. Calculate the $C_{H_3O^+}$ and the pH in $0.1\,M$ solutions of: (*a*) HCN, (*b*) H_2S, (*c*) H_3AsO_4, (*d*) HClO. *Ans.* (*a*) $6.32 \times 10^{-6}\,M$, 5.2; (*b*) $1.07 \times 10^{-4}\,M$, 4.0; (*c*) $2.19 \times 10^{-2}\,M$, 1.66; (*d*) $7.48 \times 10^{-5}\,M$, 4.13.

5. Calculate $C_{H_3O^+}$ and pH of $0.15\,M$ NH_4Cl solution. *Ans.* $9.13 \times 10^{-6}\,M$, 5.04.

6. Calculate C_{OH^-}, the pOH, and the pH of $0.01\,M$ NH_3 solution. *Ans.* $4.25 \times 10^{-4}\,M$, 3.4, 10.6.

7. What is $C_{H_3O^+}$ in solutions having a pH of: (*a*) 1.2, (*b*) 5.7, (*c*) 7.9, (*d*) 8.4, (*e*) 12.5. *Ans.* (*a*) $6.31 \times 10^{-2}\,M$, (*b*) $2 \times 10^{-6}\,M$, (*c*) $1.26 \times 10^{-8}\,M$, (*d*) $4 \times 10^{-9}\,M$, (*e*) $3.16 \times 10^{-13}\,M$.

8. Calculate:

$C_{CO_3^=}$ in 0.1 M H_2CO_3	*Ans.* $4.7 \times 10^{-11} M$
$C_{S^=}$ in 0.05 M H_2S	$1 \times 10^{-15} M$
$C_{HPO_4^=}$ and $C_{PO_4^{\equiv}}$ in 0.1 M H_3PO_4	$6.2 \times 10^{-8} M$; $2.26 \times 10^{-18} M$

9. The solubility in water at 25° and 1 atm. of CO_2 is 0.034 mol per liter. Calculate $C_{H_3O^+}$ (*a*) in water saturated with CO_2 at 25° and atmospheric pressure, (*b*) in a solution in equilibrium with CO_2 at 25° and 12.3 atm. (Hint: apply the Law of Henry.) *Ans.* (*a*) $1.21 \times 10^{-4} M$, (*b*) $4.24 \times 10^{-4} M$.

10. Water saturated with H_2S at 25° and 1 atm. dissolves about 0.1 mol per liter of the gas. Calculate $C_{H_3O^+}$ (*a*) in this solution, (*b*) in water in equilibrium at 25° with a gas mixture 50% H_2S and 50% H_2. *Ans.* (*a*) $1.07 \times 10^{-4} M$, (*b*) $7.58 \times 10^{-5} M$.

11. At 25° and 1 atm., water dissolves SO_2 to the extent of 1.47 mols per liter. Calculate $C_{H_3O^+}$ in water saturated with SO_2 at 25° and (*a*) 1 atm, (*b*) 4.2 atm. *Ans.* (*a*) $1.33 \times 10^{-1} M$, (*b*) $2.72 \times 10^{-1} M$.

12. Calculate $C_{H_3O^+}$ and $C_{SO_4^=}$ in H_2SO_4 (*a*) 1.5 M, (*b*) 0.01 M (Quadratic equations must be solved.) Assume the first H to be completely changed to H_3O^+. *Ans.* (*a*) $C_{H_3O^+}$, 1.51 M; (*b*) $C_{H_3O^+}$, 1.45×10^{-2}; (*a*) $C_{SO_4^=}$, 0.0118 M; (*b*) $C_{SO_4^=}$, 4.5×10^{-3}.

13. Calculate $C_{H_3O^+}$ and $C_{C_2O_4^=}$ in $H_2C_2O_4$, (*a*) at 1.0 M, (*b*) at 0.1 M. (Quadratic equations must be solved.) *Ans.* (*a*) $C_{H_3O^+}$, 0.2158 M; (*b*) $C_{H_3O^+}$, 0.0528 M; (*a*) $C_{C_2O_4^=}$, $6.36 \times 10^{-5} M$; (*b*) $C_{C_2O_4^=}$ $6.39 \times 10^{-5} M$.

14. Calculate the $C_{H_3O^+}$ in 1 liter of 1 M acetic acid to which, has been added one mol of ammonium acetate giving an "effective" concentration of acetate ion 0.6 M. *Ans.* $3.1 \times 10^{-5} M$.

15. How many mg of NH_4Cl (53.5 g per mol) must be in one ml of 2 N NH_3 solution to reduce the C_{OH^-} to 5.5×10^{-5}? *Ans.* 35 mg.

16. In a solution 0.1 M AcOH, 1.0 M in AcO^- ("effective" concentration = 0.6 M) and saturated with H_2S, *all* the following equilibria are satisfied:

$$(a)\ C_{H_3O^+} \times C_{AcO^-} = 1.8 \times 10^{-5} \times C_{AcOH}$$
$$(b)\ C_{H_3O^+} \times C_{OH^-} = 1 \times 10^{-14}$$
$$(c)\ C_{H_3O^+} \times C_{HS^-} = 1.15 \times 10^{-7} \times C_{H_2S}$$

Calculate C_{HS^-} and C_{OH^-} in the solution. (Hint: in a solution there can be only one concentration of any given ion.) *Ans.* $C_{HS^-} = 3.7 \times 10^{-3} M$; $C_{OH^-} = 3.2 \times 10^{-9} M$.

17. To 3 ml 0.6 N acetic acid is added 2 ml 0.3 N NaOH solution. Observing the dilution effect but disregarding hydrolysis, calculate $C_{H_3O^+}$ in the final solution. *Ans.* $3.7 \times 10^{-5} M$.

CHAPTER 8

HETEROGENEOUS EQUILIBRIA

EQUILIBRIUM BETWEEN A SLIGHTLY SOLUBLE SALT AND ITS SATURATED SOLUTION

It has been pointed out that true salts in solid state consist of oppositely charged ions. Each cation in the crystal is surrounded by anions and each anion is surrounded by cations. A crystal surface of such a salt consists of alternate cations and anions.

The oxygen atom is tetrahedral, and in the H_2O molecule the protons have been shown to occupy adjacent vertices of the tetrahedron. The two remaining vertices must possess a high electron density due to the unshared two pairs of the oxygen atom. In consequence the water molecule has a high electrical moment and is a dipole.

If a crystal is placed in water, the water molecules will rearrange themselves about the crystal surface in such a way that the oxygen end of a water molecule approaches a cation in the crystal and the hydrogen end of another molecule approaches an anion. If the polar forces of the water molecules are able to detach a cation from the crystal surface, an anion will be simultaneously detached. Since the removal of this first cation and anion from the crystal surface weakens the forces which hold the cations and anions adjacent to them, still other cations and anions will leave the crystal surface. These dissolved cations and anions in rapid motion through the solvent will approach or impinge on the surface of the crystal from time to time and the attractive forces within the crystal lattice will cause some of them to return again into the lattice. In this way a reversible reaction takes place, ions passing into the solution from the crystal and at the same time ions leaving the solution and again entering the crystal lattice. Evidently a state of equilibrium will be reached when ions are leaving the lattice and returning to it at exactly the same rate.

The Solubility Product Principle

Let us consider the conditions of concentration when such a state of equilibrium has been reached. If a portion of the crystal surface

of unit area is considered, we may assume that the fraction x of the surface is occupied by cations and the fraction $1 - x$ of the surface is occupied by anions. The rate, v_1 at which cations go into solution should be proportional to x, that is, equal to a constant times x.

$$v_1 = k_1 x \tag{1}$$

The rate at which cations deposit upon the surface should be proportional to the concentration of cations in the solution and also to the number of available places on the surface, that is, to $1 - x$.

$$v_2 = k_2(1 - x) \times C_{\text{cation}} \tag{2}$$

At equilibrium the rates of solution and deposition must be equal,

$$v_1 = v_2,$$

and hence

$$k_1 x = k_2(1 - x) \times C_{\text{cation}}. \tag{3}$$

In the same way the rate at which anions leave the surface is given by

$$v_3 = k_3(1 - x), \tag{4}$$

and the rate at which anions return to the surface is given by

$$v_4 = k_4 x \times C_{\text{anions}}. \tag{5}$$

At equilibrium

$$v_3 = v_4$$

and

$$k_3(1 - x) = k_4 x \times C_{\text{anions}}. \tag{6}$$

Multiplying (6) by (3), we obtain

$$C_{\text{cations}} \times C_{\text{anions}} = \frac{k_1 k_3}{k_2 k_4}. \tag{7}$$

Since k_1, k_3, k_2, and k_4 are all fixed numbers at a fixed temperature, the ratio of their products is a constant. Hence equation (7) states that at equilibrium the product of the molar concentration of the cations in solution by the molar concentration of the anions in solution will be a constant. This constant is called the solubility product[1] constant of the salt and is usually designated by $K_{s.p.}$

[1] The above deduction of the constancy of the ion products in *saturated* solutions of slightly soluble salts is due to Butler, J. Phys. Chem., **28**, 438 (1924). It is noteworthy in that it does not involve the older assumption of partial ionization of the dissolved salt.

So long as the solution is unsaturated, ions will be leaving the surface of the solid in greater numbers than ions are returning from the solution into the crystal lattice. As soon as the solution is saturated the rates of dissolution and deposition become equal.

Calculation of solubility product from solubility. The relation between the *measured* molar solubility, s,

$$\frac{m \text{ mg/ml}}{n \text{ mg/m.mol}} = s \text{ m.mol/ml},$$

of a slightly soluble salt and its solubility product constant depends upon the relative number of cations and anions in the salt. If such salts are classified according to this number, it becomes evident that their solubility product constants ($K_{s.p.}$) expressed in terms of s, take certain characteristic forms for each class.

ELECTROLYTE	$K_{s.p.}$
1. Two-ion ($AgCl$, $CuCl$, $BaSO_4$, $FePO_4$)	s^2 (mol/l)^2
2. Three-ion (Ag_2CO_3, PbI_2, Hg_2Cl_2, Ag_2S, SnS_2)	$4s^3$ (mol/l)^3
but for $MgNH_4PO_4$, $K_{s.p.} = s^3$ (mol/l)^3	
3. Four-ion (Ag_3AsO_4, $Ag_3Co(CN)_6$)	$27s^4$ (mol/l)^4
but for $K_2Na[Co(NO_2)_6]$, $K_{s.p.} = 4s^4$ (mol/l)^4	
4. Five-ion ($Ca_3(PO_4)_2$, Fe_2S_3, Bi_2S_3)	$108s^5$ (mol/l)^5

Class 1. Since each molecule dissolved forms *one* cation and *one* anion, if the fraction s of a mol of salt dissolves to form 1 liter of saturated solution, the concentration of the cation will be s mol per liter and the concentration of the anion will also be s mol per liter. The product of these two ion concentrations will be s mol/l $\times$ s mol/l or s^2 (mol/l)^2. The unit (mol/l)^2 has no physical significance. It indicates only that the numbers multiplied were *both* expressed in the unit mol/l.

Class 2. If s mol/l of the salt has dissolved when the solution becomes saturated,

$$\underline{Ag_2CO_3} \rightleftarrows 2Ag^+ + CO_3^=,$$

$C_{CO_3^=} = s$ mol/l and $C_{Ag^+} = 2s$ mol/l, since $2Ag^+$ enter the solution for each $CO_3^=$. Since the balanced chemical equation contains $2Ag^+$, any C_{Ag^+} appearing in the solubility product must be *squared*. That is, the solubility product, $C^2_{Ag^+} \times C_{CO_3^=}$ becomes

$$(2s)^2 \times s = 4s^3 \text{ (mol/l)}^3.$$

Similarly for $\underline{PbI_2} \rightleftarrows Pb^{++} + 2I^-$, the ion concentration product, $C_{Pb^{++}} \times C^2_{I^-}$, becomes

$$s \times (2s)^2 = 4s^3 \text{ (mol/l)}^3.$$

But notice that for the three-ion electrolyte, $MgNH_4PO_4$,

$$\underline{MgNH_4PO_4} \rightleftarrows Mg^{++} + NH_4^+ + PO_4^{-3},$$

the ion product is

$$s \times s \times s = s^3 \text{ (mol/l)}^3,$$

since each molecule dissolved furnishes *one ion only* of each of the three ionic species.

Class 3. It should now be obvious to the student that if s is the molar solubility of the salts,

$$\underline{Ag_3AsO_4} \rightleftarrows 3Ag^+ + AsO_4^{-3}$$
$$\underline{Ag_3Co(CN)_6} \rightleftarrows 3Ag^+ + [Co(CN)_6]^{-3},$$

the solubility product will be for both

$$(3s)^3 \times s = 27s^4 \text{ (mol/l)}^4.$$

But notice that for

$$\underline{K_2NaCo(NO_2)_6} \rightleftarrows 2K^+ + Na^+ + Co(NO_2)_6^{-3}$$

the solubility product is

$$(2s)^2 \times s \times s = 4s^4 \text{ (mol/l)}^4.$$

Class 4. Since

$$\underline{Ca_3(PO_4)_2} \rightleftarrows 3Ca^{++} + 2PO_4^{-3} \text{ and} \qquad (8a)$$
$$\underline{Fe_2S_3} \rightleftarrows 2Fe^{+3} + 3S^=, \qquad (9a)$$

the solubility products will be

$$(3s)^3 \times (2s)^2 = 108s^5 \text{ (mol/l)}^5 \qquad (8b)$$
$$(2s)^2 \times (3s)^3 = 108s^5 \text{ (mol/l)}^5. \qquad (9b)$$

These relations make it possible readily to calculate the $K_{s.p.}$ of a difficultly soluble salt if its solubility in mg/ml is known, or its solubility if its $K_{s.p.}$ is known.

Limitations of the Solubility Product Principle

It is to be understood that the solubility product constant gives the product of the ion concentrations in a solution which contains *no other ions* than those of the difficultly soluble salt. It is now known that the solubility *increases* with increasing total concentration of ions in the solution. For instance, AgCl is more soluble in a solution of $NaNO_3$ than it is in water. It is not to be expected, therefore, that, in moderately concentrated solutions containing many different ions, the product of the ion concentrations of a given salt will be exactly, or even very closely, that in pure water. If the activities of the ions are substituted for their concentrations and the total ionic strength of the solution can be computed, the ion product is approximately constant over a much greater range of concentrations. The values of the solubility product constants listed in Table 5 give a rough idea of the relative solubilities of various compounds, but they must not be considered to apply very exactly to solutions containing large concentrations of other electrolytes.

The validity of the solubility product principle has been discussed at length by McAlpine and Soule.[2] They point out that in determinations of the solubility of highly insoluble salts, the constancy of the ion product has been *assumed* as a starting point for calculation. Furthermore, the solubilities of such extremely insoluble substances can be determined only by indirect methods, the validity of which is highly questionable, inasmuch as the values found by individual workers for a given compound may differ by as much as $10^{-4}\,M$. In such determinations there is evidence that important factors such as the presence of CO_2 in the distilled water used, the presence of complex ions, and the time required to reach equilibrium have been neglected. For example, the stated $K_{s.p.}$ of CdS indicates that it should be practically completely precipitated in $6\,N$ HCl. Actually, precipitation is barely visible at about $1\,N$. But this difference is accounted for if the presence of a complex ion, $CdCl_4^{=}$, having an instability constant of the order 10^{-2} is assumed. Probably for the same reason, PbS is visible at smaller concentration than is the far more insoluble HgS. CaC_2O_4 is stated to be only slightly more insoluble than MgC_2O_4. Yet CaC_2O_4 free from Mg^{++} can be precipitated from solutions containing moderately

[2] Prescott and Johnson's *Qualitative Chemical Analysis*, pp. 87–137, Van Nostrand, 1933.

large $C_{Mg^{++}}$. The reason appears to be that MgC_2O_4 precipitates with extreme slowness. Pink MnOHSH is visibly formed at concentrations at which the certainly far more insoluble ZnS does not appear. This is ascribed to the slowness with which ZnS forms.

Common-ion effect. According to the solubility product principle, in a saturated solution of a slightly soluble salt the *product* of the ion concentrations should be a constant at a fixed temperature, but each ion concentration may have any value, one varying inversely as the other. For example, for $BaSO_4$

$$C_{Ba^{++}} \times C_{SO_4^{--}} = K_{s.p.} = 9.9 \times 10^{-11},$$

and in pure water saturated with pure $BaSO_4$

$$C_{Ba^{++}} = C_{SO_4^{--}} = 9.95 \times 10^{-6} M.$$

In the precipitation of Ba^{++} by SO_4^{--} in analysis, if, when precipitation of $BaSO_4$ ceases, $C_{SO_4^{--}}$ in the solution is $0.01 M$, then $C_{Ba^{++}}$ will have to be

$$\frac{9.9 \times 10^{-11}}{1 \times 10^{-2}} = 9.9 \times 10^{-9}.$$

The small excess of SO_4^{--} reduces one thousandfold the $C_{Ba^{++}}$ in the solution. In other words, the precipitation of Ba^{++} is made more complete if a small excess of the precipitating ion is added. Similarly, in precipitating SO_4^{--} by Ba^{++}, a small excess of Ba^{++} should be added.

Effect of a large excess of precipitant. Since in a saturated solution the product of the ion concentrations is fixed, although the ion concentrations themselves may take any value, it follows that increase of one ion concentration must cause corresponding decrease of the other. This would lead to the conclusion that in precipitation the larger the excess of the precipitating ion the more completely the precipitated ion would be removed from the solution.

This conclusion is fallacious for at least two reasons. It has been stated that the solubility and solubility product *increase* decidedly if considerable concentrations of other ions are present. Furthermore, many anions—particularly the halides—are strong complex formers and may change the ion to be precipitated into an unexpected form.

As an example consider the effect of a small excess of I^- in precipitating HgI_2. The solubility at 25° of HgI_2 is 6×10^{-2} gram

per liter, or $0.06/454.5 = 1.32 \times 10^{-4}$ mol/l. and

$$K_{s.p.} = 1.32 \times 10^{-4} \times (2.64 \times 10^{-4})^2 = 9.2 \times 10^{-12} \text{ (mol/liter)}^3.$$

In precipitating Hg^{++} by I^-, we should expect that, if C_{I^-} in the solution were made $0.1\,M$, $C_{Hg^{++}}$ would be reduced to

$$C_{Hg^{++}} = \frac{(9.2 \times 10^{-12})}{0.01} = 9.2 \times 10^{-10} M$$

so that the precipitation of Hg^{++} would be unusually complete. But in the precipitation of Hg^{++} by KI solution, if we continued to add the reagent until C_{I^-} became even $0.01\,M$, we should be astonished by seeing the scarlet precipitate *completely disappear*. This would be due to formation of the very stable anion, $[HgI_4]^=$.

Complex ions are in equilibrium with their component parts,

$$[HgI_4]^= \rightleftarrows Hg^{++} + 4I^-.$$

In the solution

$$\frac{C_{Hg^{++}} \times C^4_{I^-}}{C_{[HgI_4]^=}} = K_{equil.} = 5.3 \times 10^{-31}.$$

In a solution $0.01\,M$ in (free) I^-,

$$C_{Hg^{++}} \times (10^{-2})^4 = 5.3 \times 10^{-31} \times C_{[HgI_4]^=}$$

and $C_{HgI_4^=}$ would have to be about 2×10^{22} times the $C_{Hg^{++}}$ in the solution when equilibrium was reached. This shows that so long as even a minute C_{I^-} was in solution any solid HgI_2 would have to dissolve to form the iodomercurate anion.

$$\underline{HgI_2} + 2I^- = HgI_4^=$$

Such stable complex anions are formed by the halides, the pseudohalides CN^- and NCS^-, and by $C_2O_4^=$ and $S_2O_3^=$. It follows that in the use of any of these anions as precipitants a large excess is to be carefully avoided.

Metastable Equilibrium

Supersaturation. It is to be kept in mind that while the solubility product principle gives the ion concentrations in equilibrium with the solid phase, it says nothing about the *time required* to reach

equilibrium. As a matter of fact, several hours, or even months, may be required to reach equilibrium. Many substances, particularly those containing water of crystallization, are able to remain dissolved in concentrations far beyond that corresponding to their solubilities. The solution has reached a state of *false equilibrium*. If into a supersaturated solution a tiny crystal of the solute is introduced, crystal formation will proceed until the product of the ion concentrations becomes equal to the solubility product. Instances of such false equilibria are occasionally met in analysis. They are overcome by centrifugation, by vigorous stirring, or by rubbing the inner walls of the container with a glass rod. The slight scratches produced by the latter on the walls of the container apparently provide tiny sharp surfaces which serve as nuclei for crystal growth. However, the same effect is produced when the end of the glass rod is covered with a rubber "policeman." In this case the surface of the glass container cannot be abraded. It has been suggested that even the cleanest glass is covered by a thin film of foreign matter and that the removal of this film is all that is necessary to start crystallization.

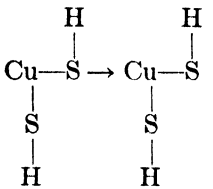
Precipitation of the Metallic Sulfides

The commonly accepted mechanism of precipitation of sulfides by concentrations of sulfide ion of the order 10^{-15} to $10^{-25}\,M$ seems rather incredible.

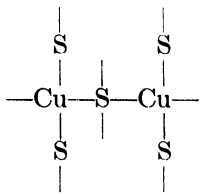
Considering the vanishingly small $C_{S^=}$ in $0.3\,N$ HCl saturated with H_2S, it seems highly improbable that this ion is the precipitating agent. It has been repeatedly noticed that during washing, sulfides continuously lose H_2S in amounts far greater than that which could be absorbed on the surface of the precipitate. Much evidence will be found in the laboratory manual of this text that sulfides change solubility very decidedly during washing. It would seem more probable that HS^- is the precipitating ion. Considering the great similarity of the molecules H_2S and H_2O, it would seem reasonable that the first step in the mechanism of precipitation should be replacement of H_2O in the hydrated ions either by H_2S or by HS^-, followed by linking of metal ions (Me) by HS^- exactly as, in hydroxides, metal ions are linked by OH^-. On aging, HS^- links may become —Me—S—Me— links exactly as —Me—O—Me— links have been shown to form during aging of hydroxides.

$$[Cu(H_2O)_4]^{++} \rightarrow [Cu(H_2O)_3HS]^{+} \rightarrow [(HS)_2Cu(H_2O)_2]$$

On flocculation, water might be squeezed out and such a three-dimensional covalent structure result as



Upon aging, analogy with hydroxide gels would lead to



forming a three-dimensional lattice.

The freshly precipitated sulfides, like the hydroxides, must undergo continuous change of composition and rearrangement of structure on standing and drying. *Changes of solubility must result.* There is no reason to suppose that the solubility of the dry aged sulfide bears much relation to that of the freshly precipitated moist substance.

Validity of the solubility product constants of the sulfides. Many of the values given in Table 5 (p. 110) appear fantastically small. If the C_{S^-} in $0.3N$ H^+ saturated with H_2S is of the order $10^{-22}M$, many of the sulfides should precipitate in concentrations of acid in which no trace of precipitate is formed. The fallacy of applying solubility product constants to precipitation of sulfides appears in the following examples:

Study of the reaction

$$\underline{As_4S_6} + 8H_2O \rightleftarrows 4HAsO_2 + 6H_2S$$

leads to a solubility product "constant" of 2×10^{-23}. From solubility determinations the "constant" for Fe_2S_3 has been reported as 10^{-88}, that of Bi_2S_3 as 10^{-72}. But H_2S precipitates As^{+3} practically completely even from hot $12N$ HCl. Bi_2S_3 is completely precipitated by H_2S from $5N$ HCl, while Fe_2S_3 can be precipitated only in

basic solutions. Experiments show that the following sulfides can be precipitated practically completely in acid of the concentration stated:

Hot	12 *N* HCl	As_4S_{10}, As_4S_6
Cold	" " "	$Hg_3Cl_2S_2$ (white)
"	10 " "	HgS, CuS
"	8 " "	Sb_2S_3
"	5 " "	Bi_2S_3, SnS_2
"	2 " "	SnS
"	0.3 " "	PbS, CdS
Acetic acid		ZnS
Buffered acetic acid		FeS, CoS, NiS (more or less completely, according to extent of buffering)

These experimental results show that the published values of the solubility product constants of these sulfides bear no close relation to the conditions in which the latter are precipitated completely by H_2S.

Table 5 gives presently accepted values of some solubility product constants mostly at 25°. Most of the values have been taken from Latimer's *Oxidation Potentials*.[3]

The Mutual Relation of Precipitation and Dissolution

The dissolution of a solid is the exact converse of its precipitation. According to the solubility product principle, dissolution must take place whenever in the solution the product of the ion concentrations is kept less than the $K_{s.p.}$. It follows then that presence of any substance which will remove one of the ions of the dissolving substance will promote the dissolution of that substance. $BaSO_4$, although nearly insoluble in water, dissolves largely in 36 *N* H_2SO_4 because

$$\underline{BaSO_4} + H_2SO_4 \rightleftarrows Ba^{++} + 2HSO_4^-.$$

AgCl although nearly insoluble in water, dissolves readily in NH_3 solution because

$$\underline{AgCl} + 2NH_3 \rightleftarrows Ag(NH_3)_2^+ + Cl^-.$$

[3] W. M. Latimer, *The Oxidation States of the Elements and their Potentials in Aqueous Solutions*, Prentice-Hall, 1938.

TABLE 5
SOLUBILITY PRODUCTS

SUBSTANCE	$K_{s.p.}$ (25°)	SUBSTANCE	$K_{s.p.}$ (25°)
Acetate		**Hydroxides** (*Cont.*)	
$AgC_2H_3O_2$	1.9×10^{-3}	$Ca(OH)_2$	7.9×10^{-6}
Bromides		$Co(OH)_2$	2×10^{-16}
CuBr	5.3×10^{-9}	$Co(OH)_3$	2.5×10^{-43}
Hg_2Br_2	5.2×10^{-23}	CuOH	1.2×10^{-15}
$PbBr_2$	6.3×10^{-6}	$Cu(OH)_2$	5.6×10^{-20}
AgBr	3.3×10^{-13}	$Fe(OH)_2$	1.7×10^{-15}
Carbonates		$Pb(OH)_2$	2.8×10^{-16}
$BaCO_3$	4.9×10^{-9}	$Mg(OH)_2$	3.4×10^{-11}
$CdCO_3$	2.5×10^{-14}	$Mn(OH)_2$	7.1×10^{-15}
$CaCO_3$	4.8×10^{-9}	$Hg_2(OH)_2$	1.6×10^{-23}
$CuCO_3$	1.4×10^{-10}	$Hg(OH)_2$	1.7×10^{-26}
$FeCO_3$	2.1×10^{-11}	$Ni(OH)_2$	1.6×10^{-14}
$PbCO_3$	1.5×10^{-13}	AgOH	2×10^{-8}
Li_2CO_3	4×10^{-3}	$Sr(OH)_2 \cdot 8H_2O$	3.2×10^{-4}
$MgCO_3 \cdot 3H_2O$	ca. 1×10^{-5}	$Sn(OH)_2$	5×10^{-26}
$MnCO_3$	8.8×10^{-11}	$Zn(OH)_2$	4.5×10^{-17}
Hg_2CO_3	9×10^{-17}	**Iodides**	
$NiCO_3$	1.4×10^{-7}	CuI	1.1×10^{-12}
Ag_2CO_3	8.2×10^{-12}	Hg_2I_2	4.5×10^{-29}
$Sr(HCO_3)_2$	1.8×10^{-6}	PbI_2	8.7×10^{-9}
$SrCO_3$	9.4×10^{-10}	AgI	8.5×10^{-17}
$ZnCO_3$	6×10^{-11}	**Nitrate**	
Chlorides		$Ba(NO_3)_2$	4.5×10^{-3}
BiOCl	7×10^{-9}	**Nitrite**	
CuCl	1.85×10^{-7}	$AgNO_2$	2.4×10^{-4}
Hg_2Cl_2	1.1×10^{-18}	**Oxalates**	
$PbCl_2$	1.7×10^{-5}	$BaC_2O_4 \cdot 2H_2O$	1.1×10^{-7}
AgCl	1.7×10^{-10}	$CaC_2O_4 \cdot H_2O$	2.3×10^{-9}
Chromates		MgC_2O_4	8.6×10^{-5}
$BaCrO_4$	2×10^{-10}	$Hg_2C_2O_4$	1×10^{-13}
$PbCrO_4$	1.8×10^{-14}	$Ag_2C_2O_4$	1.1×10^{-11}
Hg_2CrO_4	2×10^{-9}	$SrC_2O_4 \cdot H_2O$	5.6×10^{-8}
Ag_2CrO_4	1.1×10^{-12}	**Phosphates**	
$SrCrO_4$	3.6×10^{-5}	$CaHPO_4$	ca. 5×10^{-6}
Fluorides		$PbHPO_4$	4×10^{-12}
BaF_2	1.7×10^{-6}	$MgNH_4PO_4$	2.5×10^{-13}
CaF_2	3.9×10^{-11}	**Potassium Salts**	
PbF_2	3.7×10^{-8}	$KClO_4$	1.1×10^{-2}
LiF	5.2×10^{-3}	K_2PtCl_6	1.1×10^{-5}
MgF_2	6.4×10^{-9}	$K_2NaCo(NO_2)_6 \cdot H_2O$	ca. 2.2×10^{-11}
SrF_2	3×10^{-9}	**Sulfates**	
Hydroxides		$BaSO_4$	9.9×10^{-11}
SbOOH	ca. 10^{-17}	$CaSO_4 \cdot 2H_2O$	2.4×10^{-5}
$Ba(OH)_2 \cdot 8H_2O$	5×10^{-3}	$PbSO_4$	1.8×10^{-8}
BiOOH	ca. 1×10^{-12}	Hg_2SO_4	6.2×10^{-7}
$Cd(OH)_2$	1.2×10^{-14}	$SrSO_4$	2.8×10^{-7}

TABLE 5.—(*Continued*)
SOLUBILITY PRODUCTS

SUBSTANCE	$K_{s.p.}$ (25°)	SUBSTANCE	$K_{s.p.}$ (25°)
Sulfides		**Sulfides** (*Cont.*)	
$Sb_4S_6 + 4H_2O + 4H^+ \leftrightarrows 4SbO^+ + 6H_2S$	10^{-30}	Hg_2S	1×10^{-45}
		HgS	3×10^{-53}
$As_4S_6 + 8H_2O \leftrightarrows 6H_2S + 4HAsO_2$	2×10^{-23}	NiS	3×10^{-21}
		NiS	1×10^{-26}
Bi_2S_3	1.6×10^{-72}	NiS	2×10^{-28}
CdS	1.4×10^{-28}	Ag_2S	1×10^{-51}
CoS	7×10^{-23}	SnS	8×10^{-29}
CoS	1.9×10^{-27}	SnS_2	ca. 10^{-46}
Cu_2S	2.5×10^{-50}	ZnS	4.5×10^{-24}
CuS	4×10^{-38}	**Thiocyanates**	
FeS	1×10^{-19}	CuNCS	4×10^{-14}
Fe_2S_3	1×10^{-88}	$Hg_2(NCS)_2$	3×10^{-20}
PbS	1×10^{-29}	AgNCS	1×10^{-12}
MnS	5.6×10^{-16}	TlNCS	5.8×10^{-4}

Calcium phosphate is highly insoluble in water but readily and largely soluble in acetic acid because all primary phosphates are very soluble,

$$Ca_3(PO_4)_2 + 4AcOH \rightleftarrows 3Ca^{++} + 2H_2PO_4^- + 4AcO^-.$$

When the solid salts are in the presence of their saturated solutions, the ion concentration products equal the respective solubility product constants.

$$C_{Ba^{++}} \times C_{SO_4^-} = K_{s.p.}\ BaSO_4$$
$$C_{Ag^+} \times C_{Cl^-} = K_{s.p.}\ AgCl$$
$$C^3_{Ca^{++}} \times C^2_{PO_4^{-3}} = K_{s.p.}\ Ca_3(PO_4)_2$$

If to the saturated solutions any substance be added which lowers the concentration of one of the ions, the ion concentration product in the solution becomes less than the $K_{s.p.}$ and more solid must dissolve. This must continue as long as the ion concentration product in the solution is *kept less* than the $K_{s.p.}$ In the above cases SO_4^- is changed to HSO_4^-, Ag^+ to $Ag(NH_3)_2^+$, and PO_4^{-3} to $H_2PO_4^-$. So long as excess of the reagent is present, the solid must continue to dissolve.

Ions can be removed from saturated solutions, and hence

insoluble compounds made more soluble, in the following ways:

1. *By formation of a less ionized substance.*
$$\underline{CaC_2O_4} + H_3O^+ + Cl^- \rightleftarrows Ca^{++} + HC_2O_4^- \text{ (or } H_2C_2O_4) + Cl^- + H_2O$$
2. *By formation of a slightly soluble and slightly ionized gas.*
$$\underline{FeS} + 2H_3O^+ \rightleftarrows Fe^{++} + \overline{H_2S} + 2H_2O$$
3. *By formation of a complex ion.*
$$\underline{AgCl} + 2NH_3 \rightleftarrows Ag(NH_3)_2^+ + Cl^-$$
4. *By oxidizing one of the ions.*
$$\underline{CuS} + H_3O^+ + NO_3^- \rightarrow Cu^{++} + \underline{S} + \overline{NO} + H_2O$$
5. *By ampholytes (amphoteric gels) becoming more soluble in either acids or bases.*
$$\underline{(H_2O)_3Al(OH)_3} + H_3O^+ \rightleftarrows [(H_2O)_4Al(OH)_2]^+, \text{ etc.}$$
$$\underline{(H_2O)_3Al(OH)_3} + OH^- \rightleftarrows [(H_2O)_2Al(OH)_4]^-, \text{ etc.}$$

Dissolution may be caused by the simultaneous effect of two or more of the above actions:

$$\underline{Sb_2S_3} + 2H_3O^+ \rightleftarrows 2SbO^+ + \overline{3H_2S} \text{ (2 and 3)}$$
$$\underline{HgS} + \overline{Cl_2} + Cl^- \rightleftarrows [HgCl_3]^- + \underline{S} \text{ (3 and 4)}$$

Metathesis of slightly soluble salts with sodium carbonate solution. In analysis for anions it is customary to bring into solution the anions of sparingly soluble salts by boiling with $3N$ Na_2CO_3 solution. The carbonates or hydroxides of most cations except Na^+, K^+, and NH_4^+ are rather insoluble in water. Boiling with moderately concentrated Na_2CO_3 solution tends to precipitate the cations, which might interfere with the anion analysis and bring into solution the anions. For example,

$$\underline{FeSO_4 \cdot 7H_2O} + CO_3^= \rightarrow \underline{FeCO_3} + SO_4^=$$
$$\underline{Fe[FeCl_6]} + 6CO_3^= + 4H_2O \rightarrow \underline{2FeOOH} + 6HCO_3^- + 6Cl^-$$

To what extent a slightly soluble salt will give up its anions to the solution must depend on the ratio of its $K_{s.p.}$ to that of the carbonate of its cation. This dependence becomes evident when the following three cases are considered.

Case 1. The $K_{s.p.}$ (at 25°) of $BaSO_4$ is given as 9.9×10^{-11}. The $K_{s.p.}$ of $BaCO_3$ is given as 4.9×10^{-9}. If $BaSO_4$ is boiled with

$3N$ Na_2CO_3 solution until the latter is *in equilibrium* with both salts, the following equations must become simultaneous since but one $C_{Ba^{++}}$ can be in the solution.

$$C_{Ba^{++}} \times C_{SO_4^{=}} = 9.9 \times 10^{-11} \quad (10)$$
$$C_{Ba^{++}} \times C_{CO_3^{=}} = 4.9 \times 10^{-9} \quad (11)$$

Dividing (10) by (11) we obtain for the state of equilibrium,

$$\frac{C_{SO_4^{=}}}{C_{CO_3^{=}}} = \frac{9.9 \times 10^{-11}}{4.9 \times 10^{-9}} = 2 \times 10^{-2}.$$

That is, when the solution is saturated with respect to both salts, $C_{SO_4^{=}}$ should be about 0.02 that of $C_{CO_3^{=}}$.

If excess of $BaSO_4$ is boiled with $3N$ Na_2CO_3 solution until equilibrium is reached,

$$\underline{BaSO_4} + CO_3^{=} \rightleftarrows \underline{BaCO_3} + SO_4^{=}.$$

Since for each $SO_4^{=}$ entering the solution a $CO_3^{=}$ is precipitated, if at equilibrium $C_{SO_4^{=}} = x\,M$, then $C_{CO_3^{=}}$ remaining will be $(1.5 - x)\,M$. Then

$$\frac{x}{(1.5 - x)} = 0.02$$

and $x = 2.94 \times 10^{-2} M$. If 5 ml of $3N$ Na_2CO_3 were taken and the same volume were maintained throughout the transposition, the weight of $SO_4^{=}$ in the 5 ml would be

$$2.94 \times 10^{-2} \frac{\text{m.mol}}{\text{ml}} \times 96 \frac{\text{mg}}{\text{m.mol}} \times 5 \text{ ml.} = 14.11 \text{ mg.}$$

One ml of the solution would contain about 2.8 mg of $SO_4^{=}$, ample to secure a good test for the ion.

Case 2. That silver halides are scarcely affected by $3N$ Na_2CO_3 is shown by the following calculation for AgCl. At equilibrium

$$C_{Ag^+} \times C_{Cl^-} = 1.7 \times 10^{-10} \text{ and}$$
$$C^2_{Ag^+} \times C_{CO_3^{=}} = 8.2 \times 10^{-12}.$$

Squaring the first equation, we obtain for equilibrium

$$\frac{C^2_{Cl^-}}{C_{CO_3^{=}}} = \frac{2.89 \times 10^{-20}}{8.2 \times 10^{-12}} = 3.53 \times 10^{-9}.$$

The value of the $K_{equil.}$ shows that very little Cl^- will be formed and, consequently, that at equilibrium $C_{CO_3^{=}}$ will not differ appre-

ciably from 1.5 M. Hence, placing $x = C_{Cl^-}$, we may write $x^2 = 1.5 \times 3.53 \times 10^{-9}$, whence $x = 7.3 \times 10^{-5} M$. One ml of the Na_2CO_3 solution would contain only 0.0026 mg of Cl^-.

Case 3. A quite insoluble salt may be practically completely transposed by 3 N Na_2CO_3. An example is PbI_2. At equilibrium

$$C_{Pb^{++}} \times C^2_{I^-} = 8.7 \times 10^{-9} \text{ and}$$
$$C_{Pb^{++}} \times C_{CO_3^=} = 1.5 \times 10^{-13}.$$

At equilibrium

$$\frac{C^2_{I^-}}{C_{CO_3^=}} = 5.8 \times 10^4.$$

The very large value, 58,000, of the $K_{equil.}$ shows that in this case practically all the $CO_3^=$ will be precipitated as $PbCO_3$. Solving

$$\frac{x^2}{1.5 - x} = 58{,}000 \textit{ as a quadratic,}$$

$1.5 - x$, the $C_{CO_3^=}$ remaining, would be less than $10^{-5} M$. This indicates that excess of PbI_2 would react as long as more than a trace of $CO_3^=$ remained in the solution.

PARTITION OF A SOLUTE BETWEEN TWO IMMISCIBLE SOLVENTS

In Chapter 6, page 69, it was pointed out that partition of a solute between two immiscible solvents constitutes a heterogeneous equilibrium, since the two solutions (phases) are separated by a definite boundary surface. The Law of Equilibrium when applied to this case is frequently called the *Partition Law.*

The Law of Partition. At any given temperature, when equilibrium is reached, the molar concentration of the solute in one solvent bears a fixed ratio to its molar concentration in the other solvent. This ratio is independent of the relative amounts of the two solvents and also of the total amount of solute, *provided* that its molecular weight is the same in both solvents.[4] The value of the ratio varies with temperature, the nature of the solute, and the natures of the two solvents employed. It must be determined by experiment for each case and for each desired temperature.

[4] Organic molecules are sometimes polymerized in certain organic solvents For example, the molecular weight of acetic acid dissolved in benzene approximates closely that of the doubled formula $(AcOH)_2$.

The following consideration of the equilibrium conditions between iodine in water and iodine in CCl_4 will make it evident that this variety of heterogeneous equilibrium differs in no essential particular from that between a solid and its saturated aqueous solution.

If a suspension of iodine in water is shaken with CCl_4, some of the iodine will pass from the water into the CCl_4. If a solution of iodine in CCl_4 is shaken with water, some iodine will pass into the water. The reaction

$$I_2 \text{ (water)} \rightleftarrows I_2(CCl_4)$$

is therefore reversible and when the iodine is entering and leaving the water phase with equal velocities the opposing reactions are in a state of equilibrium and

$$\frac{C_{I_2}(CCl_4)}{C_{I_2}(\text{water})} = K_{\text{equil.}}$$

If the value of the $K_{\text{equil.}}$ can be determined by experiment, it is possible to calculate the amount removed from a given volume of one solvent[5] when shaken with a given volume of the other solvent. This is best understood by an example.

Example. Iodine is 85 times as soluble in CCl_4 as in water. If 10 mg iodine suspended in 4 ml of water is shaken with 1 ml of CCl_4 until equilibrium is reached, how many mg should pass into the CCl_4?

Solution. Since the molecular weight of I_2 is the same in both solvents, concentrations may be expressed in mg per ml instead of

[5] For partition of acetic acid between benzene and water, the chemical reaction would be

$$2AcOH \text{ (water)} \rightleftarrows (AcOH)_2 \text{ (benzene)}.$$

The equilibrium expression would be

$$\frac{C_{(AcOH)_2} \text{ (benzene)}}{C^2_{AcOH} \text{ (water)}} = K_{\text{equil.}}$$

In general, if the solute has the molecular formula A in water and the molecular formula $(A)_n$ in the solvent S, then, at equilibrium,

$$\frac{C^n_A \text{ (water)}}{C_{(A)_n} (S)} = K_{\text{equil.}}$$

in m.mols per ml. We have then *at equilibrium*

$$\frac{\frac{x \text{ mg}}{1 \text{ ml}}}{\frac{10 - x \text{ mg}}{4 \text{ ml}}} = 85, \text{ whence } \frac{4x}{10 - x} = 85.$$

Solving, $x = 9.55$ mg and $10 - x = 0.45$ mg. At equilibrium 9.55 mg I_2 will be in the 1 ml of CCl_4 and 0.45 mg will remain in the 4 ml of water.

PROBLEMS

1. From the solubility product constants in Table 5 and the Table of Atomic Weights calculate the solubilities of the following compounds (1) in m.mols per ml, (2) in mg per ml:

$BaCrO_4$	$BiOCl$	$AgNO_2$	$Ca(OH)_2$	Bi_2S_3
$PbCrO_4$	Hg_2Cl_2	$Ag_2C_2O_4$	$Mg(OH)_2$	SnS_2

2. Given the following solubilities in mg per ml, calculate the solubility products (data from Lange's Handbook [1934]).

$BaCO_3$	0.022	AgBr	8.4×10^{-5}	$PbCl_2$	6.73
$CaCO_3$	0.065	Ag_2CrO_4	0.014	PbI_2	0.442

3. $Pb_3(PO_4)_2$ is soluble to the extent of 1.4×10^{-5} g per 100 ml H_2O. Calculate a value for the $K_{s.p.}$. *Ans.* $1.65 \times 10^{-32} M$.

4. If the $K_{s.p.}$ of $Mg(OH)_2$ is 3.4×10^{-11}, what is the largest C_{OH^-} that could be in a solution $0.03 M$ in Mg^{++} without a precipitate forming? *Ans.* $3.36 \times 10^{-5} M$.

5. Assume that the K_{ion} of $(AcO)_2Pb$ is 1.66×10^{-4} and that the $K_{s.p.}$ of $PbSO_4$ is 1×10^{-8}. In a solution $0.02 M$ in $(AcO)_2Pb$ and $0.02 M$ in $SO_4^{=}$, what C_{AcO^-} should just prevent precipitation of $PbSO_4$? *Ans.* $2.577 M$.

6. If the $K_{s.p.}$ of $BaCrO_4$ is 2.25×10^{-10}, what is the largest $C_{Ba^{++}}$ (137.4) that can be in a solution $0.0025 M$ in $CrO_4^{=}$ without precipitating? What fraction of a mg of Ba^{++} would this be in 1 ml of solution? *Ans.* (1) $9 \times 10^{-8} M$, (2) 1.237×10^{-5} mg.

7. A solution is $0.02 M$ in Ba^{++} and $0.3 M$ in Sr^{++}; to this is slowly added solid Na_2SO_4. Assuming no volume change as the solid is added, and having given $K_{s.p.}$ $SrSO_4 = 2.9 \times 10^{-7}$ and $K_{s.p.}$ $BaSO_4 = 1.1 \times 10^{-10}$, (*a*) what is $C_{Ba^{++}}$ when $SrSO_4$ begins to

precipitate? (*b*) when $C_{Sr^{++}} = 0.02$ what is $C_{Ba^{++}}$? *Ans.* (*a*) $1.138 \times 10^{-4} M$, (*b*) $7.59 \times 10^{-6} M$.

8. The $K_{s.p.}$ of Bi_2S_3 is said to be 10^{-72}. Given a solution which is $0.001\,M$ in Bi^{+3} and $0.3\,N$ in H^+, calculate the $C_{Bi^{+3}}$ left in solution after saturation with H_2S. The ion product of H_2S is 1.15×10^{-23} in a saturated solution at 25°. *Ans.* $6.92 \times 10^{-4} M$.

9. Two ml of a solution is $0.2\,M$ in Mg^{++} and $0.4\,M$ in NH_4^+. If 1 ml of $1N$ NH_3 solution is added, will $Mg(OH)_2$ precipitate? K_{ion} NH_3 solution $= 1.8 \times 10^{-5}$; $K_{s.p.}$ $Mg(OH)_2 = 3.4 \times 10^{-11}$. *Ans.* Yes. $C_{Mg^{++}}$ left in solution $= 6.71 \times 10^{-2} M$.

10. When 1 ml of solution $0.3\,N$ in H^+ was saturated with H_2S, 1.7×10^{-5} mg of Pb^{++} escaped precipitation. Calculate the $K_{s.p.}$ of PbS. *Ans.* 1.05×10^{-29}.

11. In a solution saturated with the very slightly soluble salt $Pb_3(PO_4)_2$, the $C_{PO_4^{-3}}$ is $3 \times 10^{-7} M$. Considering the dissolved portion as completely ionized, what is the $C_{Pb^{++}}$ in this solution? *Ans.* $C_{Pb^{++}} = 4.5 \times 10^{-7} M$.

12. What $C_{C_2O_4^{=}}$ is necessary to just start precipitation of CaC_2O_4 from a saturated solution of $CaSO_4$? *Ans.* $4.7 \times 10^{-7} M$.

13. Solid $Pb(NO_3)_2 \cdot H_2O$ is slowly added to 5 ml of $0.001\,M$ K^+I^- solution. How many mg of the salt would need to be added before PbI_2 started to precipitate? *Ans.* 15.2 mg.

14. The $K_{s.p.}$ of Ag_3PO_4 is 1.8×10^{-18} and that of AgI is 8.5×10^{-17}. Show by calculation which of these salts has the greater molar solubility.

15. The solubility of bromine in CCl_4 is 26 times that in water. If 15 mg of Br_2 in 5 ml of water is shaken with 1 ml of CCl_4, how many mg should pass into the CCl_4? *Ans.* 12.6 mg.

16. If the CCl_4 layer obtained in problem 15 is drawn off and the water layer again shaken with 1 ml of fresh CCl_4, how many mg of Br_2 should remain in the water layer? *Ans.* 0.4 mg.

17. If 50 mg of Br_2 are in 8 ml of water, show by calculation whether more Br_2 would be removed by shaking once with 3 ml of CCl_4 or by shaking with three successive 1 ml portions of CCl_4, the CCl_4 layer being removed after each shaking.

18. A solution contains 2 mg/ml of Cu^{++} (at. wt. Cu = 63.6) and is $2\,M$ in AcOH. To 1 ml of it is added 0.5 ml $3\,N$ NaOH, and

the resulting solution is saturated with H_2S. (A saturated solution of H_2S is 0.1 *M*.)

$$K_I\ H_2S = 1.15 \times 10^{-7};\ K_{II}\ H_2S = 1.0 \times 10^{-15}$$
$$K_{s.p.}\ CuS = 4.0 \times 10^{-38};\ K\ AcOH = 1.85 \times 10^{-5}$$

Show by calculation:

	Ans.
(*a*) C_{H^+} in the solution.	6.2×10^{-6} *M*.
(*b*) The ion product of H_2S.	1.15×10^{-23} " .
(*c*) C_{S^-} in the solution.	3.025×10^{-13} " .
(*d*) C_{HS^-} in the solution.	1.86×10^{-3} ".
(*e*) Whether or not a precipitate is obtained.	Yes.
(*f*) $C_{Cu^{++}}$ left in the solution.	1.32×10^{-25} ".

19. If the $K_{s.p.}$ of CaF_2 is 3.9×10^{-11} and that of $CaCO_3$ is 4.8×10^{-9}, what C_{F^-} (at. wt. = 19) in (*a*) m.mol/ml, and (*b*) mg/ml should be in 3 *N* Na_2CO_3 solution which has reached equilibrium with an excess of CaF_2? *Ans.* (*a*) 0.106 m.mol/ml, (*b*) 2.02 mg/ml.

20. State the effect of prolonged boiling with 3 *N* Na_2CO_3 upon arsenious sulfide, ammonium alum, ferric phosphate, lead chromate, calcium fluoride, bismuth sulfide. Write (and underscore) formulas of insoluble compounds formed and formulas of ions in solution.

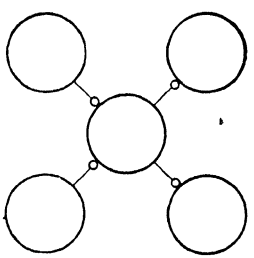
21. If excess of solid Ag_2CrO_4 is boiled with 5 ml of 3 *N* Na_2CO_3 until equilibrium is reached and then cooled to 25°, how many mg of CrO_4^- should be in each ml of the solution? What fraction of the CO_3^- should have been precipitated as Ag_2CO_3? *Ans.* 20 mg. About 0.12.

CHAPTER 9

HYDROLYSIS

As a strongly dipolar molecule, water has a marked tendency to coordination. In conformity with the maximum coordination number 4 for oxygen (Period 2), ice at very low temperatures[1] is indicated by X-ray investigations to have as the lattice unit $(H_2O)_5$, four molecules being attached to the fifth molecule by hydrogen bonds.[2]

In the three-dimensional lattice each oxygen appears to be coordinated to two H_2O molecules through its own hydrogen atoms and to two other molecules through one of their hydrogen atoms.



ICE MOLECULE

Liquid water probably consists of minute broken-down fragments of the ice structure, as is evidenced by its boiling point. Uncoordinated H_2O would be a low boiling gas. In ice at 0° appreciable amounts of three-coordinated and two-coordinated molecules are present. In the range 25–90° the average molecular weight is slightly greater than that for two-coordinated molecules. According to present views the increased apparent ionization of water at temperatures near 100° is due partly to decoordination of water complexes increasing the actual concentration of the molecule H_2O.

PROTON EXCHANGE IN AQUEOUS SOLUTION

According to the modern definitions of acid, base, and salt (Chapter 7), both neutralization and its opposed reaction, hydrolysis, become simply cases of *proton exchange.*

[1] Only at extremely low temperatures could the strength of hydrogen bonds approach that of ordinary covalent bonds.

[2] Bernal and Fowler, J. Chem. Phys., **1**, 515 (1933); Leighton, *et al.*, J. Am. Chem. Soc., **59**, 1134 (1937).

$$\underset{\text{ACID}_1}{H_3O^+} + \underset{\text{BASE}_2}{OH^-} \underset{\text{hydrolysis}}{\overset{\text{neutralization}}{\rightleftharpoons}} \underset{\text{ACID}_2}{H_2O} + \underset{\text{BASE}_1}{H_2O}$$

$$NH_4^+ + H_2O \underset{\text{neutralization}}{\overset{\text{hydrolysis}}{\rightleftharpoons}} H_3O^+ + NH_3$$

$$H_2O + CO_3^= \underset{\text{neutralization}}{\overset{\text{hydrolysis}}{\rightleftharpoons}} HCO_3^- + OH^-$$

The following illustrations show how the varying tendency of different acids to release protons and the varying tendency of different bases to take up protons can cause similar reactions to proceed very differently.

$$\underset{A_1}{HCl} + \underset{B_2}{H_2O} \rightarrow \underset{A_2}{H_3O^+} + \underset{B_1}{Cl^-} \qquad (1)$$

$$HCN + H_2O \leftarrow H_3O^+ + CN^- \qquad (2)$$

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3 \qquad (3)$$

Reaction (1) proceeds almost completely to the right because H_2O has a far greater tendency to add protons than has Cl^-. Contrariwise, reaction (2) tends to proceed to the left because CN^- as a stronger base than H_2O takes protons from H_3O^+ to form HCN. Reaction (3) will proceed only to a slight extent in either direction because NH_4^+ has little more tendency to donate protons than does H_3O^+ and because in proton accepting power NH_3 and H_2O do not differ greatly.

As potential proton donors, all molecules and ions such as those listed below must be considered to be *acids*.

NEUTRAL MOLECULES	ANIONS	CATIONS
HCl	$H_2PO_4^-$	H_3O^+
AcOH	$HPO_4^=$	NH_4^+
H_2O	$HC_2O_4^-$	$[Zn(H_2O)_4]^{++}$
H_3PO_4	HSO_4^-	$[Fe(H_2O)_6]^{+3}$
$[(H_2O)_3Al(OH)_3]$		

As potential proton acceptors, all molecules and ions such as the following must be considered to be *bases*.

NEUTRAL MOLECULES	ANIONS	CATIONS
H_2O	OH^-	$[(H_2O)_3Zn\ OH]^+$
NH_3	PO_4^{-3}	$[(H_2O)_5Al\ OH]^{++}$
$[(H_2O)_3Al(OH)_3]$	$HPO_4^=$	
	CN^-	
	$[Al(OH)_6]^{-3}$	

BEHAVIOR OF SALTS IN AQUEOUS SOLUTION

Many aqueous solutions of salts are not neutral, that is, their *p*H is not exactly 7. Some salt solutions are acidic, others are basic. This was formerly explained as being caused *solely* by one or both ions of the salt taking H^+ or OH^- from water molecules. The modern view attributes it to competition for protons by *all* the various bases present, of which water is merely one.

Any aqueous solution of an electrolyte (salt) will be acid if the ions have a greater *net* tendency to give protons to water than to take them from water. It will be basic if the ions have a greater *net* tendency to take protons from water than to donate them to water.

In the following pages hydrolysis will be considered as competition for protons. From this point of view, it appears necessary to consider the behavior of salts in aqueous solutions as classifiable into six types.

Type I. The cation has no appreciable tendency to give up protons and the anion has no appreciable affinity for protons.

Example. A solution of Na^+Cl^-.

$$Na^+ + Cl^- + H_2O \rightleftarrows Na^+ + Cl^- + H_2O$$

Na^+ cannot donate protons to H_2O to form H_3O^+, and Cl^- has practically no affinity for protons. In consequence, when pure Na^+Cl^- is dissolved in water, no proton exchange takes place and $C_{H_3O^+}$ and C_{OH^-} in equilibrium with H_2O remain unchanged from what they were in the solvent water.

Type II. The anion of the salt tends to take on protons while the cation has little or no tendency to give off protons.

Example. A solution of Na^+CN^-.

$$\underset{B_1}{Na^+} + \underset{A_2}{CN^-} + \underset{}{H_2O} \rightleftarrows \underset{A_1}{HCN} + \underset{B_2}{OH^-} + \underset{}{Na^+}$$

Since the anion is able to take protons from H_2O, OH^- accumulates in the solution, which therefore shows a basic reaction.

Type III. The cation is able to give off protons while the anion has little or no tendency to acquire them.

Example 1. A solution of $NH_4^+Cl^-$.

$$\underset{A_1}{NH_4^+} + \underset{B_2}{Cl^-} + \underset{}{H_2O} \rightleftarrows \underset{A_2}{H_3O^+} + \underset{B_1}{NH_3} + \underset{}{Cl^-}$$

Example 2. A solution of $AlCl_3 \cdot 6H_2O$.

$$\underset{A_1}{[Al(H_2O)_6]^{+3}} + 3Cl^- + \underset{B_2}{H_2O} \rightleftarrows \underset{B_1}{[Al(H_2O)_5\,OH]^{++}} + \underset{A_2}{H_3O^+} + 3Cl^-$$

Cl^- has little or no affinity for protons, but NH_4^+ and $[Al(H_2O)_6]^{+3}$ have a greater tendency to yield them than has H_3O^+. In consequence, H_2O will take protons from NH_4^+ and from $[Al(H_2O)_6]^{+3}$ to a certain extent to form H_3O^+ making the solutions slightly acidic.

Type IV. The anion is amphoteric and the cation is not a proton donor.

Example 1. A solution of $Na^+H_2PO_4^-$.

$$\begin{array}{llll} \underset{A_1}{H_2PO_4^-} + \underset{B_2}{H_2O} & \rightleftarrows \underset{B_1}{HPO_4^=} + \underset{A_2}{H_3O^+} & (4a) \\ \underset{B_2}{H_2O} + \underset{A_1}{H_2PO_4^-} & \rightleftarrows \underset{B_1}{OH^-} + \underset{A_2}{H_3PO_4} & (4b) \end{array}$$

Since the anion of the salt acts simultaneously as proton donor and proton acceptor, in this type of salt solution there is competition for protons among *four* bases, $H_2PO_4^-$, $HPO_4^=$, OH^-, and H_2O. The result of the competition will depend on the ionization constants of the acids involved. These are

$$H_3PO_4 = 7.5 \times 10^{-3} \qquad H_2PO_4^- = 6.2 \times 10^{-8}$$
$$HPO_4^= = 1 \times 10^{-12} \qquad H_2O = 1 \times 10^{-14}$$

The values of the constants indicate that $H_2PO_4^-$ has little tendency to take protons from H_2O since H_3PO_4 is shown by its K_{ion} to be a moderately strong proton donor. H_2O evidently has much greater affinity for protons than has $H_2PO_4^-$ and somewhat greater than has $HPO_4^=$. We may predict then that reaction 4*b* will tend to proceed chiefly toward the left and that reaction 4*a* will proceed to some extent toward the right. Since 4*a* forms H_3O^+ and 4*b* (toward the left) removes OH^-, we can expect that at equilibrium the solution will be somewhat *acidic*.

Example 2. A solution of $Na^+HCO_3^-$.

$$\begin{array}{llll} \underset{A_1}{HCO_3^-} + \underset{B_2}{H_2O} & \rightleftarrows \underset{B_1}{CO_3^=} + \underset{A_2}{H_3O^+} & (5a) \\ \underset{B_2}{H_2O} + \underset{A_1}{HCO_3^-} & \rightleftarrows \underset{B_1}{OH^-} + \underset{A_2}{H_2CO_3} & (5b) \end{array}$$

The competitors for protons are the four bases HCO_3^-, $CO_3^=$, OH^-, and H_2O. The ionization constants of the acids are

$$H_2CO_3 = 4.3 \times 10^{-7} \qquad HCO_3^- = 4.7 \times 10^{-11}$$
$$H_2O = 1 \times 10^{-14}$$

Since water as a base has a proton affinity comparable to that of $CO_3^{=}$, reaction 5*a* can be expected to proceed to the right to some extent. But since H_2CO_3 is shown by its K_{ion} to be a much weaker proton donor than H_3PO_4 (Example 1), it will evidently have far less power to remove OH^- from the solution than had H_3PO_4 in 4*b*. We may predict then that a solution of $NaHCO_3$ will probably be slightly *basic*. Whether these predictions are fulfilled will be shown by the computations set forth under this type of salt solution.

Type V. The anion is a proton acceptor and the cation is a proton donor. The salt solution is a mixture of two buffers.

Example 1. A solution of $NH_4^+CN^-$.

$$\underset{}{A_1} \quad \underset{}{B_2} \quad \underset{}{A_3} \quad \underset{}{B_4} \quad \underset{}{A_2} \quad \underset{}{B_1} \quad \underset{}{A_4} \quad \underset{}{B_3}$$

$$\underset{0.4591}{NH_4^+} + \underset{0.4590}{CN^-} + H_2O + H_2O \rightleftarrows \underset{0.5410}{HCN} + \underset{0.5409}{NH_3} + \underset{4.7 \times 10^{-10}}{H_3O^+} + \underset{2.1 \times 10^{-5}}{OH^-}$$

The numbers in both Example 1 and Example 2 are the concentrations at equilibrium in 1 *M* solution as calculated by methods shortly to be discussed. The salts were assumed to be completely ionized.

Whether the solution of $NH_4^+CN^-$ is acidic or basic depends upon the relative ionization constants of the three acids: NH_4^+, HCN, and H_2O and upon the relative proton accepting powers of the three bases CN^-, NH_3, and H_2O. The solution is basic—that is, it contains more OH^- than H_3O^+—because CN^- will have taken protons from water as well as from NH_4^+.

Example 2. A solution of $AcO^-NH_4^+$.

$$\underset{0.9944}{NH_4^+} + \underset{0.99455}{AcO^-} + H_2O + H_2O \rightleftarrows \underset{0.00545}{AcOH} + \underset{0.00557}{NH_3} + \underset{1.015 \times 10^{-7}}{H_3O^+} + \underset{9.86 \times 10^{-8}}{OH^-}$$

Here the three bases AcO^-, NH_3, and H_2O similarly compete with one another for protons which are furnished by the three acids NH_4^+, AcOH, and H_2O in proportions depending upon their respective ionization constants.

This solution is practically neutral because both AcO^- and NH_3 are relatively weak bases as compared with water. Since their proton-accepting powers are almost identical (K_a AcOH = 1.85×10^{-5}, K_b $NH_3 = 1.8 \times 10^{-5}$), AcO^- will take few protons from NH_4^+.

Type VI. The anion of the salt is either amphoteric or is the anion of a polybasic acid, and the cation is a proton donor. The salt solution is a mixture of two buffers.

Examples. Solutions of $(NH_4^+)_2HPO_4^=$, $(NH_4^+)_2S^=$, $NH_4^+HS^-$, $(NH_4^+)_2CO_3^=$, or $NH_4^+HCO_3^-$.

The equilibrium in solutions of salts of this type is rather complicated. The equilibrium factors will be discussed in the following section on calculations.

The equilibrium in $(NH_4^+)_2CO_3^=$ solutions has been worked out by R. Wegscheider.[3]

CALCULATION OF PROTON EXCHANGE (HYDROLYSIS) IN AQUEOUS SALT SOLUTIONS

Salt Type II

The anion is a proton acceptor and the cation is not a proton donor.

Example 1. Calculate (1) the fraction and the per cent of CN^- in 0.1 *M* Na^+CN^- solution which is changed to HCN, (2) the C_{OH^-} in the solution at equilibrium and the *p*H of the solution.

$$\underset{B_1}{CN^-} + \underset{A_2}{H_2O} \rightleftarrows \underset{A_1}{HCN} + \underset{B_2}{OH^-}$$

At equilibrium

$$\frac{C_{HCN} \times C_{OH^-}}{C_{CN^-}} = K_{equil.} \tag{6}$$

The competition for protons between the two bases CN^- and OH^- will proceed until *both* the following equations are satisfied by the $C_{H_3O^+}$ then in the solution.

$$C_{H_3O^+} \times C_{OH^-} = 1 \times 10^{-14}(K_w) \tag{7}$$

and

$$\frac{C_{H_3O^+} \times C_{CN^-}}{C_{HCN}} = 4 \times 10^{-10}(K_a). \tag{8}$$

Since $C_{H_3O^+}$ is identical in both, dividing (7) by (8) gives for (6),

$$\frac{C_{HCN} \times C_{OH^-}}{C_{CN^-}} = K_{equil.} = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{4 \times 10^{-10}} = 2.5 \times 10^{-5}. \tag{9}$$

As a rule the information desired about a salt solution is its *p*H. This can be calculated exactly only after solution of a quadratic equation. But in solutions of salts of Types II and III the proton

[3] Monatsh., **37**, 425, (1916); C.A., **11**, 1072 (1917).

exchange rarely involves more than 2% of the salt present. For a 1 M solution, x^2 in $\frac{x^2}{1-x}$ would not exceed 0.0004. Whether 0.0004 is divided by 1 or by 0.98 evidently makes little difference. It is also evident that the smaller the extent of proton exchange, the more nearly will the value of x obtained by approximation be that obtained by solution of a quadratic. In order to make this clear, both exact and approximate solutions for 0.1 M Na^+CN^- solution are given below.

Exact solution. The exact solution requires that the following equations be simultaneous at equilibrium.

$$C_{H_3O^+} \times C_{OH^-} = 1 \times 10^{-14} \tag{10}$$

$$\frac{C_{H_3O^+} \times C_{CN^-}}{C_{HCN}} = 4 \times 10^{-10} \tag{11}$$

$$C_{CN^-} + C_{HCN} = 0.1 \tag{12}$$

$$C_{CN^-} + C_{OH^-} = 0.1(C_{Na^+}) + C_{H_3O^+} \tag{13}$$

There are four variables and four equations. Combination and substitution give $C_{OH^-} = 1.568 \times 10^{-3} M$.[4] Then

$$C_{H_3O^+} = 6.379 \times 10^{-12} M,$$
$$C_{CN^-} = 0.09843 M,$$
$$C_{HCN} = 1.569 \times 10^{-3} M.$$

Verify that these concentrations satisfy *all* the equations (10)–(13) above.

Compare the results of this laborious computation with those obtained by the rapid approximate method which follows.

Approximate solution. In (9) the small value of $K_{equil.}$ shows x to be small and the quotient of x^2 by 0.1 not to differ greatly from that by $0.1 - x$. Then $x^2/0.1 = 2.5 \times 10^{-5}$ and $x^2 = 2.5 \times 10^{-6}$; whence $x = 1.581 \times 10^{-3} M = C_{OH^-}$, and $pH = 11.20$ in close agreement with that found by solving the quadratic.

Then at equilibrium

$$\frac{C_{HCN}}{C_{CN^-}} = \frac{6.324 \times 10^{-12}}{4 \times 10^{-10}} = 1.581 \times 10^{-2}.$$

Putting $y = C_{HCN}$ and $0.1 - y = C_{CN^-}$,

$$\frac{y}{0.1 - y} = 0.01581, \text{ and } y = 0.001578 = C_{HCN}$$
$$0.1 - y = 0.09842 = C_{CN^-}.$$

[4] It is understood that digits after the first decimal place are without physical significance. They are given only for the convenience of students using four-place log tables in verifying calculations.

The two methods of computation give the following comparative results.

	C_{OH^-}	$C_{H_3O^+}$	C_{HCN}	C_{CN^-}
By exact solution	$1.568 \times 10^{-3} M$	$6.379 \times 10^{-12} M$	$1.569 \times 10^{-3} M$	$0.09843 M$
By approximation	$1.58 \times 10^{-3} M$	$6.3 \times 10^{-12} M$	$1.578 \times 10^{-3} M$	$0.0984 M$

It is obvious that approximation gives sufficiently accurate results.

Example 2. Calculate the C_{OH^-} and the pH of $0.1\,M$ $Na_2^+CO_3^=$ solution. Calculate the fraction and per cent of $CO_3^=$ changed into HCO_3^-. At equilibrium in the reaction

$$\underset{B_1}{CO_3^=} + \underset{A_2}{H_2O} \rightleftarrows \underset{A_1}{HCO_3^-} + \underset{B_2}{OH^-}$$

$$\frac{C_{HCO_3^-} \times C_{OH^-}}{C_{CO_3^=}} = K_{equil.}$$

the following equations become simultaneous:

$$C_{H_3O^+} \times C_{OH^-} = 1 \times 10^{-14} (K_w) \tag{14}$$

and

$$\frac{C_{H_3O^+} \times C_{CO_3^=}}{C_{HCO_3^-}} = 4.7 \times 10^{-11} (K_a). \tag{15}$$

Dividing (14) by (15),

$$\frac{C_{HCO_3^-} \times C_{OH^-}}{C_{CO_3^=}} = K_{equil.} = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{4.7 \times 10^{-11}} = 2.128 \times 10^{-4}.$$

Let $x = C_{HCO_3^-} = C_{OH^-}$; then $C_{CO_3^=} = 0.1 - x$ and

$$\frac{x^2}{0.1 - x} = 2.128 \times 10^{-4}.$$

Neglecting x in $0.1 - x$,

$$x^2 = 2.128 \times 10^{-5},$$

whence $x = 4.613 \times 10^{-3} M = C_{OH^-}$. The $p\text{H} = 7.6640 - 10 + 14 = 11.66$.

Then,

$$C_{H_3O^+} = \frac{1 \times 10^{-14}}{4.613 \times 10^{-3}} = 2.167 \times 10^{-12}$$

Substituting this value in (15),

$$\frac{2.167 \times 10^{-12} \times C_{CO_3^-}}{C_{HCO_3^-}} = 4.7 \times 10^{-11},$$

whence $\frac{C_{HCO_3^-}}{C_{CO_3^-}} = \frac{2.16 \times 10^{-12}}{4.7 \times 10^{-11}} = 4.612 \times 10^{-2}$. Then,

$$\frac{y}{0.1 - y} = 0.04612,$$

whence $y = C_{HCO_3^-} = 0.00441\,M$, and $0.1 - y = C_{CO_3^-} = 0.09559\,M$. 4.41% of the CO_3^- is changed to HCO_3^-.

Salt Type III

No hydrolysis is involved. The anion has no tendency to add protons, but the cation can donate protons to water. The solution will be more acidic the more the ionization constant of the cation exceeds that of water.

Example 1. Calculate $C_{H_3O^+}$ and pH of 0.1 M $NH_4^+Cl^-$ solution and the per cent of NH_4^+ changed to NH_3.

$$\underset{}{\overset{A_1}{Cl^-} + \overset{B_2}{NH_4^+} + \overset{}{H_2O} \rightleftarrows \overset{A_2}{H_3O^+} + \overset{B_1}{NH_3} + Cl^-}$$

At equilibrium

$$\frac{C_{H_3O^+} \times C_{NH_3}}{C_{NH_4^+}} = K_{equil.}$$

Treating the problem as one of hydrolysis, the constants to be satisfied at equilibrium are

$$C_{H_3O^+} \times C_{OH^-} = 1 \times 10^{-14} (K_w) \tag{16}$$

and

$$\frac{C_{NH_4^+} \times C_{OH^-}}{C_{NH_3}} = 1.8 \times 10^{-5} (K_b). \tag{17}$$

Dividing (16) by (17),

$$\frac{C_{H_3O^+} \times C_{NH_3}}{C_{NH_4^+}} = K_{equil.} = \frac{K_w}{K_b} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.555 \times 10^{-10}.$$

This value of the $K_{equil.}$ is identical with that of the ionization constant of NH_4^+ given in Table 4, page 84. Solutions of NH_4^+

salts of strong acids are slightly acidic because NH_4^+ has a slightly greater proton potential than has water. The hydrolysis of these salts, therefore, is really a slight ionization of NH_4^+ as a very weak acid. Problem 1 then becomes a matter of ionization rather than of hydrolysis.

$$\frac{C_{H_3O^+} \times C_{NH_3}}{C_{NH_4^+}} = 5.555 \times 10^{-10}$$

Putting $x = C_{H_3O^+} = C_{NH_3}$ and $C_{NH_4^+} = 0.1$ very closely, $\frac{x^2}{0.1} = 5.5555 \times 10^{-10}$, whence $x = 7.454 \times 10^{-6} M = C_{H_3O^+}$. The pH of the solution is 5.93.

The per cent of the NH_4^+ changed to NH_3, $\frac{7.4554 \times 10^{-6}}{0.1} \times 100$, is $7.5 \times 10^{-3}\%$.

Example 2. Calculate the pH of 0.1 M $Al(H_2O)_6^{+3}Cl_3^-$ solution.

$$\underset{A_1}{Al(H_2O)_6^{+3}} + \underset{B_2}{3Cl^-} + \underset{B_1}{H_2O} \rightleftarrows \underset{B_1}{[OH\,Al(H_2O)_5]^{++}} + \underset{A_2}{3Cl^-} + \underset{A_2}{H_3O^+}$$

The K_{ion} of $Al(H_2O)_6^{+3}$ (Table 4) shows that it is a considerably stronger proton donor than is NH_4^+. In consequence 0.1 M $AlCl_3$ solution should be much more acidic than 0.1 M NH_4Cl solution.

$$\frac{C_{H_3O^+} \times C_{[OHAl(H_2O)_5]^{++}}}{C_{Al(H_2O)_6^{+3}}} = K_{equil.} = K_a = 1.4 \times 10^{-5}.$$

Taking

$$x = C_{H_3O^+} = C_{[OHAl(H_2O)_5]^{++}}$$

$$\frac{x^2}{0.1} = 1.4 \times 10^{-5}$$

$$x = 1.183 \times 10^{-3} = C_{H_3O^+}, \text{ and } p\text{H} = 2.93.$$

Salt Type IV

The anion of the salt is amphoteric and the cation is not a proton donor. The $C_{H_3O^+}$ at equilibrium is independent of the concentration of the salt and equal to the square root of the product of the two ionization constants involved.

That, in solutions of salts of this type, the $C_{H_3O^+}$ at equilibrium is equal to the square root of the product of the two ionization constants involved results from the following considerations.

Case 1. The acid is bibasic, H_2CO_3, $H_2PO_4^-$, $H_2C_2O_4$, and so on.

$$\begin{array}{cccccc} A_1 & & B_2 & A_2 & & B_1 \\ H_2O & + & HA^- & \rightleftarrows H_2A & + & OH^- \end{array} \quad (18)$$

$$HA^- + H_2O \rightleftarrows H_3O^+ + A^- \quad (19)$$

$$H_3O^+ + OH^- \rightleftarrows H_2O + H_2O \quad (20)$$

The sum of (18), (19), and (20) is

$$2HA^- \rightleftarrows H_2A + A^-. \quad (21)$$

At equilibrium one $C_{H_3O^+}$ must satisfy both of the following equations.

$$\frac{C_{H_3O^+} \times C_{HA^-}}{C_{H_2A}} = K_1 \quad (22)$$

and

$$\frac{C_{H_3O^+} \times C_{A^-}}{C_{HA^-}} = K_2. \quad (23)$$

Multiplying (22) by (23),

$$\frac{C^2_{H_3O^+} \times C_{A^-}}{C_{H_2A}} = K_1 \times K_2.$$

But since, from (21), $C_{H_2A} = C_{A^-}$ at equilibrium,

$$C_{H_3O^+} = \sqrt{K_1 \times K_2}.$$

To calculate C_{H_2A}, C_{HA^-}, and C_{A^-} *at equilibrium:*

In (21), putting $C_{A^-} = C_{H_2A} = x$, C_{HA^-} becomes $C_{salt} - 2x$. Substituting these values and $\sqrt{K_1 \times K_2}$ $(= C_{H_3O^+})$ in (23),

$$\sqrt{K_2K_1} \times \frac{x}{C_{salt} - 2x} = K_2.$$

Squaring,

$$K_2K_1 \times \frac{x^2}{(C_{salt} - 2x)^2} = K^2_2$$

and

$$\frac{x^2}{(C_{salt} - 2x)^2} = \frac{K^2_2}{K_2K_1} = \frac{K_2}{K_1}$$

and

$$\frac{x}{C_{salt} - 2x} = \sqrt{\frac{K_2}{K_1}} \quad (24)$$

Example. (*a*) Calculate the *p*H of any $Na^+HCO_3^-$ solution. (*b*) Calculate $C_{CO_3^=}$ and $C_{HCO_3^-}$ at equilibrium in 0.1 *M* solution.

$$\begin{array}{cccc} A_1 & B_2 & A_2 & B_1 \\ HCO_3^- + H_2O & \rightleftarrows & H_3O^+ + CO_3^= \\ H_2O + HCO_3^- & \rightleftarrows & H_2CO_3 + OH^- \\ H_3O^+ + OH^- & \rightleftarrows & H_2O + H_2O \end{array}$$

(*a*) As shown above, at equilibrium $C_{H_3O^+} = \sqrt{K_1 \times K_2}$. For H_2CO_3, $K_1 = 4.3 \times 10^{-7}$ and $K_2 = 4.7 \times 10^{-11}$. Then $C_{H_3O^+} = \sqrt{4.3 \times 10^{-7} \times 4.7 \times 10^{-11}} = 4.5 \times 10^{-9}$. The $p\text{H} = 0.0 - (1.6528 - 10) = 8.35$. (The experimentally measured *p*H of $NaHCO_3$ solution is 8.3.)

(*b*) For 0.1 *M* $Na^+HCO_3^-$, putting $x = C_{CO_3^=} = C_{H_2CO_3}$ and $0.1 - 2x$ for $C_{HCO_3^-}$ in (24),

$$\frac{x}{C_{salt} - 2x} = \sqrt{\frac{K_2}{K_1}}$$

becomes

$$\frac{x}{0.1 - 2x} = \sqrt{\frac{4.7 \times 10^{-11}}{4.3 \times 10^{-7}}} = 0.01045,$$

whence $x = 0.001024\,M$ and $0.1 - 2x = 0.09795$.

Since $C_{H_3O^+}$ is independent of the concentration of the salt solution, $C_{H_2CO_3}$, $C_{CO_3^=}$, and $C_{HCO_3^-}$ in 0.1 *M* solution will *all* be 0.1 of those calculated for a 1 *M* solution.

Case 2. The acid is tribasic, $HPO_4^=$, $HAsO_4^=$.

$$\begin{array}{cccc} A_1 & B_2 & A_2 & B_1 \\ H_2O + HA^= & \rightleftarrows & H_2A^- + OH^- & (25) \\ HA^= + H_2O & \rightleftarrows & H_3O^+ + A^{-3} & (26) \\ H_3O^+ + OH^- & \rightleftarrows & H_2O + H_2O & (27) \end{array}$$

The sum of (25), (26), and (27) is

$$2HA^= \rightleftarrows H_2A^- + A^{-3}.$$

At equilibrium

$$\frac{C_{H_3O^+} \times C_{HA^=}}{C_{H_2A^-}} = K_2, \text{ and}$$

$$\frac{C_{H_3O^+} \times C_{A^{-3}}}{C_{HA^=}} = K_3$$

become simultaneous. Then by the same reasoning as in Case 1

$$C_{H_3O^+} = \sqrt{K_2 \times K_3}. \qquad (28)$$

Example. (*a*) Calculate the *p*H of any $Na_2^+HPO_4^-$ solution. (*b*) Calculate $C_{H_2PO_4^-}$, $C_{HPO_4^-}$, and $C_{PO_4^{-3}}$ at equilibrium in $0.2M$ solution.

The reactions involved are:

$$\begin{array}{cccccc} A_1 & B_2 & A_2 & B_1 & \\ HPO_4^- + H_2O & \rightleftarrows & H_3O^+ + PO_4^{-3} & & (29) \\ H_2O + HPO_4^- & \rightleftarrows & H_2PO_4^- + OH^- & & (30) \\ H_3O^+ + OH^- & \rightleftarrows & H_2O + H_2O & & (31) \end{array}$$

The sum of (29), (30), and (31) is

$$2HPO_4^- \rightleftarrows H_2PO_4^- + PO_4^{-3}.$$

(*a*) At equilibrium, from (28), $C_{H_3O^+} = \sqrt{K_2 \times K_3} = 2.49 \times 10^{-10}$. $p\text{H} = 0.0 - (0.3962 - 10) = 9.6$.

(*b*) For a $0.2M$ Na_2HPO_4, putting $x = C_{H_2PO_4^-} = C_{PO_4^{-3}}$ and $C_{HPO_4^-} = 0.2 - 2x$ in (24),

$$\frac{x}{C_{salt} - 2x} = \sqrt{\frac{K_3}{K_2}}$$

becomes

$$\frac{x}{0.2 - 2x} = \sqrt{\frac{1 \times 10^{-12}}{6.2 \times 10^{-8}}} = 0.004016,$$

whence $x = C_{H_2PO_4^-} = C_{PO_4^{-3}} = 8 \times 10^{-4}$. $0.2 - 2x = C_{HPO_4^-} = 0.0184$.

Salt Type V

The anion is a proton acceptor and the cation is a proton donor.

Example. Calculate C_{OH^-} and *p*H of $1.0M$ $NH_4^+CN^-$ solution. Then calculate the molar concentrations at equilibrium of NH_4^+, NH_3, HCN, and CN^-.

$$\begin{array}{cccccccc} A_1 & B_2 & A_3 & B_4 & A_2 & B_1 & A_4 & B_3 \\ NH_4^+ + CN^- + H_2O + H_2O & \rightleftarrows & HCN + NH_3 + H_3O^+ + OH^- \end{array}$$

Since $2H_2O = H_3O^+ + OH^-$, the equation for equilibrium is

$$\frac{C_{HCN} \times C_{NH_3}}{C_{CN^-} \times C_{NH_4^+}} = K_{equil.}$$

That water, H_3O^+, and OH^- do not appear in this equation indicates

that the pH of $NH_4^+CN^-$ solutions is the same at all concentrations of the salt. It does *not* indicate that $C_{H_3O^+} = C_{OH^-}$.

At equilibrium a certain $C_{H_3O^+}$ must satisfy both of the following equations:

$$\frac{C_{H_3O^+} \times C_{CN^-}}{C_{HCN}} = 4 \times 10^{-10} \tag{32}$$

$$\frac{C_{H_3O^+} \times C_{NH_3}}{C_{NH_4^+}} = 5.555 \times 10^{-10} \tag{33}$$

Dividing (32) by (33),

$$\frac{C_{HCN} \times C_{NH_3}}{C_{CN^-} \times C_{NH_4^+}} = \frac{5.555 \times 10^{-10}}{4 \times 10^{-10}} = 1.389.$$

Since $C_{H_3O^+}$ is independent of the concentration of the salt solution, we may assume as a first approximation that

$$C_{NH_3} = C_{HCN} = x \text{ and}$$
$$C_{NH_4^+} = C_{CN^-} = 1 - x,$$

then $\frac{x^2}{(1-x)^2} = 1.389$ and $\frac{x}{1-x} = 1.178$, whence $x = 0.541 = C_{HCN} = C_{NH_3}$. $1 - x = 0.459 = C_{CN^-}$.

At equilibrium

$$\frac{C_{H_3O^+} \times \overset{(0.459\,M)}{C_{CN^-}}}{\underset{(0.541\,M)}{C_{HCN}}} = 4 \times 10^{-10},$$

whence $C_{H_3O^+} = 4.715 \times 10^{-10}$ and $p\text{H} = 0.0 - (0.6735 - 10) = 9.33$. At equilibrium

$$\frac{C_{H_3O^+} \times C_{NH_3}}{C_{NH_4^+}} = 5.555 \times 10^{-10}.$$

Substituting $y = C_{NH_3}$, $1 - y = C_{NH_4^+}$, and $C_{H_3O^+} = 4.715 \times 10^{-10}$,

$$\frac{1-y}{y} = \frac{4.715 \times 10^{-10}}{5.555 \times 10^{-10}} = 0.8488.$$

Solving, $y = 0.5409\,M = C_{NH_3}$ and $1 - y = 0.4591\,M = C_{NH_4^+}$.

The calculations above are for $1\,M$ solution. Since in this type of salt $C_{H_3O^+}$ is independent of the concentration of the salt, in a $0.1\,M$ solution $C_{H_3O^+}$ will be $4.715 \times 10^{-10}\,M$ and C_{OH^-} will be

$2.121 \times 10^{-5} M$, the same as in $1 M$ solution. In other words, the pH of any solution of $NH_4^+CN^-$ is 9.3. In $0.1 M$ solution, C_{NH_3}, $C_{NH_4^+}$, C_{HCN}, and C_{CN^-} will have 0.1 the values calculated above for the $1.0 M$ solution. All equilibria will be satisfied by the following concentrations:

$$\underset{4.715 \times 10^{-10} M.}{C_{H_3O^+}} = 5.555 \times 10^{-10} \times \frac{\overset{0.04591\ M}{C_{NH_4^+}}}{\underset{0.05409\ M}{C_{NH_3}}} = 4 \times 10^{-10} \times \frac{\overset{0.05410\ M}{C_{HCN}}}{\underset{0.04590\ M}{C_{CN^-}}} = \frac{10^{-14}}{\underset{2.121 \times 10^{-5} M}{C_{OH^-}}}.$$

As a stronger base than NH_3, the CN^- has removed protons from more than half of the NH_4^+ present. As a base not infinitely weaker than OH^-, it has taken protons to a slight extent from H_2O also, leaving a small C_{OH^-} in the solution.

In $0.1 M$ Na^+CN^- solution the concentrations at equilibrium would be

$$\underset{6.843 \times 10^{-12}}{C_{H_3O^+}} = 4 \times 10^{-10} \times \frac{\overset{0.001581}{C_{HCN}}}{\underset{0.09242}{C_{CN^-}}} = \frac{10^{-14}}{\underset{1.46 \times 10^{-3}}{C_{OH^-}}}$$

In this solution, where the competition for protons is between CN^- and OH^- only, a far smaller fraction of the CN^- has acquired protons than in the $0.1 M$ $NH_4^+CN^-$ solution, but a much larger C_{OH^-} has accumulated in the solution.

Salt Type VI

The anion is either amphoteric or the anion of a polybasic acid, and the cation is a proton donor.

The equilibria in solutions of salts of this type are too complicated for simple mathematical treatment. However, by assuming (1) a definite *sum* of the concentrations of the anions and (2) an arbitrary $C_{H_3O^+}$, the ion concentrations can be calculated for any set of these arbitrarily fixed conditions. Such calculations are shown below for so-called "ammonium sulfide" solutions and for solutions of $(NH_4)_2HPO_4$.

Equilibrium in Solutions Containing Ammonia and Hydrogen Sulfide

All such solutions will contain several proton donors and several proton acceptors.

$$\begin{array}{llll} A_1 & B_2 & A_2 & B_1 \\ NH_4^+ & + HS^- & \rightleftarrows H_2S & + NH_3 \\ H_2O & + HS^- & \rightleftarrows H_2S & + OH^- \\ HS^- & + H_2O & \rightleftarrows H_3O^+ & + S^= \\ 2H_3O^+ & + 2OH^- & \rightleftarrows 2H_2O & + 2H_2O \\ H_2O & + NH_3 & \rightleftarrows NH_4^+ & + OH^- \\ NH_4^+ & + H_2O & \rightleftarrows H_3O^+ & + NH_3 \\ HS^- & + NH_3 & \rightleftarrows NH_4^+ & + S^= \end{array} \qquad \begin{array}{r} (34) \\ (35) \\ (36) \\ (37) \\ (38) \\ (38a) \\ (38b) \end{array}$$

The sum of equations (34) to (38*b*) is

$$4HS^- \rightleftarrows 2H_2S + 2S^= \quad \text{or} \quad 2HS^- \rightleftarrows H_2S + S^=,$$

and at equilibrium

$$\frac{C_{H_2S} \times C_{S^=}}{C^2_{HS^-}} = K_{equil.}, \tag{39}$$

which shows that the H_2S equilibria are independent of the $NH_4^+ \rightleftarrows NH_3$ equilibrium. At equilibrium the following equations become simultaneous, since there can be only one $C_{H_3O^+}$ in the solution.

$$\frac{C_{H_3O^+} \times C_{HS^-}}{C_{H_2S}} = 1.15 \times 10^{-7} \tag{40}$$

$$\frac{C_{H_3O^+} \times C_{S^=}}{C_{HS^-}} = 1 \times 10^{-15} \tag{41}$$

Dividing (41) by (40) gives 8.7×10^{-9} as the value of the $K_{equil.}$ in (39). Then dividing (39) by (40),

$$\frac{C^2_{H_2S} \times C_{S^=}}{C^3_{HS^-} \times C_{H_3O^+}} = \frac{8.7 \times 10^{-9}}{1.15 \times 10^{-7}} = 7.562 \times 10^{-2}, \tag{42}$$

which shows the relation of the H_2S equilibria to the $C_{H_3O^+}$. *This equation must be satisfied in all solutions containing H_2S.*

Example. Calculate the ion concentrations in "ammonium hydrosulfide" in which total sulfur ($C_{H_2S} + C_{HS^-} + C_{S^=}$) is $1\,M$, $C_{H_3O^+}$ is $10^{-8}\,M$ and $C_{NH_3} + C_{NH_4^+} = 1\,M$.

Solution. (*a*) The equilibrium $H_2S \rightleftarrows HS^- \rightleftarrows S^=$. Substituting the stated $C_{H_3O^+}$ in equations (40) and (41) and multiplying (40) by (41),

$$(10^{-8})^2 \times C_{S^=} = 1.15 \times 10^{-22} \times C_{H_2S},$$

whence

$$C_{S^=} = (1.15 \times 10^{-6})C_{H_2S}.$$

Substituting this value in (41),

$$10^{-8} \times (1.15 \times 10^{-6})C_{H_2S} = (1 \times 10^{-15})C_{HS^-},$$

whence

$$C_{HS^-} = 11.5 \times C_{H_2S}.$$

Substituting values of $C_{S^=}$ and C_{HS^-} in

$$C_{H_2S} + C_{HS^-} + C_{S^=} = 1\,M,$$
$$C_{H_2S} + 11.5C_{H_2S} + (1.15 \times 10^{-6})C_{H_2S} = 1\,M,$$

or, closely enough,

$$12.5C_{H_2S} = 1\,M.$$

Solving, $C_{H_2S} = 0.08\,M$, and $C_{HS^-} = 0.92\,M$ practically. $C_{S^=}$ can be calculated by substituting in (41)

$$\frac{10^{-8} \times C_{S^=}}{0.92} = 1 \times 10^{-15},$$

from which $C_{S^=} = 9.2 \times 10^{-8}\,M$.

(*b*) The $NH_3 \rightleftarrows NH_4^+$ equilibrium. Substituting the given $C_{H_3O^+}$ in

$$\frac{C_{H_3O^+} \times C_{NH_3}}{C_{NH_4^+}} = 5.555 \times 10^{-10}, \qquad (43)$$

$$\frac{C_{NH_3}}{C_{NH_4^+}} = \frac{5.56 \times 10^{-10}}{10^{-8}} = 5.56 \times 10^{-2}.$$

Putting $x = C_{NH_3}$ and $1 - x = C_{NH_4^+}$,

$$\frac{x}{1-x} = 0.0556,$$

whence $x = 0.0526\,M$, C_{NH_3} and $1 - x = 0.9474\,M$, $C_{NH_4^+}$.

Similar calculations for other selected concentrations of H_3O^+ in the above solution (total sulfur $= 1\,M$ and $C_{NH_3} + C_{NH_4^+} = 1\,M$) gave the concentrations tabulated below. These show the effect of small changes of $C_{H_3O^+}$ on the other concentrations.

$C_{H_3O^+}$	$C_{NH_4^+}$	C_{HS^-}	C_{NH_3}	C_{H_2S}	$C_{S^=}$
10^{-8}	0.9474	0.92	0.0526	8.0×10^{-2}	9.2×10^{-8}
10^{-9}	.6428	.9914	.3572	8.62×10^{-3}	9.91×10^{-7}
10^{-10}	.1525	.9991	.8475	8.688×10^{-4}	1×10^{-5}
10^{-11}	.0175	.9995	.9825	8.688×10^{-5}	1×10^{-4}
10^{-12}	.0018	.9995	.9982	8.688×10^{-6}	1×10^{-3}

Ratios valid for all mixtures of NH_3 and H_2S. By substituting various concentrations of H_3O^+ in equations (40), (41), and (43), the ratios tabulated below are obtained. They facilitate considerably calculation of ion concentrations in such mixtures, since they readily give, for each $C_{H_3O^+}$, the substituents in

$$C_{H_2S} + C_{HS^-} + C_{S^{--}} = \text{total } C_{\text{sulfur}}$$

and

$$C_{NH_3} + C_{NH_4^+} = \text{total } C_{\text{ammonia}}.$$

These ratios depend only on $C_{H_3O^+}$ and are independent of the proportions of NH_3 and H_2S except as this proportion actually fixes the $C_{H_3O^+}$ in a given mixture.

$C_{H_3O^+}$	$\frac{C_{S^{--}}}{C_{H_2S}}$	$\frac{C_{HS^-}}{C_{H_2S}}$	$\frac{C_{NH_3}}{C_{NH_4^+}}$
10^{-8}	1.15×10^{-6}	1.15×10^{1}	5.56×10^{-2}
10^{-9}	" 10^{-4}	" 10^{2}	" 10^{-1}
10^{-10}	" 10^{-2}	" 10^{3}	" 10^{0}
10^{-11}	" 10^{0}	" 10^{4}	" 10^{1}
10^{-12}	" 10^{2}	" 10^{5}	" 10^{2}

Reagent "ammonium sulfide." The composition of the reagent, made by saturating half of a volume of NH_3 solution with H_2S and adding the other half, must be extremely uncertain. The quantity of H_2S absorbed varies greatly with temperature, and considerable NH_3 is volatilized. To emphasize further the dependence of all ion concentrations on the $C_{H_3O^+}$ in these solutions, calculations have been made for three mixtures having widely varying proportions of NH_3 and H_2S. Solution (*a*) is assumed to approximate $1\,M$ NH_4HS, solution (*b*) to approximate $1\,M$ $(NH_4)_2S$, solution (*c*) is $0.1\,M$ NH_3 saturated with H_2S ($C_{H_2S} = 0.1\,M$). The *p*H of (*a*) will be about 8.0, that of (*b*) about 11.0, that of (*c*) about 6.9.

SOLUTION	$C_{H_3O^+}$	$C_{NH_4^+}$	C_{NH_3}	C_{H_2S}	C_{HS^-}	$C_{S^{--}}$
(*a*)	10^{-8}	0.9474	0.0526	0.08	0.92	9×10^{-8}
(*b*)	10^{-11}	0.0336	1.966	8.7×10^{-5}	0.9998	1×10^{-4}
(*c*)	1.24×10^{-7}	0.0995	4.5×10^{-4}	0.1	0.9256	1×10^{-4}

Solution (*b*), for which the formula $(NH_4)_2S$ is commonly written, is seen to be essentially a mixture of $2\,M$ NH_3 and $1\,M$ HS^-. Nevertheless, it contains a $C_{S^{--}}$ more than a thousand times that ($8.7 \times 10^{-8}\,M$) in water saturated with H_2S at 25°.

Equilibrium in Solutions Containing NH_3 and HPO_4^-

The following reactions take place:

$$\begin{array}{llll} A_1 & B_2 & B_1 & A_2 \\ NH_4^+ + HPO_4^- & \rightleftarrows NH_3 + H_2PO_4^- & & (44) \\ H_2O + HPO_4^- & \rightleftarrows OH^- + H_2PO_4^- & & (45) \\ HPO_4^- + H_2O & \rightleftarrows PO_4^{-3} + H_3O^+ & & (46) \\ 2H_3O^+ + 2OH^- & \rightleftarrows 2H_2O + 2H_2O & & (47) \\ H_2O + NH_3 & \rightleftarrows OH^- + NH_4^+. & & (48) \\ HPO_4^- + NH_3 & \rightleftarrows PO_4^{-3} + NH_4^+ & & (48a) \\ NH_4^+ + H_2O & \rightleftarrows NH_3 + H_3O^+ & & (48b) \end{array}$$

Adding equations (44) to (48*b*),

$$4HPO_4^- \rightleftarrows 2PO_4^{-3} + 2H_2PO_4^- \quad \text{or} \quad 2HPO_4^- \rightleftarrows PO_4^{-3} + H_2PO_4^-.$$

By combination of the ionization equations exactly as for H_2S above, we obtain

$$\frac{C_{PO_4^{-3}} \times C^2_{H_2PO_4^-}}{C^3_{H_2PO_4^-} \times C_{H_3O^+}} = \frac{K_3}{(K_2)^2} = 259.5.$$

Similarly, the ratios $\frac{C_{PO_4^{-3}}}{C_{H_2PO_4^-}}$ and $\frac{C_{HPO_4^-}}{C_{H_2PO_4^-}}$ can be shown to change with increasing basicity as follows:

$C_{H_3O^+}$	$\frac{C_{PO_4^{-3}}}{C_{H_2PO_4^-}}$	$\frac{C_{HPO_4^-}}{C_{H_2PO_4^-}}$
10^{-7}	6.2×10^{-6}	6.2×10^{-1}
10^{-8}	" 10^{-4}	" 10^{0}
10^{-9}	" 10^{-2}	" 10^{1}

At pH = 7.0 and pH = 8.0, the concentrations in 1 M $(NH_4)_2HPO_4$ should be approximately as follows:

$C_{H_3O^+}$	$C_{NH_4^+}$	C_{NH_3}	$C_{H_2PO_4^-}$	$C_{HPO_4^-}$	$C_{PO_4^{-3}}$
10^{-7}	1.989	0.011	0.6173	0.3827	3.8×10^{-6}
10^{-8}	1.8947	0.1053	0.1389	0.8612	8.6×10^{-5}

BUFFER SOLUTIONS

Any solution containing a weak acid and a considerable concentration of its anion, or a weak base and a considerable concentration of its cation, is able to protect itself against small additions of

either H_3O^+ or OH^-. Such a solution is said to be buffered. On addition of either H_3O^+ or OH^-, the following changes occur:

A_1	B_2	A_2	B_1	
HA	$+ OH^-$	$\rightleftarrows H_2O$	$+ A^-$	(49*a*)
H_3O^+	$+ A^-$	$\rightleftarrows HA$	$+ H_2O$	(49*b*)
H_3O^+	$+ BOH$	$\rightleftarrows B^+$	$+ H_2O$	(50*a*)
B^+	$+ OH^-$	$\rightleftarrows H_2O$	$+ BOH$	(50*b*)

Illustrations:

A_1	B_2	A_2	B_1	
$H_2PO_4^-$	$+ OH^-$	$\rightleftarrows H_2O$	$+ HPO_4^=$.	(49*c*)
H_3O^+	$+ HPO_4^=$	$\rightleftarrows H_2PO_4^-$	$+ H_2O$	(49*d*)
H_3O^+	$+ NH_3$	$\rightleftarrows NH_4^+$	$+ H_2O$	(50*c*)
NH_4^+	$+ OH^-$	$\rightleftarrows H_2O$	$+ NH_3$	(50*d*)

Notice that neither H_3O^+ nor OH^- appears as *product* in any of the four reactions. In the $H_2PO_4^- \rightleftarrows HPO_4^=$ buffer a small addition of OH^- forms H_2O and a little more $HPO_4^=$; a small addition of H_3O^+ increases slightly the $H_2PO_4^-$. In neither case is the *p*H of the solution changed perceptibly.

Equilibrium in Buffer Solutions

Acid buffers. For a weak acid,

$$HA + H_2O \rightleftarrows H_3O^+ + A^-,$$

equations (49*a*) and (49*b*) above show that if the solution is to be equally protected against small additions of either H_3O^+ or OH^-, the concentration of the anion (A^-) should nearly equal that of the weak acid (HA). For such a solution, if C_{A^-} equals C_{HA},

$$C_{H_3O^+} = K_a \times \left(\frac{C_{HA}}{C_{A^-}} = 1\right); \tag{51}$$

that is, if $C_{A^-} = C_{HA}$ in a buffer, the $C_{H_3O^+}$ in the solution will be equal to the K_{ion} of the weak acid. This shows that buffers covering a considerable *p*H range can be prepared by selecting various weak acids.

By inverting equation (51) and taking logs, we obtain

$$p\text{H} = \log \frac{1}{C_{H_3O^+}} = \log \frac{1}{K_a} + \log \frac{C_{A^-}}{C_{HA}}. \tag{52}$$

It is apparent that small changes in $C_{H_3O^+}$, equation (51), and pH, equation (52), can be made by varying the proportions of acid and anion in the buffer.

Note that equations (51) and (52) are identical. If $C_{H_3O^+}$ is being considered, (51) is more convenient. If pH is being considered, (52) is more convenient.

Basic buffers. For a weak base such as an $NH_3 \rightleftarrows NH_4^+$ solution, since

$$\frac{C_{NH_4^+} \times C_{OH^-}}{C_{NH_3}} = K_b = 1.8 \times 10^{-5},$$

$$C_{OH^-} = K_b \times \frac{C_{NH_3}}{C_{NH_4^+}} \tag{53}$$

and

$$p\text{OH} = \log \frac{1}{C_{OH^-}} = \log \frac{1}{K_b} + \log \frac{C_{NH_4^+}}{C_{NH_3}}. \tag{54}$$

To make the C_{OH^-} in an NH_3 solution equal 1.8×10^{-5}, enough NH_4^+ salt should be added so that $C_{NH_4^+}$ equals C_{NH_3}. Note that, like equations (51) and (52) for acid buffers, equations (53) and (54) for basic buffers are identical.

Note also that buffer solutions are examples of the "common-ion effect" and that equations (51) and (53) are useful forms for computing common-ion effect problems, as the following examples show.

Example 1. To 5 ml of 1 M acetic acid what weight of AcONa·$3H_2O$ (mol. wt. = 136) should be added to make $C_{H_3O^+}$ become $5 \times 10^{-6}\,M$? Neglect volume change. Assume the salt completely ionized.

Substituting in (51),

$$K_a = 1.85 \times 10^{-5} \text{ and } C_{HA} = 1\,M,$$

$$5 \times 10^{-6} = 1.85 \times 10^{-5} \times \frac{1}{C_{A^-}},$$

whence

$$C_{A^-} = \frac{1.85 \times 10^{-5}}{5 \times 10^{-6}} = 3.7 \frac{\text{m.mol}}{\text{ml}}$$

For 5 ml of the acid,

$$5 \text{ ml} \times 3.7 \frac{\text{m.mol}}{\text{ml}} \times 136 \frac{\text{mg}}{\text{m.mol}} = 2516 \text{ mg}$$

or 2.516 g of AcONa·$3H_2O$ must be added.

Example 2. It is desired to buffer a $0.2\,M$ NH_3 solution to a pOH of 5.0. What should $C_{NH_4^+}$ be made in the solution? If 0.5 l is to be buffered, what weight of NH_4Cl should be added?

Substituting in (53), $K_b = 1.8 \times 10^{-5}$ and $C_{NH_3} = 0.2\,M$,

$$5 = \log \frac{1}{1.8 \times 10^{-5}} + \log \frac{C_{NH_4^+}}{0.2},$$

$$5 = \log 1 - \log (1.8 \times 10^{-5}) + \log C_{NH_4^+} - \log 0.2$$

$$5 + \log (1.8 \times 10^{-5}) + \log 0.2 = \log C_{NH_4^+}$$

$$5 + (5.2553 - 10) + (9.3010 - 10) = \log C_{NH_4^+} = 9.5563 - 10$$

$$C_{NH_4^+} = 0.36\,M.$$

To buffer 0.5 l of $0.2\,M$ NH_3 to a pOH of 5 will require 0.5 l $\times$ 0.36 mol/l $\times$ 53.5 g/mol = 9.63 g of NH_4Cl.

Example 3. (*a*) If a drop (0.05 ml) of $1\,M$ HCl accidentally fell into 10 ml of an acetic acid–acetate buffer of pH 4.6 and $0.1\,M$ in acid, what would be the resulting pH of the solution? (*b*) What would the pH become if a drop of $1\,M$ NaOH fell into 10 ml of the buffer?

To solve this problem, C_{AcO^-} in the buffer must first be calculated by inserting the data of the problem in (52).

$$4.6 = \log \frac{1}{1.85 \times 10^{-5}} + \log \frac{C_{AcO^-}}{0.1},$$

whence

$$C_{AcO^-} = 0.07365\,M.$$

(*a*) 0.05 ml of 1 m.eq./ml HCl = 0.05 m.eq. of H_3O^+ which diluted to 10 ml makes 0.005 m.eq./ml.

$$AcO^- + H_3O^+ \rightleftarrows AcOH + H_2O$$

Since 1 m.eq. of H_3O^+ removes 1 m.eq. of A^- and forms 1 m.eq. of HA, 0.07365 m.eq./ml AcO^- + 0.005 m.eq./ml H_3O^+ gives $0.06865\,N$ AcO^- and $0.105\,N$ AcOH. Then, at the new equilibrium, (52) becomes

$$p\text{H} = \log \frac{1}{1.85 \times 10^{-5}} + \log \frac{0.06865}{0.105},$$

whence

$$p\text{H} = 4.55.$$

(*b*) Similarly, it can be calculated that 1 drop of $1\,N$ NaOH diluted to 10 ml will give $0.005\,N$ OH^-.

$$AcOH + OH^- \rightleftarrows H_2O + AcO^-$$

Then 0.1 m.eq./ml AcOH + 0.005 m.eq./ml of OH^- will form 0.005 m.eq./ml of AcO^-. The resulting concentrations will be $C_{AcOH} = 0.095N$ and $C_{AcO^-} = 0.0765N$.

Then (52) becomes

$$pH = \log \frac{1}{1.85 \times 10^{-5}} + \log \frac{0.07865}{0.095} = 4.65.$$

The effect of 1 drop of HCl was to decrease the pH by 0.05 of a unit, that of 1 drop of NaOH to increase it by 0.05 of a unit.

PROBLEMS

1. Calculate the fraction hydrolyzed and the pH for each of the following $0.2M$ salt solutions:

(*a*) NH_4NO_3 (*d*) NaH_2PO_4 (*g*) Na_2CO_3
(*b*) KCN (*e*) K_2HPO_4 (*h*) $Ba(NO_2)_2$ (Assume $Ba(OH)_2$
(*c*) $AcONH_4$ (*f*) $NaHC_2O_4$ to be completely ionized)

Ans.

	pH	Fraction Hydrolyzed		pH	Fraction Hydrolyzed
(*a*)	5.0	5.3×10^{-5}	(*e*)	9.6	8.06×10^{-3}
(*b*)	11.3	1.12×10^{-2}	(*f*)	2.7	1.03×10^{-3}
(*c*)	7.0	5.46×10^{-3}	(*g*)	11.8	3.3×10^{-2}
(*d*)	4.7	2.88×10^{-3}	(*h*)	8.5	1.49×10^{-5}

2. List the acids and bases that are present in a solution of $(NH_4)_2HAsO_4$.

3. How many grams of NaCN must be added to 100 ml of water to give an OH^- ion concentration of 10^{-2} mol/liter? *Ans.* 19.6 g NaCN.

4. An NH_4Cl solution has a pH of 5.6. How many mg of NH_4Cl in 10 ml? *Ans.* 6.03 mg.

5. Show by calculation whether FeS or $Fe(OH)_2$ will be precipitated when $0.1M$ Na_2S solution and $0.1M$ $FeSO_4$ solution are mixed.

6. Calculate the pH of a $0.15M$ NH_4CN solution. What is the percentage of hydrolysis? *Ans.* pH = 9.33; 53.33%.

7. (*a*) Write an ionic equation for the action of water on $NaAsO_2$.

(*b*) Calculate the hydrolysis constant. The ionization constant of arsenious acid is 6×10^{-10}. *Ans.* $K_h = 1.67 \times 10^{-5}$.

(*c*) Calculate C_{OH^-}, C_{H^+}, and *p*H of 0.25 *M* $NaAsO_2$.

(*d*) What fraction and what per cent of $NaAsO_2$ is hydrolyzed in 0.25 *M* solution?

8. A solution 0.05 *M* in H_2CO_3 and 0.1 *M* in $NaHCO_3$ has $C_{H^+} = 1.75 \times 10^{-7}$. What will C_{H^+} become (*a*) if to 50 ml of the solution 1 ml of 0.01 *M* HCl is added? (*b*) If to 50 ml of the solution 1 ml of 0.01 *M* NaOH is added?

9. Calculate the *p*H of 1 *M* $NaHCO_3$ solution. For H_2CO_3, $K_1 = 4.3 \times 10^{-7}$; $K_2 = 4.7 \times 10^{-11}$.

10. What fraction and what per cent of $NaBO_2$ is hydrolyzed in 0.35 *M* solution?

CHAPTER 10

EQUILIBRIUM IN COMPLEX IONS

In Chapter 4 it was shown that sharing of electrons results in the formation of both covalent molecules (nonelectrolytes) and complex ions. It was there stated briefly that the stability of the latter varied over a wide range. The extent of this variation is shown in Table 6 (page 151).

Even in the simplest complex ions, H_3O^+ and NH_4^+, a marked difference of stability appears. H_3O^+ gives up protons much more readily than does NH_4^+. Great differences of stability are apparent among similar complexes. For instance, $Co(NH_3)_6^{++}$ gives most of the reactions of Co^{++} about as readily as if no NH_3 were present. On the other hand, $Co(NH_3)_6^{+3}$ gives no reactions for cobalt, and acids do not remove NH_3 from it. Addition of I^- to a solution containing $Ag(NH_3)_2^+$ causes nearly all the Ag^+ to precipitate. It precipitates no Ag^+, however, from a solution containing $Ag(CN)_2^-$. It is evident that a solution containing $0.1\,M$ $Ag(CN)_2^-$ must contain far fewer silver ions than does $0.1\,M$ $Ag(NH_3)_2^+$.

When AgCl is treated with NH_3 solution, it dissolves, forming a solution of $Ag(NH_3)_2^+$ and Cl^-.

$$\underline{AgCl} + 2NH_3 \rightleftarrows Ag(NH_3)_2^+ + Cl^- \qquad (1)$$

Addition of Cl^- to this solution causes AgCl to precipitate. Addition of more NH_3 causes this precipitate to redissolve.

Reaction (1) is clearly reversible and can reach a state of equilibrium. The experimental fact that from a solution containing $Ag(NH_3)_2^+$ some Ag compounds can be precipitated shows that it contains Ag^+. If we consider the decomposition of $Ag(NH_3)_2^+$ into its components,

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

we have for the state of equilibrium between the complex ion and its components

$$\frac{C_{Ag^+} \times C^2_{NH_3}}{C_{Ag(NH_3)_2^+}} = K_{equil.} \qquad (3)$$

The equilibrium in this ion has been very exactly determined and the value of the $K_{equil.}$ at 25° found to be 6.0×10^{-8}. The equilibrium constant of complex ions is usually called the *instability constant* and denoted by $K_{inst.}$ The reason for this term is apparent from equation (3). The more the complex decomposes into its components, that is, the more *unstable* it is, the larger will be the numerator in (3) and the smaller the denominator. In other words, the larger the value of the constant the more unstable is the complex. Notice that inversion of the ratio in (3) would give a *stability* constant. This inverted form, which gives a large number for the constant, has been preferred by German chemists.

Inspection of equation (3) suggests three important deductions concerning the properties of $Ag(NH_3)_2^+$.

1. From the value of the $K_{inst.}$ it is evident that C_{Ag^+} should be *much smaller* in a solution of $Ag(NH_3)_2^+NO_3^-$ than in one of $Ag^+NO_3^-$ of the same concentration.

2. A small C_{Ag^+} must always be in the solution. If C_{Ag^+} became zero, $C_{Ag^+} \times C^2_{NH_3}/C_{Ag(NH_3)_2^+}$ would become infinity.

3. The C_{Ag^+} should vary inversely with the amount of NH_3 (not in the complex) contained by the solution.

CALCULATIONS INVOLVING COMPLEX IONS

That the chemical behavior of $Ag(NH_3)_2^+$ is in accord with these three deductions is shown by the following calculations which illustrate all the types of problems concerning complex ions. Quantitative lecture experiments which strikingly confirm the calculations were devised by Julius Stieglitz.[1]

If to 100 ml of 0.1 *M* $Ag^+NO_3^-$ solution there be added gradually 20 ml of 1 *M* NH_3 solution, the precipitate of $AgOH \rightleftarrows Ag_2O$ will have just about redissolved when the last drops of NH_3 are added.

$$Ag^+ + NH_3 + H_2O \rightleftarrows \underline{AgOH} + NH_4^+$$
$$\underline{AgOH} + NH_3 + NH_4^+ \rightleftarrows Ag(NH_3)_2^+ + H_2O$$

Since 0.02 mol of NH_3 reacts rather exactly with 0.01 mol of Ag^+, the composition of the complex must correspond rather closely to $Ag(NH_3)_2^+$. If the solution be diluted with water to 200 ml, a solution 0.05 *M* in $Ag(NH_3)_2^+NO_3^-$ will result.

[1] *Elements of Qualitative Chemical Analysis*, Vol. I, pp. 217–223, Appleton-Century, 1911.

Problem 1. Calculate C_{Ag^+} (*a*) in 0.05 *M* $Ag(NH_3)_2^+NO_3^-$ solution, (*b*) in 0.05 *M* $Ag^+NO_3^-$, assuming both salts completely ionized.

(*a*) Assuming the salt to be completely ionized into $Ag(NH_3)_2^+$ and NO_3^-, let $x = C_{Ag^+}$. Then C_{NH_3} will be $2x$, since in this case all NH_3 in the solution is assumed to come from dissociation of the complex according to equation (2). In the 0.05 *M* solution at equilibrium

$$\frac{x \times (2x)^2}{0.05 - x} = K_{inst.} = 6.0 \times 10^{-8}.$$

The value of the constant shows that x is negligible in comparison with 0.05 and that without appreciable error we may write

$$4x^3 = (6 \times 10^{-8} \times 5 \times 10^{-2}) = 3 \times 10^{-9},$$

whence

$$x = C_{Ag^+} = 9.08 \times 10^{-4}\,M.$$

(*b*) In 0.05 *M* $Ag^+NO_3^-$ completely ionized, C_{Ag^+} would be $5 \times 10^{-2}\,M$, more than fifty times the calculated C_{Ag^+} in the $Ag(NH_3)_2^+NO_3^-$.

Problem 2. The $K_{s.p.}$ of $AgBrO_3$ is stated to be 5.2×10^{-5} $(mol/l)^2$. Should a precipitate of $AgBrO_3$ form in either solution when 5 ml of 1 *M* $NaBrO_3$ solution is added to

(*a*) 50 ml of 0.05 *M* $Ag^+NO_3^-$ solution;

(*b*) 50 ml of 0.05 *M* $Ag(NH_3)_2^+NO_3^-$ solution?

[Assume in (*a*) that only 0.8 of the C_{Ag^+} and $C_{BrO_3^-}$ is "effective" in producing equilibrium. In (*b*) make the same assumption for $C_{Ag(NH_3)_2^+}$ and $C_{BrO_3^-}$.]

(*a*) In a mixture of 50 ml of 0.05 *M* $Ag^+NO_3^-$ and 5 ml of 1 *M* $Na^+BrO_3^-$,

$$C_{Ag^+} = \frac{50}{55} \times 0.05\,M = 0.045\,M, \text{ of which 0.8, or } 0.036\,M, \text{ is "effective";}$$

$$C_{BrO_3^-} = \frac{5}{55} \times 1.0\,M = 0.09\,M, \text{ of which 0.8, or } 0.072\,M, \text{ is "effective."}$$

The "effective" ion product, $0.036 \times 0.072 = 2.6 \times 10^{-3}(mol/l)^2$, is considerably larger than 5.2×10^{-5}, the $K_{s.p.}$ of $AgBrO_3$. A precipitate should form.

(*b*) In a mixture of 50 ml of 0.05 *M* $Ag(NH_3)_2^+NO_3^-$ and 5 ml of 1 *M* $Na^+BrO_3^-$,

$$\text{effective } C_{Ag(NH_3)_2^+} = \frac{50}{55} \times 0.05\,M = 0.045M \times 0.8 = 0.036\,M;$$

$$C_{Ag^+}\left(= x \text{ in } \frac{x \times (2x)^2}{0.036} = 6 \times 10^{-8} \right) = 8.14 \times 10^{-4}\,M;$$

$$\text{effective } C_{BrO_3^-} = \frac{5}{55} \times 1\,M = 0.09\,M \times 0.8 = 0.072\,M.$$

The ion product, $C_{Ag^+} \times C_{BrO_3^-}$, $= (8.14 \times 10^{-4}) \times (7.2 \times 10^{-2}) = 5.86 \times 10^{-5}$ (mol/l)^2, which barely exceeds the $K_{s.p.}$, 5.2×10^{-5}. No immediate precipitate should form.

If solutions of the concentrations specified, are mixed in the proportions used in the above calculations, no precipitate of $AgBrO_3$ appears within an hour in the $0.05\,M$ $Ag(NH_3)_2^+NO_3^-$, while in the $0.05\,M$ $Ag^+NO_3^-$ a considerable precipitate immediately forms. Thus, experiment confirms deduction 1 (page 144) that the C_{Ag^+} is much smaller in the solution containing the complex ion $Ag(NH_3)_2^+$.

Problem 3. If to the solution of $Ag(NH_3)_2^+NO_3^-$ from which no $AgBrO_3$ precipitated, 5 ml of $0.1\,M$ Na^+Cl^- be added, should AgCl precipitate?

The $K_{s.p.}$ of AgCl is 1.5×10^{-10}. After adding 5 ml of Na^+Cl^- solution to 55 ml of $Ag(NH_3)_2^+$ solution

$$\text{effective } C_{Ag(NH_3)_2^+} = \frac{55}{60} \times 0.036 = 0.033\,M;$$

$$C_{Ag^+} = \left(x \text{ in } \frac{x \times (2x)^2}{.033} = 6 \times 10^{-8} \right) = 7.91 \times 10^{-4}\,M;$$

$$\text{effective } C_{Cl^-} = \frac{5}{60} \text{ of } 0.1\,M = 0.0083\,M \times 0.8 = .0064\,M.$$

The ion product, $(7.91 \times 10^{-4}) \times (6.4 \times 10^{-3}) = 5.1 \times 10^{-6}$ (mol/l)^2, *greatly exceeds* the $K_{s.p.}$ of AgCl, 1.5×10^{-10}. We should expect a rather heavy precipitate of AgCl to form.

When 5 ml of $0.1\,M$ Na^+Cl^- solution is added to the 55 ml of $Ag(NH_3)_2^+BrO_3^-$, which gave no precipitate of $AgBrO_3$, a large precipitate of AgCl immediately appears. This confirms deduction 2. While the C_{Ag^+} in the $Ag(NH_3)_2^+$ solution is too small to cause any immediate precipitation of the moderately soluble $AgBrO_3$, it is amply large to permit precipitation of the less soluble AgCl.

If $6\,M$ NH_3 solution is added to the mixture of AgCl and solution obtained above, the precipitate dissolves as deduction 3 (page 144) led us to expect.

Problem 4. What volume of $6\,M$ NH_3 should be required to just dissolve the precipitate of AgCl formed in confirmation of Problem 3?

Neglecting the small increase of volume due to addition of the $6\,M$ NH_3 to 60 ml of solution, the effective C_{Cl^-} when the precipitate of AgCl has just dissolved will be:

$$\text{effective } C_{Cl^-} = \frac{5}{60} \times 0.1\,M = 0.0083\,M \times 0.8 = 0.0064\,M;$$

$$C_{Ag^+} = \frac{K_{s.p.}}{C_{Cl^-}} = \frac{1.5 \times 10^{-10}}{0.0064} = 2.34 \times 10^{-8}\,M;$$

$$\text{effective } C_{Ag(NH_3)_2^+} = 0.033\,M \text{ as calculated above.}$$

Then $\frac{(2.34 \times 10^{-8} \times C^2_{NH_3})}{0.033} = 6 \times 10^{-8}$, whence $C_{NH_3} = 0.291\,M$. By adding x ml of $6\,M$ NH_3 there will result $(60 + x)$ ml of $0.291\,M$ NH_3. Therefore, x ml $\times$ 6 m. mol/ml must equal $(60 + x)$ ml $\times$ 0.291 m.mol/ml, whence $x = 3.1$ ml of $6\,M$ NH_3 required.

Experiment shows that this calculated volume of $6\,M$ NH_3, 3.1 ml, just about dissolves the precipitate of AgCl.

If to the solution, to which NH_3 was added until $C_{Ag^+} \times C_{Cl^-}$ just equaled $K_{s.p.}$ AgCl, more Cl^- is added, more AgCl precipitates, which in turn dissolves if more NH_3 is added.

Thus, deduction 3 (page 144) is fully verified and it becomes clear that the C_{Ag^+} in a solution containing $Ag(NH_3)_2^+$ can be *controlled* within rather wide limits by adding the complex-forming molecule NH_3 in smaller or larger excess.

If a few drops of K^+I^- solution are added to a solution containing $Ag(NH_3)_2^+Cl^-$ and so large C_{NH_3} that C_{Ag^+} is kept smaller than the value necessary to make $C_{Ag^+} \times C_{Cl^-} = K_{s.p.}$ of AgCl, a precipitate of AgI at once forms. The solubility product of AgI,

$$C_{Ag^+} \times C_{I^-} = 8.5 \times 10^{-17},$$

is so much smaller than that of AgCl that the minute C_{Ag^+} in the solution of $Ag(NH_3)_2^+Cl^-$ is sufficient to cause a precipitate of AgI. Addition of even $15M$ NH_3 will not completely dissolve the AgI. If, however, a precipitate of AgI is treated with a little $1\,M$ Na^+CN^- solution, it instantly dissolves.

$Ag(CN)_2^-$ ($K_{inst.} = 3.8 \times 10^{-19}$) is a far more stable complex than is $Ag(NH_3)_2^+$ ($K_{inst.} = 6 \times 10^{-8}$), so that in a solution containing even a minute C_{CN^-} (not in the complex) the C_{Ag^+} is far smaller than that in saturated AgI solution and the solid AgI must continuously give up Ag^+ to form $Ag(CN)_2^-$. If AgI be first dissolved in CN^- according to

$$\underline{AgI} + 2CN^- \rightleftarrows Ag(CN)_2^- + I^-,$$

so that the resulting solution is $0.01\,M$ in I^- and in $Ag(CN)_2^-$, the C_{Ag^+} in the solution is given by

$$\frac{K_{s.p.}\ AgI}{C_{I^-}} = \frac{8.5 \times 10^{-17}}{0.01} = 8.5 \times 10^{-15} M.$$

To dissolve exactly the AgI would require that at equilibrium

$$\frac{8.5 \times 10^{-15} \times C^2_{CN^-}}{0.01} = 3.8 \times 10^{-19}.$$

Solving this equation, $C_{CN^-} = 6.7 \times 10^{-4} M$. To dissolve 0.01 m.mol of AgI into 1 ml of solution requires that when the AgI has just dissolved, no more than this very small excess of CN^- need be in the solution.

That even a solution containing the very stable $Ag(CN)_2^-$ still contains Ag^+ can be demonstrated by adding a little sulfide solution. An immediate precipitate of $AgHS \rightleftarrows Ag_2S$ is formed.

The $K_{s.p.}$ of Ag_2S is given as 1×10^{-51}. If the $K_{s.p.}$ of AgHS is about 1×10^{-35}, the C_{Ag^+} (8.5×10^{-15}) in the above $0.01 M$ $Ag(CN)_2^-$ solution should require a C_{HS^-} not much greater than $1 \times 10^{-35}/(8.5 \times 10^{-15}) = 10^{-21} M$ to form a precipitate of AgHS.

Summary

The preceding statements and calculations involving the stabilities of two complex ions, $Ag(NH_3)_2^+$ and $Ag(CN)_2^-$, convincingly demonstrate properties which experiment shows to belong in varying degrees to all complex ions. These may be summarized as follows.

1. The values of the instability constants given in Table 6 (page 151) indicate to what extent the complex decomposes into its components. They also indicate the extent to which the usual reactions of the central ion of the complex will not be given by the complex.

For example, the central ions in $[Co(NH_3)_6]^{+3}$ ($K_{inst.} = 10^{-34}$), $[Fe(CN)_6]^{-4}$ (10^{-37}), $[Fe(CN)_6]^{-3}$ (10^{-44}), $[Hg(CN)_4]^=$ (10^{-42}) can be expected to show none, or at most very few, of their common reactions. On the other hand, $[Co(NH_3)_6]^{++}$ (10^{-5}), $[Ag(NH_3)_2]^+$ (10^{-8}), $[Zn(NH_3)_4]^{++}$ (10^{-10}), $[Cd(CN)_4]^=$ (10^{-17}), $[HgCl_4]^=$ (10^{-16}) may be expected to show some, but not all, of the usual reactions. Aquo complexes, such as $[Cu(H_2O)_4]^{++}$ and $[Al(H_2O)_6]^{+3}$, are so little stable that they give all the reactions characteristic of their central ions.

2. In solutions containing complex ions, the concentration of the central ion is never *zero*, although for the most stable complex ions it is too small to give any chemical reactions.

3. For complex ions of medium stability the equilibrium concentration of the central ion is rapidly decreased as the concentration of the complex-forming ion or molecule is increased. Adding NH_3 caused AgCl to dissolve. Addition of a sufficiently large C_{CN^-} causes even the extremely insoluble AgHS or Ag_2S to dissolve due to formation of $[Ag(CN)_3]^-$ (10^{-23}) even more stable than $[Ag(CN)_2]^-$ (10^{-19}).

ANALYTICAL APPLICATIONS OF COMPLEX ION FORMATION

Among many instances of practical use of the properties of complex ions to be found in the laboratory manual, may be mentioned the following:

In Cation Group I		Separation of Ag^+ from Hg_2^{++}
" " "	II	" " Subgroup A from Subgroup B.
		" " Sb from Sn^{+4}
		" " BiO^+ from Cu^{++} and Cd^{++}
		Detection of Cd^{++} in presence of Cu^+.
" " "	III	" " Fe^{+3} by thiocyanate
		" " Co^{++} " "
		" " Ni^{++} in cobalt salts

A single one of these applications, the detection of Cd^{++} in presence of (possibly) a rather large amount of Cu^+, will be discussed by means of the following problems.

Problem 5. A small excess of CN^- reduces $Cu(NH_3)_4^{++}$ to $Cu(CN)_3^=$, of which the $K_{inst.}$ is 5×10^{-28}. At the same time $Cd(NH_3)_4^{++}$ forms $Cd(CN)_4^=$, of which the $K_{inst.}$ is 1.4×10^{-17}. In a solution $0.05\,M$ in $Cu(CN)_3^=$ and $0.05\,M$ in $Cd(CN)_4^=$ what C_{CN^-} (outside the complex ions) would have to be present to prevent precipitation of Cu_2S, of which the $K_{s.p.}$ is said to be 2.5×10^{-50} $(mol/l)^3$, when the $C_{S^=}$ was made $1 \times 10^{-3} M$ in the solution?

To just prevent precipitation of Cu_2S by $0.001\,M$ $S^=$, $C^2_{Cu^+} \times C_{S^=}$ $(= 0.001) = 2.5 \times 10^{-50}$, whence $C_{Cu^+} = 5 \times 10^{-24} M$. To reduce C_{Cu^+} to $5 \times 10^{-24} M$ in a solution $0.05\,M$ in $Cu(CN)_3^=$ the C_{CN^-} must be made large enough so that

$$\frac{5 \times 10^{-24} \times C^3_{CN^-}}{0.05} = 5 \times 10^{-28}.$$

Solving, $C^3_{CN^-} = 5 \times 10^{-6} M$ and $C_{CN^-} = 1.71 \times 10^{-2} M$. An excess C_{CN^-} less than $0.02\,M$ should prevent precipitation of any Cu_2S.

Problem 6. Should any CdS precipitate from the solution in Problem 1 if the $K_{s.p.}$ of CdS is 1.4×10^{-28} $(mol/l)^2$?

$$\frac{C_{Cd^{++}} \times (1.71 \times 10^{-2})^4}{0.05} = 1.4 \times 10^{-17}, \text{ whence } C_{Cd^{++}} = 8.18 \times 10^{-2} M.$$

Since $C_{Cd^{++}}$ $(0.082) \times C_{S^{=}}$ $(1 \times 10^{-3}) = 8.2 \times 10^{-5}$ $(mol/l)^2$, far larger than the $K_{s.p.}$ of CdS, practically all the Cd^{++} should precipitate as CdS.

THE IRON BLUES

The strong color of Prussian blue and Turnbull's blue, entirely different from the colors of the component ions, makes very probable that they are high polymers. Davidson[2] has devised interesting experiments which throw new light on these compounds.

When Fe^{+3} and $[Fe(CN)_6]^{-4}$ are mixed, two reactions take place:

$$Fe^{+3} + [Fe(CN)_6]^{-4} \rightleftarrows Fe^{++} + Fe(CN)_6^{-3} \text{ (instantaneous)} \quad (4)$$

and

$$Fe^{+3} + [Fe(CN)_6]^{-4} \rightarrow \text{Prussian blue (slow)}. \quad (5)$$

From the molar potentials $Fe^{++} \rightleftarrows Fe^{+3} + e^-$ $(+ 0.77$ v.) and $[Fe(CN)_6]^{-4} \rightleftarrows [Fe(CN)_6]^{-3} + e^-$ $(+ 0.36$ v.), the equilibrium constant[3] of reaction (4),

$$\frac{C_{Fe^{++}} \times C_{Fe(CN)_6^{-3}}}{C_{Fe^{+3}} \times C_{Fe(CN)_6^{-4}}} = K_{equil.}, \quad (6)$$

should be about 6.8×10^6.

Calculations from equation (6) show that excess of Fe^{+3} should tend to *prevent* formation of a blue by greatly decreasing $[Fe(CN)_6]^{-4}$. (This is the "paradox".) Excess of Fe^{++} promotes its formation by at least doubling Fe^{+3} and $[Fe(CN)_6]^{-4}$ without greatly changing $[Fe(CN)_6]^{-3}$. While the solubility products of Prussian blue and Turnbull's blue are not known, from analogy it is to be expected that ferric ferrocyanide is much more insoluble than ferrous ferrocyanide or ferrous ferricyanide. The slowly forming colloidal blue should then be $K^+Fe^{+3}[Fe(CN)_6]^{-4}$ rather than $K^+Fe^{++}[Fe(CN)_6]^{-3}$, regardless of whether one starts with Fe^{+3} and $[Fe(CN)_6]^{-4}$ or Fe^{++} and $[Fe(CN)_6]^{-3}$.

[2] J. Chem. Ed., **14**, "The Prussian Blue Paradox," 238–241, 277–281 (1937).

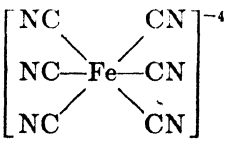
[3] Davidson gave 10^4. More recent values of the molar potentials indicate a much larger value.

TABLE 6

INSTABILITY CONSTANTS

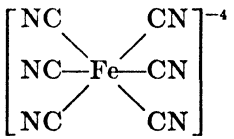
COMPLEX	EQUILIBRIUM	$K_{inst.}$
$[Cd(NH_3)_4]^{++}$	$\rightleftarrows Cd^{++} + 4NH_3$	2.5×10^{-7}
$[Co(NH_3)_6]^{++}$	$\rightleftarrows Co^{++} + 6NH_3$	1.25×10^{-5}
$[Co(NH_3)_6]^{+3}$	$\rightleftarrows Co^{+3} + 6NH_3$	2.2×10^{-34}
$[Cu(NH_3)_2]^{+}$	$\rightleftarrows Cu^{+} + 2NH_3$	1.35×10^{-11}
$[Cu(NH_3)_4]^{++}$	$\rightleftarrows Cu^{++} + 4NH_3$	4.56×10^{-14}
$[Ni(NH_3)_4]^{++}$	$\rightleftarrows Ni^{++} + 4NH_3$	4.8×10^{-8}
$[Ag(NH_3)_2]^{+}$	$\rightleftarrows Ag^{+} + 2NH_3$	6.0×10^{-8}
$[Zn(NH_3)_4]^{++}$	$\rightleftarrows Zn^{++} + 4NH_3$	9.8×10^{-10}
$[Cd(CN)_4]^{-}$	$\rightleftarrows Cd^{++} + 4CN^{-}$	1.4×10^{-17}
$[Cu(CN)_2]^{-}$	$\rightleftarrows Cu^{+} + 2CN^{-}$	1×10^{-16}
$[Cu(CN)_3]^{-}$	$\rightleftarrows Cu^{+} + 3CN^{-}$	5×10^{-28}
$[Fe(CN)_6]^{-4}$	$\rightleftarrows Fe^{++} + 6CN^{-}$	ca. 10^{-37}
$[Fe(CN)_6]^{-3}$	$\rightleftarrows Fe^{+3} + 6CN^{-}$	ca. 10^{-44}
$[Hg(CN)_4]^{-}$	$\rightleftarrows Hg^{++} + 4CN^{-}$	4×10^{-42}
$[Ni(CN)_4]^{-}$	$\rightleftarrows Ni^{++} + 4CN^{-}$	ca. 1×10^{-22}
$[Ag(CN)_2]^{-}$	$\rightleftarrows Ag^{+} + 2CN^{-}$	3.8×10^{-19}
$[Ag(CN)_3]^{-}$	$\rightleftarrows Ag^{+} + 3CN^{-}$	8×10^{-23}
$[Zn(CN)_4]^{-}$	$\rightleftarrows Zn^{++} + 4CN^{-}$	2×10^{-17}
$[Au(CN)_2]^{-}$	$\rightleftarrows Au^{+} + 2CN^{-}$	5×10^{-39}
$[AlF_6]^{-3}$	$\rightleftarrows Al^{+3} + 6F^{-}$	ca. 2×10^{-24}
$[CuCl_2]^{-}$	$\rightleftarrows Cu^{+} + 2Cl^{-}$	2.9×10^{-6}
$[HgCl_4]^{-}$	$\rightleftarrows Hg^{++} + 4Cl^{-}$	1.1×10^{-16}
$[AuCl_4]^{-}$	$\rightleftarrows Au^{+3} + 4Cl^{-}$	5×10^{-22}
$[HgBr_4]^{-}$	$\rightleftarrows Hg^{++} + 4Br^{-}$	2.3×10^{-22}
$[CdI_4]^{-}$	$\rightleftarrows Cd^{++} + 4I^{-}$	ca. 5×10^{-7}
$[HgI_4]^{-}$	$\rightleftarrows Hg^{++} + 4I^{-}$	5.3×10^{-31}
$[Au(NCS)_4]^{-}$	$\rightleftarrows Au^{+3} + 4CNS^{-}$	3×10^{-38}
$[Fe(NCS)_6]^{-3}$	$\rightleftarrows Fe^{+3} + 6CNS^{-}$	8×10^{-10}
$[Hg(NCS)_4]^{-}$	$\rightleftarrows Hg^{++} + 4CNS^{-}$	1×10^{-22}
$[Fe(C_2O_4)_3]^{-3}$	$\rightleftarrows Fe^{+3} + 3C_2O_4^{-}$	ca. 10^{-10}
$[Zn(C_2O_4)_3]^{-4}$	$\rightleftarrows Zn^{++} + 3C_2O_4^{-}$	1×10^{-9}
$[Ag(S_2O_3)_2]^{-3}$	$\rightleftarrows Ag^{+} + 2S_2O_3^{-}$	4.2×10^{-14}
$[Ag(SO_3)_2]^{-3}$	$\rightleftarrows Ag^{+} + 2SO_3^{-}$	3.0×10^{-9}
$[Cd(S_2O_3)_4]^{-6}$	$\rightleftarrows Cd^{++} + 4S_2O_3^{-}$	4.0×10^{-8}

The commonly accepted structure of CN^- is $[:C:::N:]^-$ and it is capable of coordinating either through C or through N. In

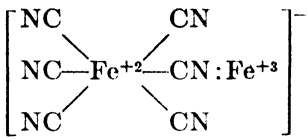


coordination is through C. The CN^- groups are at the corners of a regular octahedron, thus forming a three-dimensional figure. The

N atoms can also coordinate with metal ions. With ferric ion,

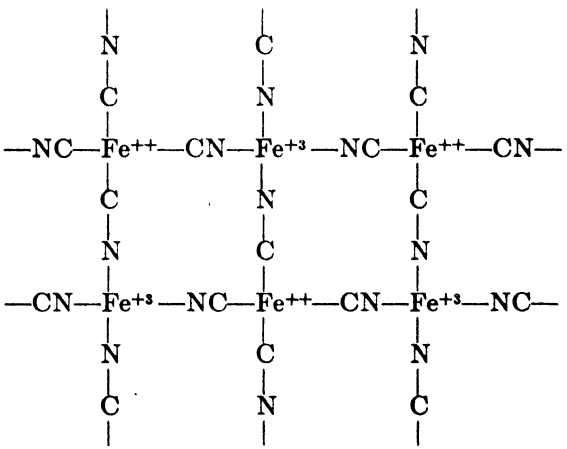


can form



univalent, since one of the four negative charges of $[Fe(CN)_6]^{-4}$ ion remains unneutralized by Fe^{+3}. This is regarded as the structural unit of the iron blues, and the name "berlinate" ion is suggested for it from the German name Berlinerblau, for Prussian blue. Soluble (colloidal) Prussian blue would then be the largely polymerized K^+ salt of this ion, $(K^+[Fe^{++}(CN)_6Fe^{+3}]^-)_x$, *potassium berlinate.*

Insoluble Prussian blue would be *ferric berlinate*, $Fe^{+3}[Fe(CN)_6Fe]_3^-$. Turnbull's blue would be *ferrous berlinate*, $Fe^{++}[Fe(CN)_6Fe]_2^-$. As actually precipitated, the latter is usually a mixture varying between $K^+Fe^{++}[Fe(CN)_6Fe]_3^-$ and $K^+Fe_2^{++}[Fe(CN)_6Fe]_5^-$. The lattice of Prussian blue is very probably about as represented in the following cross section. Cyanide ions are to be imagined in front of and behind each iron atom. The lattice, of course, extends indefinitely in *three* directions.[4]



[4] A later X-ray examination of cupric ferrocyanides (R. Rigamonti, Gazz. chim. ital., 67, 137 [1937]; C. A., 31, 6574) lends support to Davidson's views.

COMBINATION OF SIMULTANEOUS EQUATIONS IN SOLVING PROBLEMS

Many of the following problems concern either precipitation from solutions containing complex ions or dissolution of solids to form complex ions. In such problems it is important to bear in mind that in *saturated* solutions at equilibrium, the equation for the ion-concentration product and that for the $K_{inst.}$ of the complex ion become simultaneous. For example, in NH_3 solution *saturated* with AgCl,

$$\underline{AgCl} + 2NH_3 \rightleftarrows Ag(NH_3)_2^+ + Cl^-,$$

the equations

$$C_{Ag^+} \times C_{Cl^-} = 1.7 \times 10^{-10} \tag{7}$$

$$\frac{C_{Ag^+} \times C^2_{NH_3}}{C_{Ag(NH_3)_2^+}} = 6 \times 10^{-8} \tag{8}$$

must become simultaneous, since more than one C_{Ag^+} cannot be in the same solution. By dividing equation (8) by equation (7), we obtain

$$\frac{C^2_{NH_3}}{C_{Ag(NH_3)_2^+} \times C_{Cl^-}} = \frac{6 \times 10^{-8}}{1.7 \times 10^{-10}} = 353. \tag{9}$$

But in this solution $C_{Ag(NH_3)_2^+} = C_{Cl^-}$ practically (since C_{Ag^+} must be negligibly small), and hence

$$\frac{C_{NH_3}}{C_{Cl^-}} = \sqrt{353} = 18.79. \tag{10}$$

In words, an NH_3 solution can dissolve AgCl until the C_{NH_3} not in the complex ion is 18.79 times the C_{Cl^-}. This relation is true for every *saturated* solution of AgCl in NH_3 but not for unsaturated solutions.

In solving problems involving solubility products and instability constants, it is usually advantageous to combine the two equations into one, provided it is certain from inspection of the problem that they are simultaneous.

PROBLEMS

1. Using the values of the instability constants given in Table 6, calculate the concentrations of the metal ion in the following solutions. (The concentration of the metal ion is *always* negligible in comparison with that of the complex ion.)

		Ans.
(*a*)	0.01 *M* $[Zn(NH_3)_4]^{++}$ in 0.1 *M* NH_3	9.8×10^{-8} *M*
(*b*)	0.03 " $[Ni(NH_3)_4]^{++}$ " 0.1 " "	1.44×10^{-5} *M*
(*c*)	0.05 " $[Ni(CN)_4]^{=}$ " 0.01 " CN^-	5×10^{-16} "
(*d*)	0.05 " $[CdI_4]^{=}$ " 0.1 " I^-	2.5×10^{-4} "
(*e*)	0.1 " $[Fe(NCS)_6]^{-3}$ " 0.1 " CNS^-	8×10^{-5} *M*

2. Which would contain a larger $C_{Cd^{++}}$, a solution 0.05 *M* in $[Cd(NH_3)_4]^{++}$ and 0.1 *M* in NH_3, or one 0.05 *M* in $[Cd(CN)_4]^{=}$ and 0.001 *M* in CN^-?

3. Write equations and constants for all the equilibria that must be satisfied in an NH_3 solution saturated with $Cd(OH)_2$.

4. What fraction of 10 mg of AgBr should dissolve when shaken with 10 ml of 2 *N* NH_3 until equilibrium is reached? What should be C_{NH_3} at equilibrium? *Ans.* About 0.88; about 1.99 *N*.

5. What is the molar concentration of a CN^- solution 1 ml of which *just* dissolves 20 mg of AgI? *Ans.* About 0.17 *N*.

6. Explain why a solution of $Hg(CN)_2$ gives no reactions for CN^- until Hg has been removed by H_2S.

7. If the salt $Ag(NH_3)_2{}^+Cl^-$ could be prepared and 0.1 mol of it dissolved in 1 liter of pure water, should any AgCl precipitate? What per cent of the Ag^+ should precipitate? *Ans.* About 90%.

8. In an NH_3 solution *saturated* with AgBr, how many times as large as C_{Br^-} must C_{NH_3} be? *Ans.* 426.5.

9. To exactly dissolve 20 mg $Cd(OH)_2$ in 2 ml of 6 *N* NH_3, how many mg of NH_4Cl must be added? *Ans.* Slightly less than 0.4 mg.

Directions for Solving Problem 9

1. Assume that *all* Cd is in complex, and calculate *molar concentration* of the complex ion in 2 ml of solution.

2. Calculate fraction of a mol of NH_3 required to form the complex and the C_{NH_3} not in the complex.

3. Using the $K_{inst.}$, calculate $C_{Cd^{++}}$ in equilibrium with the complex.

4. Using the $K_{s.p.}$ of $Cd(OH)_2$, calculate how small the C_{OH^-} in the solution must be made to *just* dissolve the $Cd(OH)_2$.

5. Using K_b of NH_3, calculate $C_{NH_4^+}$ required to be in the NH_3 solution to reduce C_{OH^-} to the required value.

6. Calculate required $C_{NH_4^+}$ to weight of NH_4Cl required for 2 ml.

CHAPTER 11

EQUILIBRIUM IN REDOX REACTIONS

It is generally accepted at the present time that the reversible reaction, atom $\rightleftarrows$ ion, consists of a gain or loss of electrons, units of negative electricity. *Oxidation* is now understood to be *loss* of electrons; *reduction*, *gain* of electrons. In $Na \rightarrow Na^+ + e^-$, Na is oxidized. In $Cl_2 + 2e^- \rightarrow 2Cl^-$, chlorine is reduced.

As was stated in Chapter 4, the inert gases with their stable outer energy levels of 8 electrons are not affected by chemical forces. They are neither oxidized nor reduced. The halogens, which immediately precede inert gases, tend most strongly to gain electrons. They are the strongest *oxidants*. Their oxidizing power decreases with increasing radius of the ion regularly from F_2 to I_2. The alkali metals, which immediately follow inert gases, tend most strongly to lose an electron and hence are the strongest *reductants*. Their strength as reductants varies somewhat irregularly as is shown by their electrode potentials (see Table 7, page 174). Oxygen and sulfur are weaker oxidants than the halogens, and the alkaline earth metals are weaker reductants than the alkali metals, Be being weakest and Ba strongest.

Elements in the middle of long periods K to Kr, Rb to Xe, Cs to Rn, show variable valence and their ions gain or lose electrons to form ions in other valence states. For example, $Cu^+ \rightleftarrows Cu^{++} + e^-$, $Fe^{++} \rightleftarrows Fe^{+3} + e^-$, $MnO_4^{=} \rightleftarrows MnO_4^- + e^-$.

Since all electron-transfer reactions are reversible, the law of equilibrium applies to them and it should be possible to calculate the values of their equilibrium constants. These reactions, however, differ from those considered in previous chapters in that electrons are reactants or products of the reactions and have to be taken into account.

THE NERNST EQUATION

About 1890, ten years before the discovery of the electron, a young German, Walter Nernst, formulated the equation which relates electricity to chemical reaction. The subsequent discovery

of electrons made clear the real basis of the equation but did not modify it at all. It is interesting that Nernst's equation is identical with that derived by consideration of the energy change involved, although the latter rejects the hypotheses on which Nernst's reasoning was based.

Nernst assumed that a metal immersed in a liquid acquired an electrical charge, either positive or negative, as a result of the magnitudes of two opposing pressures. He assumed that each element must possess as one of its characteristic properties a definite, fixed, and measurable tendency to form ions. But since ions are electrically charged, while atoms are neutral, the change, atom $\rightleftarrows$ ion, must result in electrical charge appearing somewhere in the system. Opposed to this "solution pressure," which was a fixed property of the metal, would be the osmotic pressure exerted by ions of the metal already in solution.

Let us consider the change

$$\underline{\text{Zn}} \rightleftarrows \text{Zn}^{++} + 2e^{-}.$$

(It is obvious that we may write electrons in place of Nernst's "units of negative electricity.") The solution pressure of Zn would force some Zn^{++} to form. The latter would pass out into the liquid about the metal. But formation of Zn^{++} would leave two free electrons on the metal, giving it a negative charge, whereas the liquid would acquire an equal positive charge from the presence of the Zn^{++}. Thus, a difference of electrical potential (E) would be built up between negative metal and positive solution. This potential would make entrance of a second Zn^{++} into the solution require much more work than the first Zn^{++} required, for this second ion would be attracted by the negative charge already on the metal and would also be repelled by the positive charge already on the solution. However, the solution pressure of zinc might be large enough to overbalance this potential difference and force more Zn^{++} into the solution. But, as van't Hoff had demonstrated shortly before, ions in solution must be assumed to exert an osmotic pressure increasing with their concentration according to the laws of gases. Since osmotic pressure tends to cause the solution to become more dilute and since in this case it could become more dilute only by Zn^{++} returning to Zn atom by the acquisition of two electrons, two reactions would oppose each other.

$$\text{e.s.p.}_{\text{Zn}} \rightleftarrows \text{os.p.}_{\text{Zn}^{++}} + E$$

So long as the solution pressure of the metal exceeds the osmotic pressure of the ions in solution plus the constantly increasing difference of potential between the negative metal and the positive solution, Zn^{++} would continue to form. Equilibrium would be reached when E becomes great enough so that the effect of it, plus the os.p. of Zn^{++}, just equals the effect of the (fixed) e.s.p. of Zn. As Helmholz later showed, equilibrium need be established only in a thin film of liquid adjacent to the metal and not in the liquid as a whole. Moreover, the electrical forces are enormous as compared with the atomic forces, e.s.p. and os.p., so that E is by far the chief factor in producing equilibrium.

Nernst was able to show that E would be given by

$$E = \pm\frac{RT}{n\mathrm{F}} \log_e \frac{\text{os.p.}}{K_{\text{e.s.p.}}}, \tag{1}$$

where R is the gas constant (Chapter 3), T the absolute temperature, n the number of charges involved in formation of the ion (two for Zn^{++}) and F is the faraday, 96500 coulombs per unit charge. $K_{\text{e.s.p.}}$ would be a constant for each element.

For $t = 25°C.$, pressures in atmospheres, and $\log_e$ changed to $\log_{10}$, (1) would become

$$E = \pm\frac{8.32 \dfrac{\text{volts} \times \text{coulombs}}{\text{degree}} \times 298 \text{ degrees}}{96500 \dfrac{\text{coulombs}}{\text{equiv.}} \times n \text{ equivalents}} \times 2.302,$$

which gives

$$E \text{ (volts)} = \pm\frac{0.0591}{n} \log_{10} \frac{\text{os.p. (atm.)}}{K_{\text{e.s.p.}} \text{ (atm.)}}. \tag{2}$$

For not too great pressures, pressure is proportional to concentration and C_{ion} can be substituted for os.p. The $K_{\text{e.s.p.}}$ can also be expressed in concentration units since, theoretically, there must be *some* C_{ion} the osmotic pressure of which would just equal the e.s.p. of the metal so that no difference of potential between element and solution would result. Hence, we may replace e.s.p. in equation (2) by that molar concentration of ions the osmotic pressure of which at 25° would just equal the unknown and unmeasurable e.s.p. of the element to which the equation is being applied. That this e.s.p. of the element and hence this K mol/l of the ions cannot be measured experimentally is not a serious objection. An experimental device

will now be described which permits elimination altogether of K in equation (2).

Eliminating the $K_{e.s.p.}$ from the Nernst equation. Just as chemists have *agreed* to assign the weight 16.00 to the atom of oxygen, so they have agreed to assign the potential 0.00 volt to the hydrogen electrode, a half-cell consisting of a platinum electrode plated with platinum black which is immersed in a solution $1\,M$ in H^+ kept saturated with H_2 gas at atmospheric pressure.[1] The half-cell reaction is $2H^+ + 2e^- \rightleftarrows H_2$. The potential of this half-cell is not 0.00 volt, but this value is assigned to it and other half-cells are compared with it. For the hydrogen electrode, equation (2) becomes

$$0.00 \text{ volt} = -\frac{0.059}{2} \log \frac{p_{H_2}\ (1 \text{ atm.})}{C^2_{H^+}\ (1\,M)}. \tag{3}$$

For reasons to be stated later we *arbitrarily* choose to give the logarithmic factor a *negative* sign.

If now we prepare the half-cell, $Zn - Zn^{++}$ $(1\,M)$, and place it in a potentiometer circuit against the half-cell, H_2 1 atm. $- H^+$ $1\,M$, we can find by measurement how much more positive or more negative the Zn electrode is than the hydrogen electrode. Measurement shows the Zn to be 0.76 volt more *negative* than the hydrogen electrode. We conclude that the *molar* potential, E^0, of $Zn^{++} \rightleftarrows Zn$ is -0.76 volt. This measurement has given us no information at all about the actual value of the e.s.p. (K mol/l) of Zn nor of that of H_2. All we have learned is that if we *arbitrarily* assign the value 0.00 volt to $1\,M$ $H^+ \rightleftarrows H_2$ 1 atm., then we may assign the value -0.76 volt to $1\,M$ $Zn^{++} \rightleftarrows Zn$.

We can now *calculate* the potential of Zn in Zn^{++} of *any concentration*, C mol/l, without knowing what the e.s.p. (K mol/l) of Zn actually is. For any $C_{Zn^{++}}$ the Nernst expression for the potential is

$$E = -\frac{0.059}{2} \log \frac{K_{Zn}}{C_{Zn^{++}}} \tag{4}$$

but we have found by experiment that for $C_{Zn^{++}} = 1\,M$

$$E^0 = -0.76 \text{ volt} = -\frac{0.059}{2} \log \frac{K_{Zn}}{1\,M}. \tag{5}$$

[1] In $1\,M$ OH^- ($C_{H^+} = 10^{-14}\,M$) the potential of the hydrogen electrode is -0.828 volt.

Subtracting (5) from (4) we have

$$E - E^0 = -\frac{0.059}{2} \log \frac{1}{C_{Zn^{++}}};$$

or, transposing E^0,

$$E = -0.76 \text{ volt} - \frac{0.059}{2} \log \frac{1}{C_{Zn^{++}}}, \tag{6}$$

since $\log K_{Zn} - \log C_{Zn^{++}} - (\log K_{Zn} - \log 1) = \log \frac{1}{C_{Zn^{++}}}$. We have now eliminated e.s.p. altogether from the Nernst equation.[2] We can compare the potentials of the elements in various concentrations of their ions (*a*) with the molar hydrogen electrode and (*b*) with each other, just as we compare their atomic weights relative to oxygen arbitrarily taken as 16.00.

Similarly, by actual measurement of the cell

$$\underline{\text{Carbon}} \;\Big|\; \begin{matrix} Cl_2 \text{ 1 atm.} \\ Cl^- \text{ 1 } M \end{matrix} \;\Big\|\; \begin{matrix} H_2 \text{ 1 atm.} \\ H^+ \text{ 1 } M \end{matrix} \;\Big|\; \underline{\text{Platinum}}$$

the molar potential $E^0 = +1.36$ volt is found for $Cl_2 \rightleftarrows 2Cl^-$. For a half-cell containing Cl_2 at about atmospheric pressure and Cl^- of any concentration, E is given by

$$E = +1.36 \text{ v.} - \frac{0.059}{2} \log \frac{C^2_{Cl^-}}{p_{Cl_2}}. \tag{7}$$

If the reactions be written as

$$Zn^{++} + 2e^- \rightleftarrows \underline{Zn} \qquad \text{and} \qquad Cl_2 + 2e^- \rightleftarrows 2Cl^-,$$

we may write (6) and (7)

$$E_{Zn} = -0.76 \text{ v.} - \frac{0.059}{2} \log \frac{1}{C_{\text{reactant}}} \text{ and}$$

$$E_{Cl_2} = +1.36 \text{ v.} - \frac{0.059}{2} \log \frac{C^2_{\text{product}}}{p_{\text{reactant}}},$$

where, regardless of whether the electrode is positive or negative, the products of the reactions considered are in the numerator and

[2] The Nernst equation is no longer derived by assuming hypothetical solution pressure opposed to osmotic pressure. The modern derivation leads to the same equation however.

the reactants in the denominator. The large *negative* potential of Zn shows that the reaction $Zn^{++} + 2e^- \rightleftarrows Zn$ has little tendency to proceed from left to right but a strong tendency to proceed from right to left. The large positive potential of Cl_2 indicates that the reaction tends strongly to go to the right and but slightly to go to the left.

Exercise. Show by calculation whether Zn becomes more or less negative than -0.76 v., and Cl_2 more or less positive than $+1.36$ v. under the following conditions:

$C_{Zn^{++}}$ = (*a*) $2\,M$; (*b*) $0.5\,M$. C_{Cl^-} = (*a*) $2\,M$; (*b*) $0.5\,M$
p_{Cl_2} constant at 1 atm.

MOLAR REDOX POTENTIALS AND THE ELECTROMOTIVE SERIES OF THE CHEMICAL ELEMENTS

Very careful measurements have been made by many experimenters of the difference of potential between the various elements in $1\,M$ solutions of their ions and the molar hydrogen electrode. The *average* values are tabulated in textbooks as the standard E^0 values, or the molar (or molal) potentials of the half-cell reactions.

The electromotive series is a qualitative, the table of molar potentials a *quantitative*, statement of the *decreasing* tendency of the elements and ions to *lose* electrons and their *increasing* tendency to *gain* electrons, that is, their increasing power as oxidants. Cs, as the strongest reductant, heads the table and F_2, as the strongest oxidant, ends it.

Some tables give the signs opposite to those in others. Confusion on this account will be avoided by remembering the following statement. If a table of molar potentials gives the sign of the potentials above hydrogen as $+$, the sign is that on the solution. If it gives it as $-$, the sign is that on the electrode.

In Table 7 the signs are those on the electrode. In this table the order is that of increasing strength as oxidant. In the given potentials of half-cell reactions, such as $Fe^{+3} + e^- \rightleftarrows Fe^{++}$, or $Cr_2O_7^- + 6e^- + 14H^+ \rightleftarrows 2Cr^{+3} + 7H_2O$, it is assumed that *every* ion involved in the reaction had activity equal to $1\,M$ when the potential was measured.

The arbitrary convention as to sign. In the Nernst equation (2), page 157, the sign of E is $\pm$. Evidently the sign is opposite on the solution and on the element. The sign on the solution, and also

that on the element, for a nonmetal is opposite to that for a metal. Evidently, whether one states the sign on the electrode or that on the solution is purely a matter of choice. It must be settled by *agreement.* The majority of chemists prefer to state the sign on the electrode. This convention will be adopted. In equation (3), page 158, we arbitrarily gave a negative sign to the logarithmic factor without stating a reason for the choice. The choice was based on the following considerations.

1. In the writing of equilibrium expressions for reversible reactions, it is conventional to place concentrations of products in the numerator, those of reactants in the denominator.

2. A *positive* value of the E.M.F. of a half-cell,[3] or of a cell (two half-cells in circuit), should indicate spontaneous reaction, that is, that the chemical reaction as written can proceed from left to right. A negative value of the E.M.F. should indicate a tendency of the chemical reaction to proceed spontaneously from right to left.

In accordance with the law of equilibrium the reaction should be more spontaneous (larger positive E.M.F.) the larger the concentrations of the reactants and the smaller the concentrations of the products. This will require that the logarithmic factor in[4]

$$E = E^0 \pm \frac{0.059}{n} \log \frac{\text{products}}{\text{reactants}}$$

always be given a *negative* sign, since, if the ratio $\frac{\text{products}}{\text{reactants}}$ is greater than unity, the log is positive but as the spontaneous tendency of the reaction is decreased, the logarithmic factor must be *subtracted* from E^0. Similarly if the ratio $\frac{\text{products}}{\text{reactants}}$ is less than unity

[3] Any element in contact with a solution containing its ions constitutes a half-cell. An indifferent electrode, for example Pt, in contact with a solution containing ions which can exchange electrons (for example, $Fe^{++} \rightleftarrows Fe^{+3}$ or $MnO_4^- \rightleftarrows MnO_4^-$), also constitutes a half-cell.

[4] It is to be understood that this expression represents the equilibrium expression for the *balanced* chemical equation, with concentrations raised to appropriate powers. Thus for the reaction $Fe^{+3} + e^- \rightleftarrows Fe^{++}$,

$$E = E^0 - \frac{0.059}{1} \log \frac{C_{Fe^{++}}}{C_{Fe^{+3}}}.$$

For the reaction $Cr_2O_7^- + 14H^+ + 6e^- \rightleftarrows 2Cr^{+3} + 7H_2O$,

$$E = E^0 - \frac{0.059}{6} \log \frac{C^2_{Cr^{+3}}}{C_{Cr_2O_7^-} \times C^{14}_{H^+}}.$$

(large concentrations of reactants and increased spontaneous reaction) the log of the ratio is negative, but when this negative logarithmic factor is *subtracted* from E^0, the value of E is increased.

A more important reason for giving the logarithmic factor in the Nernst equation a minus sign will appear later in physical chemistry in connection with the *free energy* of chemical reactions. Since spontaneous reactions involve loss of energy, the amount of this loss, ΔF, represents the *driving force* of the reaction. In a cell reaction this change of free energy is given by

$$-\Delta F \text{ (joules)} = 96500nE$$

where E is the E.M.F. of the cell and n the number of electrons involved in the reaction. The minus sign shows that energy is lost, that is, becomes free. If all reactants and products of the chemical reaction have unit activities, $-\Delta F$ becomes $-\Delta F^0$ just as E becomes E^0.

If we are always to write

$$E = E^0 - \frac{0.059}{n} \log \frac{\text{products}}{\text{reactants}}$$

and take the sign of E as that on the electrode, half-cell reactions must be written as *reductions*, that is, electrons appear as *reactants* as do the oxidized forms. Reduced forms become products. Compare equations (6) and (7), page 159, and exercise 1, page 160.

SIMULTANEOUS OXIDATION AND REDUCTION

Production of current. In a half-cell no current can flow. There is merely accumulation of electrons which have no place to go. In order for electrons to move, two half-cells must be combined in a circuit. The E.M.F. of a cell is the algebraic difference of the potentials (E values) of the two half-cells.

If the equation for the half-cell having the smaller E value be subtracted from the equation having the larger E value, a positive value of the cell E.M.F. is invariably obtained. Furthermore, the resulting equation is automatically arranged so that products are in the numerator and reactants in the denominator of the logarithmic factor.

Rules for calculating the E.M.F. of a cell.

1. Write the half-cell reactions as reductions and set down the E^0 values (Table 7). For example:

$$Zn^{++} + 2e^- \rightleftarrows \underline{Zn} \qquad -0.76 \text{ v.}$$
$$Ag^+ + e^- \rightleftarrows \underline{Ag} \qquad +0.80 \text{ v.}$$

2. If the half-cell reactions contain unequal numbers of electrons, multiply one or both by such factors that the resulting equations shall contain the same number of electrons. The E^0 values are *not* part of the equation and are not to be multiplied.

$$Zn^{++} + 2e^- \rightleftarrows \underline{Zn} \qquad -0.76 \text{ v.}$$
$$2Ag^+ + 2e^- \rightleftarrows \underline{2Ag} \qquad +0.80 \text{ v.}$$

3. Set down the Nernst equations for the E values of the half-cell reactions containing the same number of electrons.

$$E_{Zn} = -0.76 - \frac{0.059}{2} \log \frac{1}{C_{Zn^{++}}}$$
$$E_{Ag} = +0.80 - \frac{0.059}{2} \log \frac{1}{C^2_{Ag^+}}$$

4. Subtract algebraically the equation having the *smaller* E value from the equation having the larger E value, remembering that -4 is smaller than -2 or $+0.5$.

$$\text{E.M.F.} = E_{Ag} - E_{Zn} = +0.80 - (-0.76) - \frac{0.059}{2} (\log 1 - \log C^2_{Ag^+} - \log 1 + \log C_{Zn^{++}})$$
$$= +1.56 \text{ v.} - \frac{0.059}{2} \log \frac{C_{Zn^{++}} \text{ (product)}}{C^2_{Ag^+} \text{ (reactant)}}$$

Since Zn^{++} appears as product and Ag^+ as reactant when the E.M.F. is positive, the spontaneous reaction is shown to be

$$\underline{Zn} + 2Ag^+ \rightleftarrows Zn^{++} + \underline{2Ag}.$$

The large positive value of the cell E.M.F. shows that Zn can reduce Ag^+ very completely to Ag.

The invariably positive value obtained for the E.M.F. of the cell shows that the reaction read from left to right *can* take place. However, it is to be remembered that nothing is implied about the *rate* of reaction, which may be infinitesimal. Such a case, discussed later, is that of H_2 and O_2 at room temperature.

CALCULATION OF THE EQUILIBRIUM CONSTANT OF A REDOX REACTION

This differs from previously studied cases of equilibrium only in that transfers of electrons (electricity) are involved and must be

taken into account. The Nernst equation gives us the quantitative measure of the tendency to electron-transfer. When an oxidation-reduction reaction is at the equilibrium point, no current will flow in the circuit. If the Nernst expressions for the two half-cells are set equal to each other, the resulting equation states the conditions of equilibrium both as to concentrations and as to electron-transfer tendencies.

How the $K_{equil.}$ can be calculated directly from the E^0 values of the half-cell reactions is evident from the following considerations. For the balanced redox reaction,

$$\underset{\text{oxidant}_1}{a\,\text{A}} + \underset{\text{reductant}_2}{b\,\text{B}} \rightleftarrows \underset{\text{reductant}_1}{c\,\text{C}} + \underset{\text{oxidant}_2}{d\,\text{D}},$$

the equilibrium condition is

$$K_{equil.} = \frac{C^c_{\text{C}} \times C^d_{\text{D}}}{C^a_{\text{A}} \times C^b_{\text{B}}} = \frac{(\text{products})}{(\text{reactants})}.$$

The half-cell reactions would be

$$\text{oxidant}_1 \; a\,\text{A} + n\,e^- \rightleftarrows c\,\text{C} \; \text{reductant}_1$$
$$\text{oxidant}_2 \; d\,\text{D} + n\,e^- \rightleftarrows b\,\text{B} \; \text{reductant}_2.$$

The potentials of the half-cell reactions are given by

$$E_1 = E^0_1 - \frac{0.059}{n} \log \frac{C^c_{\text{C}}}{C^a_{\text{A}}};$$
$$E_2 = E^0_2 - \frac{0.059}{n} \log \frac{C^b_{\text{B}}}{C^d_{\text{D}}}.$$

At equilibrium $E_1 = E_2$ and hence

$$E^0_1 - \frac{0.059}{n} \log \frac{C^c_{\text{C}}}{C^a_{\text{A}}} = E^0_2 - \frac{0.059}{n} \log \frac{C^b_{\text{B}}}{C^d_{\text{D}}}$$

and, assuming that $E^0_1 > E^0_2$,

$$(E^0_1 - E^0_2)\frac{n}{0.059} = -\log \frac{C^b_{\text{B}}}{C^d_{\text{D}}} + \log \frac{C^c_{\text{C}}}{C^a_{\text{A}}}$$
$$= \log \frac{C^c_{\text{C}} \times C^d_{\text{D}}}{C^a_{\text{A}} \times C^b_{\text{B}}} = \log K_{equil.}.$$

It follows then that

$$\log K_{equil.} = \log \frac{\text{products}}{\text{reactants}} = (E^0_1 - E^0_2) \times \frac{n}{0.059}. \qquad (8)$$

This equation gives at once the $K_{equil.}$ of a redox reaction in terms of the standard potentials ($E^0_1 - E^0_2$) of the two half-cell reactions and the number of electrons transferred in the *balanced* equation for the cell reaction.

The equilibrium constant for the cell reaction

$$\underline{Zn} + 2Ag^+ \rightleftarrows Zn^{++} + 2\underline{Ag},$$

$$\frac{C_{Zn^{++}}}{C^2_{Ag^{++}}} = K_{equil.},$$

is given by

$$\log K = +1.56 \times \frac{2}{0.059} = 52.9,$$

whence

$$K = 8 \times 10^{52}.$$

Concentration Cells

The difference of potential between electrode and solution in a half-cell depends not only on the tendency of the element to gain or lose electrons but equally on the concentration of the ions in the solution around the electrode. The latter observation suggests that a current should flow when two half-cells, containing the same element as electrode but different concentrations of the ion, are connected in a closed circuit. Such cells are known as concentration cells and constitute the simplest type of primary cell or "battery." In a concentration cell (same electrodes) E^0 cancels out and the E.M.F. is given by

$$\text{E.M.F.} = \frac{0.059}{n} \log \frac{c_1}{c_2} \tag{9}$$

where c_1 is the more concentrated solution.

Consider the cell

$$\underline{Ag} \;\Big|\; \begin{matrix} Ag^+ \\ 1\,M \end{matrix} \;\Big\|\; \begin{matrix} Ag^+ \\ 0.001\,M \end{matrix} \;\Big|\; \underline{Ag}.$$

The two Ag electrodes are connected externally through a voltmeter; the two solutions are connected through a U-tube filled with solution of an indifferent electrolyte, such as NH_4NO_3 which, inverted, dips into each half-cell.

For the half-cell on the left, $E_1 = E^0$. For the half-cell on the right, $E_2 = E^0 - \frac{0.059}{1} \log \frac{1}{0.001}$. The E.M.F. of this cell should be

$$0.059 \log \frac{1}{0.001} = 0.177 \text{ v.}$$

The voltmeter would not read exactly 0.177 volt because there is an E.M.F. at the junction of the solutions c_1 and c_2 in addition to those at the electrodes. The salt bridge of concentrated NH_4NO_3, of which both ions have nearly the same mobility, reduces the junction potential to a few millivolts.

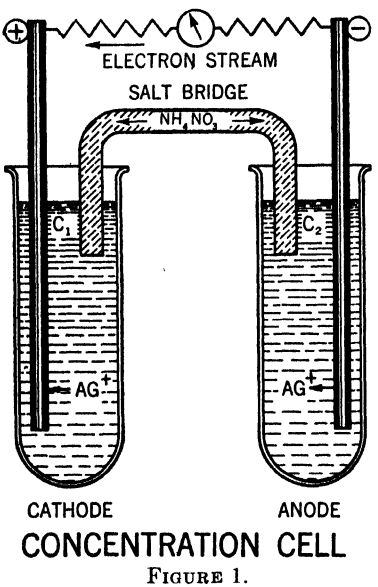


FIGURE 1.

Which electrode should be connected to the + binding post of the galvanometer is evident by considering that in the more concentrated solution, c_1, Ag^+ must be taking electrons from Ag 1000 times as rapidly as in the dilute solution if both electrodes have the same surface area in contact with solution. The electrode in the c_1 (more concentrated) solution is therefore less negative (more positive) than the electrode in the c_2 (more dilute) solution.

Oxidation always takes place at the anode. Anions move toward the anode. At the anode Ag^+ is forming, that is, Ag atoms are oxidized, leaving electrons in the anode which then stream through the external circuit to the less negative (more positive) cathode. At the latter Ag^+ is being reduced, that is, taking electrons from the cathode which consequently becomes less negative (more positive). Since the solution about the cathode becomes more dilute and that about the anode more concentrated in Ag^+, anions (in this case NO_3^-) move from the former into the latter, that is, toward the anode. It follows then that the electrode at which *reduction* takes place is to be connected to the positive binding post of the galvanometer.

Concentration cells have many important uses, two of which are the following:

1. To find the solubility of a slightly soluble salt. If the E.M.F. of the following cell is measured

$$\underline{\text{Ag}} \;\Big|\; \begin{matrix}\text{Ag}^+ \\ 0.1\,M\end{matrix} \;\Big\|\; \begin{matrix}\text{Satd.} \\ \text{AgCl}\end{matrix} \;\Big|\; \underline{\text{Ag}},$$

$$\text{E.M.F.} = 0.059 \log \frac{0.1}{C_{Ag^+}} \text{ (in satd. AgCl)}.$$

Since only C_{Ag^+} is unknown, this can be calculated. In the saturated AgCl solution, $C_{Cl^-} = C_{Ag^+}$ and the $K_{s.p.}$ of AgCl can be calculated.

2. To find the valence of an ion. Ogg[5] by this method showed that mercurous ion must be Hg_2^{++}. For the cell

$$\text{Hg} \;\Big|\; \begin{matrix}\text{mercurous nitrate } 0.001\,N \\ \text{HNO}_3\ 0.1\,N\end{matrix} \;\Big\|\; \begin{matrix}\text{mercurous nitrate } 0.01\,N \\ \text{HNO}_3\ 0.1\,N\end{matrix} \;\Big|\; \text{Hg}$$

he found E.M.F. = 0.029 volt at 18°. Then

$$0.029 = \frac{0.058}{n} \log \frac{0.01}{0.001},$$

from which $n = 2$ and the ion must contain *two* equivalents of Hg.

Reversal of Current Direction

Change of the ion concentrations in cell solutions may cause the current to flow in the opposite direction.[6] This is illustrated by the following calculations. The necessary changes of concentrations are smaller the smaller the difference between the potentials of the two half-cells composing the cell. In the cell

$$\underline{\text{Ag}} \;\Big|\; \begin{matrix}\text{Ag}^+ \\ 1\,M\end{matrix} \;\Big\|\; \begin{matrix}\text{Fe}^{+3}\ 0.1\,M \\ \text{Fe}^{++}\ 10^{-5}\,M\end{matrix} \;\Big|\; \underline{\text{Pt}}$$

[5] Z. physik. Chem., **27**, 285 (1898).

[6] In the following calculations, as well as in the problems at the end of this chapter, the approximate value 0.06 has been used instead of 0.059. This facilitates calculations considerably. Since the ion concentrations used in these calculations may differ considerably from the activities used in calculating the standard electrode potentials of Table 7, calculated values must be considered as only approximate. They serve to indicate satisfactorily the direction and completeness of redox reactions.

$$E_{Ag^+-\underline{Ag}} = +0.8 - 0.06 \log 1, \text{ and}$$

$$E_{Fe^{+3}-Fe^{++}} = +0.75 - 0.06 \log \frac{10^{-5}}{10^{-1}}.$$

The Pt electrode is 0.19 volt more positive than the Ag electrode. The cell reaction

$$Fe^{+3} + \underline{Ag} \rightleftarrows Ag^+ + Fe^{++}$$

is proceeding toward the right. Ag is being oxidized; Fe^{+3} is being reduced. Equilibrium will be reached and current cease to flow when $C_{Ag^+} = 1.01266\,M$; $C_{Fe^{+3}} = 0.08734\,M$ and $C_{Fe^{++}} = 0.01267\,M$ if the amounts of solution are assumed equal.

In the cell

$$\underline{Ag} \;\Big|\; \begin{matrix} Ag^+ \\ 0.1\,M \end{matrix} \;\Big\|\; \begin{matrix} Fe^{+3}\ 10^{-5}\,M \\ Fe^{++}\ 10^{-1}\,M \end{matrix} \;\Big|\; \underline{Pt}$$

$$E_{Ag^+-Ag} = +0.80 - 0.06 \log \frac{1}{0.1}, \text{ and}$$

$$E_{Fe^{+3}-Fe^{++}} = +0.75 - 0.06 \log \frac{10^{-1}}{10^{-5}}.$$

The Ag electrode is now 0.23 volt more positive than the Pt electrode. Ag^+ is now oxidizing Fe^{++}. Equilibrium will be reached and current cease to flow when $C_{Ag^+} = C_{Fe^{++}} = 0.06825\,M$ and $C_{Fe^{+3}} = 0.03175\,M$, amounts of solutions being assumed equal.

In the first cell above, the (*starting*) E.M.F. is 0.19 v.; in the second it is 0.23 v. Of course, in each case the E.M.F. approaches 0.0 v. as the cell reaction, $Fe^{+3} + \underline{Ag} \rightleftarrows Fe^{++} + Ag^+$, approaches equilibrium.

It was previously shown that the equilibrium constant of a cell reaction is given by

$$\log K = E \times \frac{n}{0.059}$$

where E is the algebraic difference of the E^0 values of the two half-cell reactions. For the reaction

$$Fe^{++} + Ag^+ \rightleftarrows Fe^{+3} + \underline{Ag}$$

we have $\log K = (0.80 - 0.75) \times \frac{1}{0.06} = 0.8333$, from which $K = 6.813$.

Hence the reaction can go in either direction, depending on the ion concentrations present, since at equilibrium $C_{Fe^{+3}}$ is only about seven times $C_{Fe^{++}} \times C_{Ag^{+}}$.

The current of even a Daniell cell can be reversed by adding a sufficient $C_{S^{=}}$ to the Cu^{++} solution. The cell reaction is

$$\underline{Zn} + Cu^{++} \rightleftarrows Zn^{++} + \underline{Cu}.$$

In the cell

$$\underline{Zn} \;\big|\; \begin{matrix} Zn^{++} \\ 0.1\,M \end{matrix} \;\Big\|\; \begin{matrix} Cu^{++} \\ 0.1\,M \end{matrix} \;\big|\; \underline{Cu}$$

the E.M.F. is given by

$$\text{E.M.F.} = +0.345 - (-0.76) - 0.03 \log \frac{0.1\ (C_{Zn^{++}})}{0.1\ (C_{Cu^{++}})} = 1.105 \text{ v.}$$

For equilibrium,

$$\log \frac{C_{Zn^{++}}}{C_{Cu^{++}}} = \log K = 1.105 \times \frac{2}{0.06} = 36.83,$$

whence

$$K = 6.76 \times 10^{36}.$$

If $S^{=}$ be added to the Cu^{++} solution until $C_{S^{=}}$ is $3.0\,M$, $C_{Cu^{++}}$ in the solution will become $(4 \times 10^{-38})/8 = 1.333 \times 10^{-38}\,M$. The E.M.F. becomes

$$1.105 - 0.03 \log \frac{0.1}{1.33 \times 10^{-38}} = -0.001 \text{ v.}$$

The change of sign indicates reversal of the reaction. The copper electrode is now more negative, showing that copper is dissolving and zinc plating out in spite of the enormous forward tendency of the reaction

$$\underline{Zn} + Cu^{++} \rightleftarrows Zn^{++} + \underline{Cu}.$$

Cobaltic ion is one of the most powerful oxidants, liberating oxygen even from water. Its potential is +1.84 volts. Ions such as $Co(NO_2)_6^{-3}$ and $Co(NH_3)_6^{+3}$ are so stable (that is, in equilibrium with so small $C_{Co^{+3}}$) that they can be formed in the presence of water. Similarly $Co(OH)_3$ is so insoluble that it can exist in basic solution. In the presence of H^{+} the Co^{+3} ion is instantly reduced to Co^{++}. In this respect it is different from Fe^{+3}.

Algebraic Manipulation of More Complex Half-Cells

Can CuS and HgS dissolve in HNO_3 if NO and S are formed? If CuS dissolves, the reaction is

$$3\underline{CuS} + 2NO_3^- + 8H^+ = 3\underline{S} + 3Cu^{++} + 4H_2O + 2\overline{NO}.$$

At equilibrium

$$\frac{C^3_{Cu^{++}} \times p^2_{NO}}{C^2_{NO_3^-} \times C^8_{H^+}} = K_{equil.}$$

The half-cell reactions and their molar potentials are:

$$\underline{S} + 2e^- \rightleftarrows S^= \qquad -0.51 \text{ v.} \qquad (10)$$

$$NO_3^- + 3e^- + 4H^+ \rightleftarrows \overline{NO} + 2H_2O \qquad +0.94 \text{ v.} \qquad (11)$$

Multiplying (10) by 3 and (11) by 2, and subtracting,

$$\text{E.M.F.} = +1.45 \text{ v.} - \frac{0.06}{6} \log \frac{p^2_{NO}}{C^2_{NO_3^-} \times C^8_{H^+} \times C^3_{S^=}},$$

whence

$$\frac{1.45}{0.01} = \log \frac{p^2_{NO}}{C^2_{NO_3^-} \times C^8_{H^+} \times C^3_{S^=}}$$

and

$$10^{145} = \frac{p^2_{NO}}{C^3_{S^=} \times C^2_{NO_3^-} \times C^8_{H^+}}. \qquad (12)$$

The $K_{s.p.}$ of CuS is 3.5×10^{-38}. Then

$$C^3_{Cu^{++}} \times C^3_{S^=} = 4.29 \times 10^{-113},$$

whence

$$C^3_{S^=} = \frac{4.29 \times 10^{-113}}{C^3_{Cu^{++}}}.$$

Substituting in (12),

$$4.29 \times 10^{32} = \frac{p^2_{NO} \times C^3_{Cu^{++}}}{C^2_{NO_3^-} \times C^8_{H^+}},$$

which indicates that CuS should dissolve in HNO_3.

If into (12) we introduce the $K_{s.p.}$ of HgS, 3×10^{-53},

$$C^3_{Hg^{++}} \times C^3_{S^=} = 2.7 \times 10^{-158},$$

(12) becomes

$$2.7 \times 10^{-13} = \frac{p^2_{NO} \times C^3_{Hg^{++}}}{C^2_{NO_3^-} \times C^8_{H^+}},$$

which indicates that HgS should *not* dissolve much.

REACTION POSSIBILITY AND REACTION VELOCITY

It must be remembered always that reaction velocities are unrelated to equilibrium conditions. Hence, a reaction indicated as possible by the value of its $K_{equil.}$ may actually take place at an extremely slow rate. A good example is

$$2H_2 + O_2 \rightleftarrows 2H_2O, \text{ for which } K_{equil.} = \frac{1}{p^2_{H_2} \times p_{O_2}}.$$

For $O_2 + 4H^+ + 4e^- \rightleftarrows 2H_2O$, $E^0 = +1.23$ v. (13)

For $4H^+ + 4e^- \rightleftarrows 2H_2$, $E^0 = 0.00$ v. (14)

Subtracting (14) from (13)

$$E = 1.23 + \frac{0.06}{4} \log \frac{1}{p^2_{H_2} \times p_{O_2}},$$

whence

$$10^{82} = \frac{1}{p^2_{H_2} \times p_{O_2}},$$

which indicates that at equilibrium at 25° one or both of the gases should be used up practically completely by the reaction.

Actually, no evidence of reaction is detectable after the mixed gases have been maintained under high pressure for years at room temperature. The speed of the reaction is infinitesimal at this temperature, although it proceeds with explosive velocity at sufficiently high temperatures.

The electrode potentials indicate when a reaction *cannot* take place. They give no information about the velocity of the reaction which at ordinary temperatures may proceed at an infinitesimal rate.

In Table 7 (p. 174) the given value of E^0 assumes that all gases involved in the reaction are at a pressure of 1 atm. and all dissolved substances at an activity of 1 molal (that is, 1 mol per 1000 g of water). The activities of pure solids and of water are taken as unity. The order is that of *increasing* strength as oxidant.

PROBLEMS

1. What should be the molar concentrations of Fe^{++} and Cd^{++} at equilibrium (*a*) when excess of Cd is placed in a solution 0.1 *M* in Fe^{++}? (*b*) When excess of iron is placed in 0.1 *M* Cd^{++}? $E^0_{Fe-Fe^{++}} = -0.44$ v. $E^0_{Cd-Cd^{++}} = -0.40$ v. *Ans.* (*a*) $Fe^{++} = 0.0955\,M$, $Cd = 0.0044\,M$; (*b*) $Fe^{++} = 0.0955\,M$, $Cd^{++} = 0.0044\,M$.

2. Calculate $K_{equil.}$ for $Br_2 + 2I^- \rightleftarrows I_2 + 2Br^-$. $E^0_{Br_2-Br^-} = +1.07$ v. $E^0_{I_2-I^-} = 0.54$ v. *Ans.* $K = 4.6 \times 10^{17}$.

3. (*a*) Calculate $K_{equil.}$ for $2Fe^{+3} + H_2S \rightleftarrows \underline{S} + 2Fe^{++} + 2H^+$. For $Fe^{+3} \rightleftarrows Fe^{++}$, $E^0 = +0.75$ v. For $H_2S \rightleftarrows \underline{S} + 2H^+$, $E^0 = +0.17$ v. (*b*) What should be the approximate value of $\frac{C_{Fe^{++}}}{C_{Fe^{+3}}}$ at equilibrium, when $0.1\,M$ Fe^{+3} in $0.25\,M$ H^+ is saturated with H_2S? A saturated solution of H_2S is $0.1M$. (*c*) About what will C_{H^+} become at equilibrium? *Ans.* (*a*) $K_{equil.}$ $\frac{C_{H^+} \times C_{Fe^{++}}}{C^{0.5}_{H_2S} \times C_{Fe^{+3}}}$ $= 4.642 \times 10^9$. (*b*) At equilibrium $\frac{C_{Fe^{++}}}{C_{Fe^{+3}}} = 4.19 \times 10^9$. (*c*) $0.35\,M$.

4. Calculate $K_{equil.}$ for oxidation of $Cr(OH)_3$ by H_2O_2 (HO_2^-) in basic solution. For $OH^- \rightleftarrows HO_2^-$, $E^0 = +0.87$ v. For $Cr(OH)_3 \rightleftarrows CrO_4^-$, $E^0 = -0.12$ v. *Ans.* $\frac{C^2_{CrO_4^-}}{C^3_{HO_2^-} \times C_{OH^-}} = 10^{99}$.

5. (*a*) Should HClO readily oxidize Pb^{++} to PbO_2? For $Cl^- \rightleftarrows HClO + H^+$, $E^0 = +1.5$ v. For $Pb^{++} \rightleftarrows \underline{PbO_2} + H^+$, $E^0 = +1.44$ v. Calculate $K_{equil.}$ *Ans.* $\frac{C_{Cl^-} \times C^3_{H^+}}{C_{Pb^{++}} \times C_{HClO}} = 100$.

(*b*) Would addition of some solid $AcONH_4$ promote or hinder the formation of PbO_2? Give reason for answer.

6. In basic solution the molar potentials are: $Cl^- \rightleftarrows ClO^-$, $E^0 = +0.94$ v. $HPbO_2^- \rightleftarrows PbO_2$, $E^0 = +0.3$ v. Would oxidation be more or less complete in basic solution than in acid solution? *Ans.* $K_{equil.} = \frac{C_{Cl^-} \times C_{OH^-}}{C_{ClO^-} \times C_{HPbO_2^-}} = 2.154 \times 10^{21}$.

7. Calculate $K_{equil.}$ for $\underline{Zn} + NO_3^- + OH^- \rightleftarrows NH_3 + ZnO_2^-$. For $OH^- + NH_3 \rightleftarrows NO_3^- + H_2O$, $E^0 = -0.12$ v. For $\underline{Zn} + OH^- \rightleftarrows ZnO_2^- + H_2O$, $E^0 = -1.216$ v. *Ans.* $\frac{C_{NH_3} \times C^4_{ZnO_2^-}}{C_{NO_3^-} \times C^7_{OH^-}} = 10^{146}$.

8. What should be the starting E.M.F. of the cell below?

H_2 1 atm.				O_2 (air) 0.2 atm.
(Pt)	$0.2\,M$ H^+	OH^- $0.1\,M$		(Pt)

(Partial pressures [in atmospheres] of gases may be substituted for concentrations.) *Ans.* 0.491 v.

9. Calculate the starting E.M.F. of the cell below.

Ag	Na_2CO_3	Na_2CO_3	O_2 1 atm.
	1 *M*	0.05 *M*	(Pt)

Assume $C_{CO_3^=}$ at left = 0.8 *M* and *p*H of 0.05*M* Na_2CO_3 = 11.6. For $Ag + CO_3^= \rightleftarrows Ag_2CO_3 + 2e^-$, $E^0 = +0.5$ v. For $4OH^- \rightleftarrows O_2 + 2H_2O + 4e^-$, $E^0 = +0.4$ v. *Ans.* 0.0412 v.

10. Calculate the concentration of $MnO_4^=$ (green) which should be in equilibrium with 0.1 *M* MnO_4^- in solutions containing C_{OH^-} as follows:

(*a*) 2.0 *M*, (*b*) 1.0 *M*, (*c*) 0.1 *M*, (*d*) 10^{-7} *M*.

For $MnO_4^= \rightleftarrows MnO_4^- + e^-$, $E^0 = +0.54$ v. For $MnO_2 + 4OH^- \rightleftarrows MnO_4^= + 2H_2O + 2e^-$, $E^0 = +0.58$ v. *Hints:* (1) Calculate $K_{equil.}$ for $MnO_4^= + H_2O \rightleftarrows MnO_4^- + MnO_2 + OH^-$. (2) In the equation for equilibrium insert the values assigned to $C_{MnO_4^-}$ and C_{OH^-} and calculate $C_{MnO_4^=}$ for each of the four cases. *Ans.* (*a*) 0.195, (*b*) 0.078, (*c*) 3.59×10^{-3}, (*d*) 3.59×10^{-11}.

(Observe that the stability of manganates depends mostly on alkalinity of the solution.)

11. Calculate $K_{equil.}$ for $MnO_4^- + H_2O_2 + H^+ \rightleftarrows O_2 + Mn^{++} + H_2O$. For $Mn^{++} + 4H_2O \rightleftarrows MnO_4^- + 5e^- + 8H^+$, $E^0 = +1.5$ v. For $H_2O_2 \rightleftarrows O_2 + 2H^+ + 2e^-$, $E^0 = +0.68$. Solubility of O_2 in water is negligible. *Ans.* $\dfrac{C_{Mn^{++}}}{C_{MnO_4^-} \times C^3_{H^+} \times C^{2.5}_{H_2O_2}} = 2.154 \times 10^{68}$.

12. Show that MnO_2 should dissolve readily in dilute HNO_3 and H_2O_2. For $Mn^{++} + 2H_2O \rightleftarrows MnO_2 + 4H^+ + 2e^-$, $E^0 = +1.33$ v. For $H_2O_2 \rightleftarrows O_2 + 2H^+$, $E^0 = +0.68$ v. *Ans.* $K = 4.64 \times 10^{21}$.

TABLE 7

STANDARD MOLAL POTENTIALS

ACID SOLUTIONS

Couple	E^0 volts (Sign on Electrode)
$Li^+ + e^- = Li$	−3.02
$K^+ + e^- = K$	−2.92
$Ba^{++} + 2e^- = Ba$	−2.90
$Sr^{++} + 2e^- = Sr$	−2.89
$Ca^{++} + 2e^- = Ca$	−2.87
$Na^+ + e^- = Na$	−2.712
$Mg^{++} + 2e^- = Mg$	−2.34
$Al^{+3} + 3e^- = Al$	−1.67
$Zn^{++} + 2e^- = Zn$	−0.7620
$Cr^{+3} + 3e^- = Cr$	−0.71
$Fe^{++} + 2e^- = Fe$	−0.44
$Cd^{++} + 2e^- = Cd$	−0.4020
$Co^{++} + 2e^- = Co$	−0.277
$Ni^{++} + 2e^- = Ni$	−0.250
$Sn^{++} + 2e^- = Sn$	−0.136
$Pb^{++} + 2e^- = Pb$	−0.126
$2H^+ + 2e^- = H_2$	0.000
$S + 2H^+ + 2e^- = H_2S$	+0.141
$Sn^{+4} + 2e^- = Sn^{++}$	+0.15
$SO_4^- + 4H^+ + 2e^- = H_2O + H_2SO_3$	+0.20
$SbO^+ + 2H^+ + 3e^- = Sb + H_2O$	+0.212
$HAsO_2(aq.) + 3H^+ + 3e^- = 2H_2O + As$	+0.2475
$Cu^{++} + 2e^- = Cu$	+0.3448
$[Fe(CN)_6]^{-3} + e^- = [Fe(CN)_6]^{-4}$	+0.36
$Cu^+ + e^- = Cu$	+0.522
$I_2 + 2e^- = 2I^-$	+0.5345
$I_3^- + 2e^- = 3I^-$	+0.5355
$H_3AsO_4 + 2H^+ + 2e^- = 2H_2O + HAsO_2$	+0.559
$Sb_2O_5 + 6H^+ + 4e^- = 3H_2O + 2SbO^+$	+0.64
$O_2 + 2H^+ + 2e^- = H_2O_2$	+0.682
$(CNS)_2 + 2e^- = 2CNS^-$	+0.77
$Fe^{+3} + e^- = Fe^{++}$	+0.771
$Hg_2^{++} + 2e^- = 2Hg$	+0.7986
$Ag^+ + e^- = Ag$	+0.7995
$2Hg^{++} + 2e^- = Hg_2^{++}$	+0.910
$NO_3^- + 3H^+ + 2e^- = HNO_2 + H_2O$	+0.94
$NO_3^- + 4H^+ + 3e^- = 2H_2O + NO$	+0.96
$HNO_2 + H^+ + e^- = NO + H_2O$	+0.99
$Br_2(liq.) + 2e^- = 2Br^-$	+1.0652
$IO_3^- + 6H^+ + 6e^- = 3H_2O + I^-$	+1.085
$Br_2(aq.) + 2e^- = 2Br^-$	+1.087
$IO_3^- + 6H^+ + 5e^- = \frac{1}{2}I_2 + 3H_2O$	+1.195
$O_2 + 4H^+ + 4e^- = 2H_2O$	+1.229
$MnO_2 + 4H^+ + 2e^- = 2H_2O + Mn^{++}$	+1.28
$HBrO + H^+ + 2e^- = H_2O + Br^-$	+1.33
$\frac{1}{2}Cl_2 + e^- = Cl^-$	+1.3583
$Cr_2O_7^- + 14H^+ + 6e^- = 7H_2O + 2Cr^{+3}$	+1.36
$BrO_3^- + 6H^+ + 6e^- = 3H_2O + Br^-$	+1.44
$ClO_3^- + 6H^+ + 6e^- = 3H_2O + Cl^-$	+1.45
$PbO_2 + 4H^+ + 2e^- = 2H_2O + Pb^{++}$	+1.456

TABLE 7.—(*Continued*)

STANDARD MOLAL POTENTIALS

ACID SOLUTIONS

Couple	E^0 volts (Sign on Electrode)
$HClO + H^+ + 2e^- = H_2O + Cl^-$	+1.49
$Mn^{+3} + e^- = Mn^{++}$	+1.51
$MnO_4^- + 8H^+ + 5e^- = 4H_2O + Mn^{++}$	+1.52
$HBrO + H^+ + e^- = \frac{1}{2}Br_2 + H_2O$	+1.59
$MnO_4^- + 4H^+ + 3e^- = 2H_2O + MnO_2$	+1.67
$NiO_2 + 4H^+ + 2e^- = 2H_2O + Ni^{++}$	+1.75
$H_2O_2 + 2H^+ + 2e^- = 2H_2O$	+1.77
$Co^{+3} + e^- = Co^{++}$	+1.84
$Ag^{++} + e^- = Ag^+$	+1.98
$F_2 + 2e^- = 2F^-$	+2.85
BASIC SOLUTIONS	
$Mg(OH)_2 + 2e^- = 2OH^- + Mg$	−2.67
$H_2AlO_3^- + H_2O + 3e^- = 4OH^- + Al$	−2.35
$Zn(CN)_4^- + 2e^- = 4CN^- + Zn$	−1.26
$ZnO_2^- + 2H_2O + 2e^- = 4OH^- + Zn$	−1.216
$Zn(NH_3)_4^{++} + 2e^- = 4NH_3$ (aq.) $+ Zn$	−1.03
$CNO^- + H_2O + 2e^- = 2OH^- + CN^-$	−0.96
$Sn(OH)_6^- + 2e^- = H_2O + 3OH^- + HSnO_2^-$	−0.96
$Cd(CN)_4^- + 2e^- = 4CN^- + Cd$	−0.90
$SO_4^- + H_2O + 2e^- = 2OH^- + SO_3^-$	−0.90
$Co(CN)_6^{-3} + e^- = Co(CN)_6^{-4}$	−0.83
$2H_2O + 2e^- = H_2 + 2OH^-$	−0.828
$HSnO_2^- + H_2O + 2e^- = 3OH^- + Sn$	−0.79
$AsO_4^{-3} + 2H_2O + 2e^- = 4OH^- + AsO_2^-$	−0.71
$AsO_2^- + 2H_2O + 3e^- = 4OH^- + As$	−0.68
$SbO_2^- + 2H_2O + 3e^- = 4OH^- + Sb$	−0.66
$Cd(NH_3)_4^{++} + 2e^- = 4NH_3 + Cd$	−0.597
$HPbO_2^- + H_2O + 2e^- = 3OH^- + Pb$	−0.54
$S_2^- + 2e^- = 2S^-$	−0.51
$S + 2e^- = S^-$	−0.508
$S + H_2O + 2e^- = OH^- + HS^-$	−0.478
$NO_2^- + H_2O + e^- = NO + 2OH^-$	−0.46
$BiOOH + H_2O + 3e^- = 3OH^- + Bi$	−0.46
$Mn(OH)_3 + e^- = OH^- + Mn(OH)_2$	−0.40
$CrO_4^- + 4H_2O + 3e^- = 5OH^- + Cr(OH)_3$	−0.12
$NO_3^- + 6H_2O + 8e^- = NH_3 + 9OH^-$	−0.12
$O_2 + H_2O + 2e^- = OH^- + HO_2^-$	−0.076
$NO_3^- + H_2O + 2e^- = 2OH^- + NO_2^-$	+0.01
$Co(OH)_3 + e^- = OH^- + Co(OH)_2$	+0.20
$IO_3^- + 3H_2O + 6e^- = 6OH^- + I^-$	+0.26
$O_2 + 2H_2O + 4e^- = 4OH^-$	+0.401
$NiO_2 + 2H_2O + 2e^- = 2OH^- + Ni(OH)_2$	+0.49
$MnO_4^- + e^- = MnO_4^-$	+0.54
$MnO_4^- + 2H_2O + 3e^- = 4OH^- + MnO_2$	+0.57
$MnO_4^- + 2H_2O + 2e^- = 4OH^- + MnO_2$	+0.58
$BrO_3^- + 3H_2O + 6e^- = 6OH^- + Br^-$	+0.61
$ClO_3^- + 3H_2O + 6e^- = 6OH^- + Cl^-$	+0.62
$HO_2^- + H_2O + 2e^- = 3OH^-$	+0.87
$ClO^- + H_2O + 2e^- = 2OH^- + Cl^-$	+0.94

PART II
THE LABORATORY WORK

FOREWORD

The course of qualitative analysis on a semimicro scale outlined in the following pages can be covered and two alloys and six to eight solid salt mixtures analyzed in nine clock hours per week for one semester. By omitting certain starred preliminary experiments and reducing the number of salt mixtures analyzed, the course can be covered in six hours per week. It is to be remembered that the use of small amounts of material and centrifugation instead of filtration permits at least 50 per cent more work to be done in a three-hour laboratory period than would be possible by the old macro methods.

It is advisable that the cation groups be studied in the order: alkali metals, Groups IV, III, II, I. Both the chemistry involved and the technique required increase in difficulty in this order. This gives time to treat in lectures the more difficult chemistry before it has to be applied in the laboratory.

In the Purdue laboratory the time devoted to individual parts of the work is approximately as follows:

Preliminary study of cations, group separations, six practice unknown solutions, and six unknown solutions on which the students are graded—21 periods.

Preliminary study of anions, one practice unknown, and two (graded) unknown solutions—9 periods.

Practice at preparing solutions of solid materials and removing interfering ions—2 periods.

Analysis of salt mixtures for both anions and cations—12 periods.

Analysis of alloys—2 periods.

Instead of the old "known solutions" on which group separations were practiced and the notebook records of which were essentially flow sheets of the movement of the various ions of the group, it has been found decidedly preferable to furnish the flow sheets and to give for practice unknown solutions containing two to four ions of the group. A large variety of these practice solutions is unnecessary. Laboratory supervisors carry records of these unknowns and the student is instructed to report the presence or absence of each ion of the group *as soon as* determined. He thus can be shown at each step in what respect his procedure may have been faulty. It is understood that no grades are involved. Students are unanimous

in stating that this form of exercise is very much more useful to them than the known solutions formerly used for practice. They have to use at once all the care necessary for analysis of unknowns and they learn at once where and how they may make mistakes. They admit freely that in "known solutions" they always interpret results on the basis of what they know should happen rather than on what actually does happen.

Unknowns. Students are required to analyze, record, and report unknowns in solution in three hours. This time limitation is of importance in teaching the student to plan before coming to the laboratory how he shall best economize time. He soon realizes that preliminary study of the procedures is the greatest time saver. This habit of planning for efficiency is bound to be of the greatest value to the student when he enters commercial work.

It is obvious that placing a time limitation on the student places on the instructor the duty of carefully planning unknowns that can be completed by the average student within the time limit. This means that the best students should finish in about two hours and that the poorest students will not have finished.

Our experience has shown that 1 to 2 mg of an ion in 1 ml of solution is found most readily. Large amounts cause the student much more trouble than extremely small ones. We give 0.5 mg of any ion and this amount is found readily by most students. In general 1 ml should not contain more than 3 to 4 mg of any ion. For this reason analysis of alloys, many of which contain 75 to 90 per cent of a single element, should not be undertaken until near the end of the course.

In the Purdue laboratory students are required to estimate and report relative amounts of the ions found in 1 ml of a liquid "unknown" or in 20 mg of a salt mixture or alloy. Less than 0.5 mg is reported as "trace," 0.5 to 1.0 mg as "small," 1 to 3 mg as "medium," more than 3 mg as "large." The laboratory test solutions, which contain in 1 ml 10 mg of the ion (for example, Cu^{++}, $HPO_4^{=}$) are always available for comparison. When two precipitates are gathered in compact form at the tips of centrifuge tubes of nearly equal diameter, a comparison of relative amounts can be made with rather surprising exactness.

Typical specimen group unknowns that can be analyzed in 3 hours are the following (number after each element is mg in 1 ml):

1. Bi 3, Hg 2, Sb 1
2. As 1, Sb 1, Sn 1, Hg 1

3. Al 2, Zn 1, Co 0.5, $HPO_4^=$ 3,[1] Ca 1[1]
4. Cr 2, Ni 2, Mn 2, Ba 1,[1] $HAsO_4^=$ 3[1]
5. Ca 1, Sr 2 (Two unknowns in 3 hours)
6. Ca 3, Sr 1, Ba 2 "
7. Sr 1, Ca 3, Mg 1 "

It should be realized that the methods prescribed permit detection of impurities even in "reagent grade" chemicals. When *several* students report as found an ion which was not given, it had best be assumed that they are right until they have been *proved* to be wrong.

Some of the few organic reagents employed are little stable in solution and have to be tested frequently for effectiveness. Careful attention should be given to the statements in "Preparation of Reagents," page 433.

In analysis on a semimicro scale accurate manipulation as outlined in Chapter 12 is of first importance. For this reason during the first few laboratory periods students should be closely supervised and correct technique insisted upon.

The Anion Elimination Sheets are an important part of the analysis for anions. One is required for each analysis. This sheet forms part of the notebook record. Mimeographed blank forms are convenient.

[1] Not required to be reported. Present for practice on its behavior in Group III.

CHAPTER 12

SEMIMICRO TECHNIQUE

Cleanliness. Until the beginner has had considerable experience, he is unable to realize what minute amounts of ions are detectable by many of the reagents used in analysis. Glass that to the eye appears sufficiently clean actually may have ions clinging to it in amounts capable of giving unmistakable reaction. The inexperienced analyst is more likely to find ions which were not given him than to fail to find those which were. This error arises from using chemically unclean glassware and also from inadvertently contaminating reagents. *The first requisite for accurate analysis is unremitting attention to cleanliness.*

With this in mind, a good analyst will prepare for his laboratory work by spreading a clean towel or paper on his desk top. The equipment to be used in the day's work is then thoroughly washed with tap water, using brush and cleaning powder if necessary, and finally rinsed with two or three successive portions of distilled water immediately before using.

The reagent bottles in the student's kit often become covered with a thin film of ammonium salt that has deposited on them from the air of the laboratory. These should always be washed with tap water and then rinsed with distilled water before starting the day's experimental work.

Contamination of reagents. A reagent dropper should *never* touch any surface except the reagent. Hold the tip above the mouth of the vessel to which the reagent is being added. If the tip is inadvertently touched to the wall of the vessel it should be washed off *thoroughly* with distilled water. Failure to do this is likely to ruin the reagent for subsequent use.

The stopper of a reagent bottle should *never* be laid on a desk top. Always hold the stopper in the hand while transferring reagent.

When removing a glass stopper, the hand should be placed *palm up* over it and the stopper grasped between the third and fourth fingers. Hold it thus while removing the reagent.

Solids are always transferred by pouring or shaking no more than the needed amount from the container on to a piece of paper or a watch glass. Na_2O_2 may inflame the paper. Do not introduce a glass rod or spatula into *any* reagent container lest all the reagent be contaminated.

If a reagent is accidentally contaminated, it should be taken at once to an instructor. This will be appreciated rather than penalized.

Before leaving the laboratory the student is expected to see that his desk top and the sink which he has used are *clean*. Note that a sponge is part of the apparatus kit.

ANALYTICAL OPERATIONS

Precipitation. This is usually carried out in a centrifuge tube or a test tube. The precipitating reagent (precipitant) is always added dropwise, with vigorous stirring with a glass rod after each addition, until *one drop* produces no additional precipitate. *Avoid* a large excess of reagent which is often responsible for subsequent analytical difficulties.

When precipitation appears to be complete, the mixture is centrifuged and another drop of reagent is added to the clear supernatant liquid (hereafter called centrifugate) to test for complete precipitation. If an additional precipitate forms, the mixture is thoroughly stirred and centrifuged. Repeat the test for complete precipitation until no additional precipitate forms upon addition of *one drop* of reagent.

Precipitation by H_2S. Methods of generating and using H_2S probably vary considerably in different laboratories. In large laboratories central generators are usual from which the gas is piped to outlets in the laboratory hoods. In small laboratories individual generators are often used.

Whether precipitations are made in closed or in open containers should depend on the volume of liquid to be saturated and on whether the laboratory is equipped with forced ventilation. Investigations have shown that for small animals the lethal concentration of H_2S differs little from that of HCN.[1] Where ventilation is inadequate, precipitation should invariably be made in closed vessels.

[1] W. P. Yant, J. Chem. Ed., **4**, 613 (1927).

In this method the delivery tube, which need not have a small orifice, passes through a rubber stopper to within an inch or so of the liquid surface. After the air above the liquid has been partially displaced by admission of H_2S, the vessel is tightly stoppered and then vigorously shaken. Since the partial pressure of the H_2S in the air over the liquid is considerably increased, the liquid absorbs gas more rapidly and becomes saturated with it in less time. Moreover a minimum quantity of poisonous gas escapes into the air.

If no more than 1 or 2 ml of liquid is to be saturated with the gas, it is usually quicker to bubble the gas through the liquid, using as delivery tube a long capillary pipet such as is used for removing liquids from precipitates. A fine capillary is necessary in this method, since large bubbles would very probably throw part of the liquid out of the tube. Because the amounts to be precipitated are quite small, precipitation is quickly completed and comparatively little H_2S escapes into the air.

In the Purdue laboratory precipitations are usually made in centrifuge tubes. No more than 2 ml of liquid should ever be treated in the small tubes. When these are used the gas may be passed through the solution, capillary pipets being used as delivery tubes.

If more than 2 ml of liquid has to be treated, the precipitation should be made in a 15 ml centrifuge tube. This size tube admits a number 0 one-hole rubber stopper. Delivery tubes 4 inches long are inserted into these stoppers so that they will project into the tube about half its length. The stopper is inserted loosely until air has been displaced from the connection and partially from the centrifuge tube. As soon as precipitation of sulfide at the surface of the liquid is observed, the stopper can be inserted firmly. The liquid in the centrifuge tube is then rotated or swirled (not shaken up and down) until precipitation seems to be complete. The liquid should never touch the rubber stopper nor the delivery tube. When precipitation seems to be complete, the stopper should be loosened for an instant while gas is still passing, to let air escape. Then insert it again and make sure that no more precipitate is forming.

Centrifugation. The separation of the precipitate and centrifugate is performed by placing the centrifuge tube in the holder on the rotating arm of the centrifuge. The tube must be counterbalanced by placing a tube of equal size containing approximately the same amount of liquid in the holder opposite to the reaction

tube. The lid is then closed and the centrifuge started. For most precipitates one minute is sufficient time for centrifuging. Unless individual centrifuges are available, it is advisable to remain at the centrifuge during the operation lest one's tubes be interchanged with those of another.

The centrifugate is removed by means of a capillary pipet. In doing this, great care not to disturb the precipitate is necessary. To remove the last of the centrifugate, tilt the tube to an angle of about 45°. Compress the bulb of the pipet to remove air and carefully insert pipet until the tip is *just over* the precipitate. *Slowly* release the bulb, allowing the liquid to be forced up into the tube. When the bulb is completely expanded or when all liquid has been removed from precipitate, carefully withdraw the pipet containing the centrifugate. With a little practice the student will find this operation not difficult.

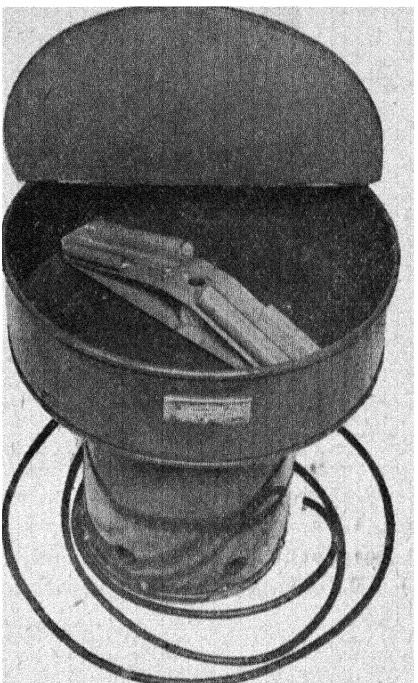


FIG. 2. CENTRIFUGE.

Washing precipitates. Precipitates are usually washed with water containing a small portion of the precipitant (common-ion effect). In most procedures the composition of the washing liquid is specified.

The washing is accomplished by adding a few drops of the washing liquid to the precipitate in the centrifuge tube and thoroughly stirring up the precipitate with it. The mixture is centrifuged and the centrifugate removed by the capillary pipet. The first washing is usually added to the original centrifugate. The washing is repeated as many times (usually specified in the directions) as necessary to prepare the precipitate for subsequent operations.

The statement, "to prepare the precipitate for subsequent operations," is of great importance. There is ample evidence that the physical structure (and, hence, the solubility) of freshly precipitated compounds is radically different from that of the same

compounds after they have been washed. We take advantage of this fact in the washing of the Group II sulfides. Considerable evidence has accumulated that freshly precipitated "sulfides" are really hydrosulfides, $M''(HS)_2$, where M'' is a bivalent cation. In this form the Group II-A "sulfides," notably copper and bismuth, have a tendency to dissolve in NaHS and NaOH (Group II-B

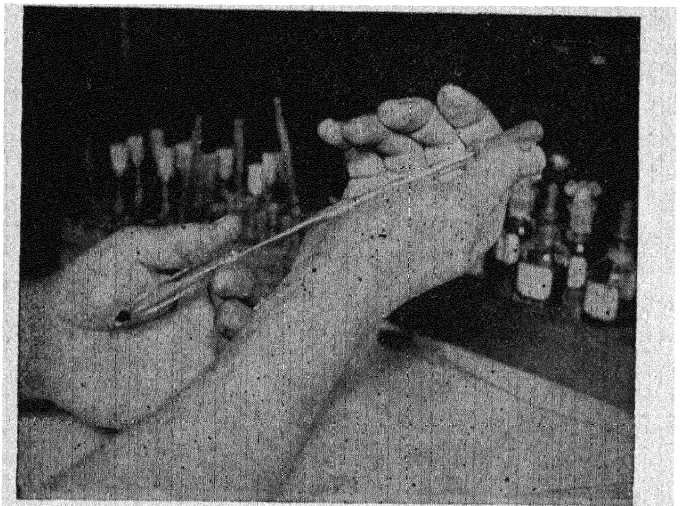


FIG. 3. USE OF CAPILLARY PIPET TO REMOVE CENTRIFUGATE.

reagent). To prevent this, we wash the Group II precipitates with 1 *N* HCl which favors the reaction

$$\underline{M''(HS)_2} \rightleftarrows \underline{M''S} + H_2S.$$

Extraction of precipitates. When a precipitate may consist of two or more compounds it is frequently necessary to dissolve one or more of the compounds, leaving the remainder unchanged. This is accomplished by using a selective solvent, one that will dissolve some compounds and not others, for example,

$$\underline{CuS} + \underline{As_2S_3} + HS^- + OH^- \rightleftarrows \underline{CuS} + 2AsS_2^- + H_2O.$$

To avoid later confusion it is essential that the separation be *complete*.

To extract a precipitate, add two or three drops of the reagent and stir thoroughly for the full time specified for each case, warming if so directed. Centrifuge and withdraw the centrifugate with a

capillary pipet. The extraction *must* be repeated with a fresh portion of reagent *until a chemical test* shows the last extract to be free from the extracted substance.

Transference of precipitates from centrifuge tube to another container. It is often necessary to transfer a part or the whole of a precipitate. This is best accomplished by adding to the precipitate in the centrifuge tube a small amount of the reagent next to be used. Then, using a dropper pipet, stir the precipitate thoroughly and withdraw precipitate and solution. Centrifuge tube and dropper pipet are then to be rinsed with two or three more drops of reagent and the process repeated until all the precipitate is removed.

Dissolution of solids. Study "Solubility Product Principle," Part I, Chapter 8 (note particularly pages 111–114).

In this operation the following facts should always be kept in mind: (1) The rate of dissolution may be slow even at 100°. Large particles dissolve more slowly than small ones. Dissolution is a *surface* reaction which soon reaches equilibrium in the film of liquid adjacent to each solid particle. Unless this equilibrium is frequently destroyed by vigorous stirring, dissolution may proceed very slowly. (2) Do not change solvents as long as reaction is perceptible. After reaction has stopped, remove the solution and try more of the same solvent before changing to another. (3) Even "soluble" salts have limited solubilities. A gram of NaCl will not dissolve in 1 ml of water. (4) A water-soluble salt may be insoluble in an acid. NaCl is but slightly soluble in 12 *N* HCl. (5) With a solvent acid a water-soluble salt may form a compound insoluble in most solvents, for example,

$$\underline{AgNO_3} + H^+ + Cl^- = \underline{AgCl},$$
$$\underline{BaCl_2} + H^+ + SO_4^{=} = \underline{BaSO_4}.$$

Heating. For all work to be carried out at a temperature above 90°C. a crucible must be used. When temperatures no higher than 90° are to be reached, the reaction vessel may be a test tube or centrifuge tube.

When instructions call for reaction tube and contents to be heated, this operation can be carried out in either of two ways. The safer way is to immerse the tube in a beaker of boiling water. A more rapid but more dangerous procedure is to pass the tube back and forth through the flame of the micro-burner. In no case should a tube be held stationary in the flame as this results in super-

heating, and the rapid formation and expansion of steam may blow out the entire contents of the tube.

All evaporations (for example, reducing the volume of a solution from 2 ml to 1 ml) should be carried out in a crucible. It is safer, and usually preferable, to place the crucible on a water bath (100 ml beaker with the water bath cover). More rapid evaporation is obtained by waving the micro flame back and forth beneath the crucible, which is placed on a wire gauze or triangle. A stationary flame must never be allowed to impinge directly on the crucible, as loss by spattering will almost certainly result.

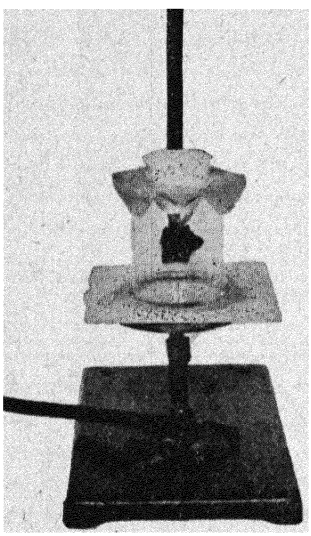


FIG. 4. SEMIMICRO WATER BATH.

Control and comparison tests. These tests are of great importance in the analysis of unknowns.

Control test for possible contamination. Many of the tests used in semimicro analysis are effective at concentrations as low as 1 part per million. With reagents so sensitive contamination is always to be feared and all reagents and test papers used must be checked before the test can be considered reliable. This procedure is called "running a blank."

The "blank" test is made by duplicating the exact procedure of the test using *all* reagents but substituting usually for the test solution the same volume of distilled water.

Comparison test for estimation of amounts. Frequently it is desirable to know roughly the weight of an ion in a precipitate. This is best done by taking two drops (1 mg) of the test solution of the ion in question and precipitating it as the compound with which it is to be compared. The volume of the unknown precipitate can then be estimated by comparing it to the volume of the centrifuged precipitate containing one mg of the ion.

Identification of gases. In the systematic analysis it is convenient at times to convert certain ions into volatile compounds and to drive these out of solution and into contact with test papers or test drops.

Experience has shown that students are careless about the technique of this type of test. Gases may be formed from certain ions

by the action of bases or acids, for example,

$$NH_4^+ + OH^- \rightarrow \overline{NH_3}$$
$$CN^- + H^+ \rightarrow \overline{HCN}$$
$$HCO_3^- + H^+ \rightarrow \overline{CO_2}$$

It is of first importance to *prove by test* that the solution is actually acidic or basic as required. Otherwise no gas-forming ion will be found even if it is present.

Many gases (for example, NH_3, SO_2, HCN) are largely soluble in water and not easily removed from it. To remove such gases, such means as prolonged heating and vigorous stirring must be resorted to. An excellent means is to generate a considerable amount of another gas which will not affect the test paper.

Closed vessel tests. These tests are carried out in a 25 ml Erlenmeyer flask the stopper of which carries on its lower end a "wedge-point" pin. In the loop of the pin is placed a small strip of test paper. The stoppered flask containing the reaction mixture and test paper is placed on a steam plate or water bath for 5 minutes.

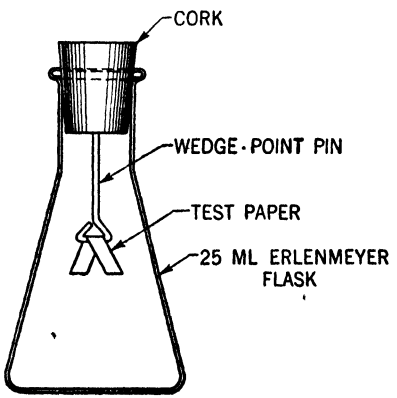


FIG. 5. GAS EVOLUTION FLASK.

Distillation tests. Occasionally it is necessary to drive a volatile liquid out of a reaction mixture and condense it for testing. Detailed directions for carrying out such tests will be found in "Test for acetate," page 407.

Flame tests. These tests are extremely important in the confirmatory tests for Ba^{++}, Ca^{++}, Sr^{++}, Na^+, and K^+ and should be carefully studied.

The chlorides are the most volatile salts and color flames most brightly. The other salts of these ions are less volatile and do not color the flame so distinctly.

The test is made by moistening the solid salt or precipitate with a drop of $12N$ HCl. A *clean* platinum wire is dipped into the mixture and then held in the edge, *near the base,* of a nonluminous flame. Note carefully and record all of the characteristics of the flame. This includes color (initial and final) and duration of flame.

The wire is best cleaned by taking a little cleaning powder ($Na_3PO_4 + NH_4Cl$) between finger and thumb and drawing the wire back and forth through it. (Not too vigorously! Fingers have been cut.) Wash the wire with water, rubbing between finger and thumb. Then dip the wire in $12N$ HCl contained in a small test tube and place in a hot flame. Repeat the alternate dipping in HCl and heating until the wire no longer colors the flame. It is then ready for flame tests.

THE NOTEBOOK

In all scientific work nothing is of greater importance than a complete and accurate record of experiments. It is a common complaint of employers of college graduates that they do not know how to keep a satisfactory notebook. Probably no course in a college curriculum affords a better opportunity to learn the essentials of good record keeping than qualitative analysis. Of all vicious habits of notebook making, the worst is failure to record the results of each separate experiment *immediately* after performing it. No one can perform even a half dozen brief experiments and then record accurately all the details of each.

The fundamental requirements of a satisfactory notebook are:

1. Name and date *on each page.* A surprising number of suits at law for infringement of patent rights have hinged upon the *date* on which an experiment was performed.

2. Exact statement of how the experiment was performed, which " . . . should be made so that any person skilled in the art can duplicate the results without requiring further research."[2]

3. A full and complete statement of what was seen.

4. Conclusions drawn from the experiment.

A student who is preparing himself for scientific work will do well, when writing his records, to imagine himself on the witness stand of a court five years hence undergoing cross examination the main purpose of which is to get him to admit that he does not remember the details of the experiment. Of course, he is allowed to have his original notes at hand for consultation, but woe betide him if his notes have omitted any important detail of the experiment.

Deductions from observations. In analysis it is of the utmost importance that *every* phenomenon connected with the presence or absence of certain ions be closely observed and an inference at once

[2] *Buckeye Incubator Co. v. Wolf*, 291 Fed. Rep. 261–262.

entered in the record. In the making of entries the force of the words *suggests, indicates,* and *proves* should be accurately distinguished and the correct word used. The possible cause of a phenomenon should be recorded as "suggested." Subsequent tests may prove the "suggestion" to have been wrong and indicate a more probable cause. The purpose of confirmatory tests is to turn "indications" into "proofs."

Consider the following examples:

1. A student is given a blue solution as an unknown. The color "suggests" to him copper. On analysis he is unable to detect any copper. But the blue color might have been due to $Ni(NH_3)_4^{++}$ or to a mixture of green and yellow ions. The "suggestion" turns out to have been quite wrong. The *blue color* was important and later must be accounted for in one way or another.

2. An unknown consisting of a not too intimate mixture of litharge (PbO, yellow), minium (Pb_3O_4, red), and lead dioxide (PbO_2, brown) "suggests" by the three colors readily observable the presence of three different compounds. Analysis shows present only Pb^{++} and no anions. The student, by making correct use of the "suggestion," will after a little reading become confident that three oxides of lead are to be reported as found.

3. A small white precipitate in Group I which dissolves when more acid is added may have "suggested" first silver and later bismuth. However it may be due to antimony. Its dissolution in more HCl strongly "indicates" but does not "prove" bismuth or antimony, or both.

It is of the utmost importance after completing an analysis to review the notebook record and be certain that all the observed facts are accounted for. Many important discoveries have resulted from noticing that certain observations were not explainable.

THE NOTEBOOK IN QUALITATIVE ANALYSIS

In the analytical laboratory a proper combination of essential completeness and brevity must be sought. An undue proportion of time must not be given to recording experiments. Much time is saved by regular use of the abbreviations listed in Table 8, page 195. The laboratory work consists of three distinct parts.

(1) Characteristic reactions of ions.
(2) Analysis of known solutions.
(3) Analysis of unknown mixtures.

The essentials of a good notebook, completeness and brevity, are the same in each of these parts of the work. Desirable forms of records for each of these divisions are suggested and discussed below.

Characteristic Reactions

The purpose of this form of notebook is to prepare *for later study* brief but sufficiently complete statements of the principal reactions of the various ions studied. As a rule these are best stated in the form of balanced ionic equations. Ions present in the solution but taking no part in the reaction should not be recorded, since they only distract attention from the essentials. In this preliminary work the student is familiarizing himself with the valences of the ions, the colors of colored compounds and ions, the solubilities of compounds, and the physical form characteristic of each: in short all those properties which furnish means of identifying the ions.

Use of signs. Discriminating use should be made of the signs $\rightarrow$, $=$, and $\rightleftarrows$. Each of these signs has its own meaning, and they should not be carelessly interchanged. Their meanings are as follows:

The sign $\rightarrow$ (read, "tends to form") indicates no more than that the reaction in question *tends* to take place in the direction indicated by the arrow, for example,

$$Ag^{+} + Fe^{++} \rightarrow Ag + Fe^{+3}.$$

This expression should be read, "ferrous ion *tends* to reduce silver ion to the metal." It indicates nothing as to the amount of reaction which may take place. In notebook writing this sign should be rather infrequently used.

The sign $=$ (read, "forms quantitatively") means that the reaction is sufficiently complete to be used for quantitative analyses. It is to be understood that no reaction is absolutely complete but many reactions proceed so nearly to completion that, practically, they may be considered quantitative. Such equations as

$$Ba^{++} + SO_4^{=} = \underline{BaSO_4}, \text{ and}$$
$$Ag^{+} + Cl^{-} = \underline{AgCl}$$

are permissible because $BaSO_4$ and AgCl are so extremely insoluble in water that for all practical purposes the removal of one of the two ions in each of the equations may be considered to be complete.

The sign $\rightleftarrows$ (read, "forms an equilibrium with") indicates that the reaction is reversible. The products of the reaction are able to

react with each other to reform the original reactants. Such reactions can be made quantitative only by exact control of conditions. For example, the reaction

$$AlO^+ + NH_3 + H_2O \rightleftarrows \underline{AlOOH} + NH_4^+ \qquad (1)$$

is commonly used for the quantitative determination of Al. The determination, however, is satisfactorily accurate only when an indicator which changes color at *p*H 6.4 is present, since at this C_{H^+} aluminum hydroxide (aluminic acid) possesses its minimum solubility. If a large excess of NH_3 is added, precipitation is incomplete. To write

$$AlO^+ + NH_3 + H_2O \underset{(p\mathrm{H}\,=\,6.4)}{=} \underline{AlOOH} + NH_4^+ \qquad (2)$$

is to imply that *at the end* of the reaction the *p*H of the solution was *known* to be very close to 6.4.

Expression (1) implies nothing as to the excess of NH_3 added and, in consequence, the amount of AlO^+ remaining unprecipitated or the amount of $Al(OH)_4^-$ formed by an excess of the reagent, since

$$\underline{HAlO_2} + NH_3 + 2H_2O \underset{\longleftarrow}{\longrightarrow} NH_4^+ + Al(OH)_4^-. \qquad (3)$$

The lengths of the arrows indicate on which side the equilibrium point lies. In (3) this is on the left. Only a very high C_{NH_3} will form much $Al(OH)_4^-$.

Essential facts to be recorded are:

1. The reagents which give reactions useful for identifying the ion studied.
2. Solubilities of slightly soluble compounds of this ion and their physical appearance.
3. Colors and color shades of colored compounds.
4. Formulas and valences of ions, both simple and complex, formed under various conditions.

Balanced ionic equations for each reaction will usually record all the information necessary for later study, provided that care is exercised to comply with all the following requirements.

1. The electrical charges of ions are an essential part of their formulas, (for example, Ca^{++}, $SO_4^{=}$).
2. *All* solids, whether reactants in or products of a reaction, should be underlined (for example, $\underline{Fe_2O_3}$).
3. All gaseous products should be overlined (for example, $\overline{CO_2}$).
4. The signs $\rightarrow$, $=$, and $\rightleftarrows$ are not interchangeable. Each should be used exactly and with understanding of its meaning.

5. Weak acids, for example, HBO_2, AcOH, and the three little-ionized salts, $HgCl_2$, $Hg(CN)_2$ and $(AcO)_2Pb$, should be written as molecules and not as ions.

Physical appearance. Solids are either crystalline or amorphous. The following terms are frequently used to describe the appearance of a precipitate not clearly crystalline. A typical example or two of each term is given.

1. Powdery. $BaSO_4$ or CaC_2O_4.
2. Granular. SnO_2 (from hot conc. HNO_3).
3. Flocculent, separating in small flocks. $Cu(HS)_2$.
4. Gelatinous, jelly like. AlOOH.
5. Curdy, descriptive of precipitates usually flocculent when first precipitated but gathering into large clots or curds when vigorously shaken.

Many powdery precipitates and some granular ones appear more or less crystalline. Flocculent, gelatinous, and curdy precipitates always appear amorphous.

Crystalline precipitates frequently reflect light from the faces of even minute crystals. Usually the form of crystals is not recognizable because they are too small. Occasionally precipitation has been slow enough for larger crystals to form. Typical forms are the *needles*, in which $PbCl_2$ deposits when its hot saturated solution cools slowly, and the lustrous *scales* or *plates* of PbI_2 formed under the same conditions. Some amorphous precipitates quickly become crystalline when left to stand in contact with the warm solution from which they were precipitated. An excellent example is the carbonates of Ca^{++}, Sr^{++}, and Ba^{++}.

Recommended Notebook Form

John Smith
Sept. 18, 19—

REACTIONS OF GROUP III CATIONS

Characteristic Reactions of Aluminum ion

EXPERIMENT
NO.

(1) *Action of ammonia solution.*

$$Al^{+3} + NH_3 + H_2O \rightleftarrows \underset{\text{(white gelatinous)}}{\underline{AlOOH}} + NH_4^+$$

(2) *Action of strong bases.*

$$\underline{AlOOH} + OH^- + H_2O \rightleftarrows Al(OH)_4^-$$

(3) *Action of ammonium salts on aluminate ion.*

$$Al(OH)_4^- + NH_4^+ \text{ (large concn.) (heated)} \rightleftarrows \underline{AlOOH} + \overline{NH_3} + 2H_2O$$

Characteristic Reactions of Ferrous Ion

(1) *Action of ammonia solution.*

$$Fe^{++} + 2NH_3 + 2H_2O \rightleftarrows Fe(OH)_2 + 2NH_4^+$$

(The precipitate is first white or pale green, then darker green, then black, and finally red brown due to oxidation by atmospheric oxygen.)

(2) *Action of air on ferrous hydroxide.*

(2*a*) $\underline{Fe(OH)_2} + OH^- \rightleftarrows \underline{FeOOH} + H_2O + e^-$ (oxidation of reductant)

(2*b*) $O_2 + 2H_2O + 4e^- \rightleftarrows 4OH^-$ (reduction of oxidant)

(2*c*) $\underline{4Fe(OH)_2} + O_2 \rightleftarrows \underline{4FeOOH} + 2H_2O$ (balanced total equation)

TABLE 8

ABBREVIATIONS

To secure brevity and to save time in writing notebooks or lecture notes, the following abbreviations should be used. They are official for *Chemical Abstracts.*

abs., absolute
addn., addition
alk., alkaline (not alkali)
amor., amorphous
anhyd., anhydrous
amt., amount
app., apparatus
approx., approximate, -ly
aq., aqueous, hydrated [aq. soln.; $CuSO_4$(aq.)]
aq. reg., aqua regia
at., atomic
atm., atmosphere(s), -ic
calc., calcd., calcn., calculate, -ed, -tion
cc., cubic centimeter(s) (also cm^3)
compd., compound
compn., composition
conc., concentrated (adj.)
concn., concentration
const., constant
cryst., crystalline
crystd., crystallized
crystn., crystallization
deliq., deliquescent
dil., dild., diln., dilute, -ed, -tion
e^-, electron(s)
effl., efflorescent
equil., equilibrium
equiv., equivalent(s)
evap., evapd., evapn., evaporate, -ed, -tion
expt., experiment
$\rightarrow$, tends to form
$=$, forms quantitatively
$\rightleftarrows$, forms incompletely or reversibly
floc., flocculent
γ (gamma), 0.001 mg
gelat., gelatinous
g, gram(s)
insol., insoluble
l, liter(s)

lab., laboratory
m.eq., milliequivalent(s)
mg, milligram(s)
ml, milliliter(s)
m.mol, millimol(s)
mixt., mixture
M, molal (of concns.)
m*M*, millimolal
mol, mole, molal, molecule
mol. wt., molecular weight
mv., millivolt(s)
N, normal (of concns.)
m*N*, millinormal, milliequivalent
no., number
p., pressure
ppt., pptd., pptg., pptn., precipitate, -ed, -ing, -ion
prep., prepd., prepg., prepn., prepare, -d, -ing, -ation
qual., qualitative (not quality)
quant., quantitative
sat., satd., satg., satn., saturate, -d, -ing, -ion
sep., sepd., sepg., sepn., separate, -d, -ing, -ion
sol., soln., soly., soluble, -ution, -ubility
subl., sublimes
temp., temperature
v., volt(s)
vac., vacuum
vol., volume
wt., weight

Known Solutions

Here the essential requirement is that the notebook give a clear picture of:

1. The reagents used to separate groups of ions from one another or the ions of a single group from each other.
2. The solid compounds or the ions formed by each reagent.
3. The reagent which is used for the final identification of each ion and the formula of the compound formed by it, unless the reagent is an organic compound, in which case formulas need not be written.

Since it is known from the first what ions are present, the compounds formed at each step should have been already learned.

In this kind of record no attempt is made to write equations nor to mention any compounds other than those containing the ions composing the group or groups.

Essentially, such a record is a *flowsheet* of the movements of ions throughout an analysis.

Recommended Notebook Form

The following brief but adequate form for recording known solutions was first proposed by William A. Noyes.

John Smith
Oct. 8, 19—

KNOWN SOLUTION—GROUP II-A
Known was a blue solution, acid to litmus

Substance	Reagent	Result	Precipitate or Residue	Solution	Conclusion
Pb^{++}(1 mg) Cu^{++}(1 mg) Bi^{3+}(1 mg) Cd^{++} (1 mg) Hg^{++} (2 mg)	Made 0.3 *N* in H^+ using M.M.O. and 3 *N* HCl. Saturated with H_2S.	Brown-black ppt.	$Pb(HS)_2$ $Cu(HS)_2$ $Bi(HS)_3$ $Cd(HS)_2$ $Hg(HS)_2$ 6 mg	Tested for complete pptn. and discarded.	Group II present.
$Pb(HS)_2$ $Cu(HS)_2$ $Bi(HS)_3$ $Cd(HS)_2$ $Hg(HS)_2$	Washed three times with 6 drops 0.3 *N* HCl.	Converted hydrosulfides to sulfides.	PbS CuS Bi_2S_3 CdS HgS	Discarded.	
PbS CuS Bi_2S_3 CdS HgS	NaHS and NaOH heat.		PbS CuS Bi_2S_3 CdS (HgS)?[a]	$HgS_2^=$ (Bi?)	Group II-A present.
$HgS_2^=$	3*N* HCl.	Black ppt.	HgS (1–2 mg)	Discarded.	Indicates Hg.

Tested for complete extraction. The second extract acidified gave a little black ppt. The third gave only a little white S.

[a] "(HgS)?" indicates that all the mercury may not have been extracted in one operation.

Unknown Solutions or Mixtures

For recording analyses of "unknowns," a form of record is recommended which in general resembles that for a known solution but differs from it in many respects. In this record observations and conclusions (suggestions, indications, proofs) are the important matters. Greatest care should be taken that the columns "Result" and "Conclusion" be complete and accurate.

Recommended Notebook Form

John Smith
Oct. 18, 19—

UNKNOWN NO. 4. IONS OF GROUP II

Substance	Reagent	Result	Ppt. or Residue and Amount	Solution	Conclusion
Unknown was a colorless solution, acid to litmus.					Indicates no large amount Cu present.
1 ml unkn. soln.	Made 0.3 *N* H^+ using M.M.O. Saturated with H_2S.	Yellow ppt. formed first which gradually changed to greenish black.	Ppt. 1, about 3 mg.	Soln. 1 Tested for complete pptn. and discarded.	Group II present; suggests As.
Ppt. 1	Washed 3 times with 0.3 *N* HCl.	No change.	Residue 2.		
Residue 2	NaHS and NaOH heat.	All dissolves.		Soln. 2	II-A absent. II-B present. Black color of ppt. 1 now indicates Hg.
Solution 2	3 *N* HCl	Yellow and black ppt.	Ppt. 3	Tested for complete pptn. and discarded.	Hg present.

Since the ions present are entirely unknown, no formulas of precipitates or ions in solutions can be written until the final identification of the various ions. All precipitates and solutions can be identified only by numbers and these should be consecutive throughout the analysis. Precipitates should be numbered consecutively 1, 2, 3, and so on, and solutions likewise consecutively 1, 2, 3. Note that the centrifugate from a precipitate will not necessarily have the same number as the precipitate (for example, in consequence of operations without result, the centrifugate from precipitate 7 might be solution 10).

The terms *precipitate* and *residue* should not be interchanged. A "precipitate" is a solid formed by the reaction of a reagent on a solution. A "residue" is the solid remaining after part of a "precipitate" has been removed by an extracting agent.

REPORTS OF ANALYSIS

A form for reporting unknowns which is convenient both for the student and for the instructor's records is shown in Figure 6. The

QUALITATIVE ANALYSIS REPORT
Name John Smith
Unknown No. 1 Date 9/20/—
Grade

Anions	Quant. Found	Quant. Present
Cations		
Na^+	m	
NH_4^+	tr	

QUALITATIVE ANALYSIS REPORT
Name John Smith
Unknown No. 1 Date 9/20/—
Grade

Anions	Quant. Found	Quant. Present
Cations		
Na^+	m	
NH_4^+	tr	

FIG. 6. FORM FOR QUALITATIVE ANALYSIS REPORT.

form is filled out by the student in duplicate, excepting the columns "Quantity Present," and handed in intact. After all the reports on a given unknown are in, they are graded and the student's half

of the duplicate returned to him. The instructor enters in the column "Quantity Present" the ions given out and the quantity of each in the volume or weight taken for analysis.

It is assumed that 2 ml of an unknown *solution* are used during an analysis and that 40 mg of a *solid* unknown (weighed out carefully) are used during the analysis of anions and another portion of the same weight used during the analysis of cations.

In the column "Quantity Found" is reported the amount of each ion found, or calculated, to be in 1 ml of solution or in 20 mg of solid material. This is reported as (*l*)arge, (*m*)edium, (*s*)mall, or (*tr*)ace. These terms represent the following amounts:

l, more than 3 mg of the ion in 1 ml of a solution or 20 mg of a solid.

m, more than 1 mg but less than 3 mg of the ion in 1 ml of a solution or 20 mg of a solid.

s, 0.5 to 1 mg of the ion in 1 ml of a solution or 20 mg of a solid.

tr, less than 0.5 mg of the ion in 1 ml of a solution or 20 mg of a solid.

Ions not found present should *not be mentioned* in the report.

Great care should be used to make sure that the report agrees ***exactly*** with the notebook record.

CHAPTER 13

PROPERTIES AND REACTIONS OF THE CATIONS

THE ALKALI-METAL IONS

No group reagent. Most salts of these cations are soluble in water and colorless unless the anion is colored. The ions are readily, and in fact best, detected by tests on solid salts at the beginning of the systematic analysis. In the systematic analysis for cations they remain in solution after all other cations have been removed. On this basis they would constitute Group V, frequently called the "soluble group." Since we shall detect them at the beginning of analyses and since they have no group reagent, it seems unnecessary to assign them a group number. They will be referred to hereafter as the Alkali-Metal Ions.

These ions form a very few salts which are not largely soluble in water. The following list includes the most important, together with their solubilities.

	Solubility in mg per ml	
$KClO_4$	16.8 (20°)	practically insoluble in absolute alcohol containing 0.2% $HClO_4$.
K_2PtCl_6	7.4 (25°)	practically insoluble in 80% alcohol.
$K_2NaCo(NO_2)_6 \cdot H_2O$	0.7 (25°)	
$KHC_4H_4O_6$	4.3 (10°)	
NH_4ClO_4	230.0 (20°)	
$(NH_4)_2PtCl_6$	5.0 (20°)	
$(NH_4)_2NaCo(NO_2)_6 \cdot H_2O$	1.0 (25°)	
$NaSb(OH)_6$[1]	3.3 (100°)	
$NaZn(UO_2)_3(AcO)_9 \cdot 6H_2O$		Practically insol. in water or dilute AcOH.

Sodium

Occurrence. Sodium is one of the most widely distributed of the elements. In order of abundance it is ranked in sixth place

[1] According to L. Pauling this is the *only* sodium antimonate. $NaSbO_3 \cdot 3H_2O$ and $Na_2H_2Sb_2O_7 \cdot H_2O$ both show identical X-ray patterns corresponding to $NaSb(OH)_6$.

following calcium. It is believed to constitute about 2.5% of the earth's lithosphere and about the same fraction of sea water. It is a constituent of many silicates. Where deposits of sea water have evaporated, enormous deposits of NaCl remain. In desert regions deposits of soluble salts may occur, such as Chile saltpeter, $NaNO_3$; borax, $Na_2B_4O_7 \cdot 10H_2O$; and trona, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$.

Dissolution of the metal. Sodium decomposes water vigorously with liberation of H_2 and formation of a strongly basic solution. The heat liberated is insufficient to inflame the H_2 (difference from K).

Reactions of Sodium Ion

1. Zinc uranyl acetate reagent[2] (I. M. Kolthoff, 1927) precipitates $NaZn(UO_2)_3(AcO)_9 \cdot 6H_2O$, small pale yellow crystals, less soluble in 50% ethyl alcohol than in water. The test is less sensitive in the presence of most of the cations if they are present in concentrations greater than 5 mg per ml.

2. Flame color. All sodium salts when brought into the Bunsen flame impart to it a brilliant yellow color. The brilliance and duration of this color are roughly proportional to the amount of sodium present. Practically all matter contains at least a trace of sodium salt. Reagents standing in glass bottles soon dissolve Na^+ out of the glass in amounts sufficient to give the yellow flame. Very minute amounts give a bright momentary flash of yellow. With larger amounts, flame persists much longer. The sodium flame completely hides the violet flame of potassium salt. Two thicknesses of blue glass completely absorb the sodium flame and permit the potassium flame color to be seen.

Potassium

Occurrence. Potassium is only slightly less abundant than sodium in the earth's lithosphere. It forms less than 0.1% of sea water because it is largely taken up by plant life as soon as it becomes soluble. It is a constituent of many silicates, especially certain feldspars and micas. Deposits from sea water contain sylvite, KCl; carnallite, $Mg(H_2O)_6Cl_2 \cdot KCl$; kainite, $K_2Mg(SO_4)_2 \cdot 3H_2O$, and other salts.

Dissolution of the metal. Potassium decomposes water more violently than does sodium. The heat of reaction raises the H_2

[2] A mixture of $(AcO)_2Zn$, $(AcO)_2UO_2$, and AcOH. The formula of the sodium salt suggests the existence in this mixture of an acid with complex anions corresponding to the Na salt. However, this has not yet been proved.

evolved to its combustion point and it burns with the pale lilac flame characteristic of potassium.

Reactions of Potassium Ion

1. Sodium hexanitrocobaltiate, $Na_3Co(NO_2)_6$, if prepared according to specific directions, precipitates $K_2NaCo(NO_2)_6 \cdot H_2O$ (yellow) insoluble in dilute acetic acid. The precipitate is decomposed by mineral acids with reduction of cobalt from 3^+ to 2^+. The corresponding salt $(NH_4)_2Na[Co(NO_2)_6] \cdot H_2O$ is only slightly more soluble than the potassium salt. As a result this reagent may not be used to precipitate potassium ion until ammonium salts have been *carefully* removed by ignition. KCl is slowly volatilized at low red heat. K_2SO_4 is not decomposed even at red heat.

2. Perchloric acid, $HClO_4$, precipitates K^+, but not Na^+ or NH_4^+. This compound is considerably more soluble than the complex nitro salt. It is, however, practically insoluble in ethyl alcohol.

3. Flame color. Potassium salts impart a pale lavender color to the Bunsen flame. The color is obscured by even small amounts of sodium. Two thicknesses of blue glass plate absorb the color due to sodium and cause the color due to potassium to appear more red. Many K^+ salts, particularly KCl, are very rapidly volatilized in the flame. In order to detect a small amount of K^+ it is absolutely necessary to be looking at the flame through the blue glass plates *at the instant* the salt is introduced into the flame. Ammonium salts impart to the Bunsen flame an extremely pale yellow-lavender tint which quickly vanishes. It is completely cut out by blue glass. The red flame colors of Sr^{++} and Ca^{++} are also absorbed by blue glass.

Ammonium

Occurrence. Salts of the ion, NH_4^+, occur infrequently in rainless regions and there only in small amounts. Ammonia, NH_3, results from decomposition of nitrogenous organic material. Commercial ammonium salts are all prepared by the absorption of NH_3 in acids.

Dissolution of the metal. There is considerable evidence that an amalgam of NH_4 can be prepared which resembles those of Na and K. Like the latter, ammonium amalgam decomposes water with liberation of H_2. This, not undisputed, formation of an

amalgam is about the only reason for considering NH_4 a metal. If accepted as such, it must be considered an alkali metal which more nearly resembles K than Na in its properties.

Reactions of Ammonium Ion

1. Effect of heat. All ammonium salts are decomposed at or below red heat.

$$NH_4Cl \rightarrow \overline{NH_4Cl}^{3} \rightarrow NH_4Cl$$

$$NH_4NO_3 \rightarrow \overline{N_2O} + 2\overline{H_2O}$$

$$(NH_4)_2Cr_2O_7 \rightarrow \overline{N_2} + Cr_2O_3 + 4\overline{H_2O}$$

$$2MgNH_4PO_4 \cdot 6H_2O \rightarrow Mg_2P_2O_7 + 2\overline{NH_3} + 13\overline{H_2O}$$

2. Strong bases—KOH, NaOH, or $Ba(OH)_2$—decompose ammonium salts with formation of water and NH_3.

$$NH_4^+ + OH^- \rightleftharpoons H_2O + NH_3 \qquad (1)$$

NH_4^+ is a very weak acid. The constant for the reaction

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3 \qquad (2)$$

is about 5.6×10^{-10} at 25°. A large concentration of OH^-, such as is furnished by any strong base, eventually will drive reaction (1) to the right. NH_3 is extremely soluble in water. If the gas be driven out of the test solution and brought into contact with a strip of moist red litmus paper, reaction (1) will be forced to the left and OH^- will turn litmus blue. This is the most commonly used test for NH_4^+.

3. Iodomercurate ion, $HgI_4^=$, in strongly alkaline solution, forms with NH_3 red-brown aquobasic ammonobasic mercuric iodide $H_2N—Hg—O—Hg—I$. (See ammonobasic salts of Hg, page 220.)

$$NH_3 + 2HgI_4^= + 3OH^- = H_2NHgOHgI + 2H_2O + 7I^-$$

With minute quantities of NH_4^+ a yellow solution is formed. The reagent is almost too sensitive for use where traces of NH_3 may be in the air (for example, when one's neighbor may be volatilizing NH_3 from a solution or solid salt mixture).

[3] If $\overline{NH_3}$ and HCl are formed, they recombine quantitatively as soon as their temperature decreases.

Sodium hexanitrocobaltiate with ammonium ion forms a yellow salt, $(NH_4)_2NaCo(NO_2)_6$, differing little in appearance and color from the corresponding potassium salt. (Compare reaction 1, potassium ion.)

THE IONS OF CATION GROUP I

[Silver, Ag^+; Mercurous, Hg_2^{++}; Lead, Pb^{++} (if present in large concentration)]

Group reagent, Cl^- in acid solution. This group includes the two ions which form extremely insoluble chlorides. (For their solubility products consult Table 5, page 109.) $PbCl_2$ is considerably more soluble and in semimicro analysis Pb^{++} is rarely precipitated in this group. The basic chlorides, BiOCl and SbOCl, occasionally precipitate in Group I but are dissolved when the group precipitate is washed with HCl. Very large C_{Cl^-} tends to form complex anions such as $[AgCl_3]^-$, $[Hg_2Cl_4]^-$, so that a large excess of precipitant should be avoided.

Silver

Occurrence. Silver, like gold, is found as free metal in the earth's lithosphere. It nearly always accompanies gold. It is also found combined with S^- as argentite, Ag_2S, and with Cl^- as horn silver, AgCl. It is usually present to a greater or less extent in copper, zinc, and lead ores and is recovered from the slimes in electrolytic refining.

Dissolution of the metal. Silver dissolves best in $8\,N$ HNO_3 and this is the usual solvent. It dissolves in hot $36\,N$ H_2SO_4 with evolution of SO_2. This reaction serves to extract silver from its alloy with Au and Pt. Silver is not strongly attacked by fused NaOH or KOH and crucibles of this metal are often used for such fusions.

The most insoluble salt of silver is the black sulfide, Ag_2S. This dissolves in hot $16\,N$ HNO_3 and in concentrated solutions of alkali cyanide.

$$\underline{Ag_2S} + 4H^+ + 2NO_3^- = \underline{S} + 2\overline{NO_2} + 2Ag^+ + 2H_2O$$

$$\underline{Ag_2S} + 6CN^- \rightleftarrows 2Ag(CN)_3^- + S^-$$

The halides, except AgF, are highly insoluble. Their solubility decreases in the order AgCl, AgBr, AgI. Insoluble also are the

"pseudohalides," cyanide, AgCN or $Ag[Ag(CN)_2]$; thiocyanate, AgNCS; and azide, AgN_3. The acetate, chlorate, nitrite, and sulfate are only sparingly soluble. Of the common salts only the nitrate and fluoride are largely soluble in water.

Several of the silver salts are colored. This fact in connection with their varying solubilities is of great importance in the detection of anions. Of the colored silver salts, AgBr (slightly yellowish white), AgI (yellow), Ag_2S (black), $Ag_3Fe(CN)_6$ (orange) are insoluble in dilute HNO_3. Ag_3AsO_3 (yellow), Ag_3PO_4 (yellow), Ag_3AsO_4 (red brown), and Ag_2CrO_4 (crimson) are insoluble in water but soluble in dilute HNO_3. $Ag_2S_2O_3$ is white and insoluble in water but decomposes very rapidly to yellow brown mixtures and finally to Ag_2S black.

Reactions of Silver Ion

1. Chloride ion, from HCl or a soluble chloride, precipitates AgCl, white, curdy, darkening on exposure to light presumably because of formation of colloidal Ag^0.

$$2AgCl \rightarrow 2Ag^0 + Cl_2$$

AgCl is somewhat soluble in concentrated HCl and in concentrated alkali chloride solutions because of formation of complex anions such as $[AgCl_3]^=$. It is readily soluble in ammonia solution because of formation of $Ag(NH_3)_2^+$. All silver salts, including even the extremely insoluble Ag_2S, dissolve in sufficient C_{CN^-} because of formation of very stable complex ions such as $[Ag(CN)_2]^-$, $[Ag(CN)_3]^=$, and the like. Both AgCl and AgBr dissolve in $Na_2S_2O_3$ solution because of formation of complexes such as $[Ag(S_2O_3)_2]^{-3}$, $[Ag_2(S_2O_3)_3]^{-4}$, and the like. This reaction is made use of in photography to dissolve unchanged AgBr off the photographic plate or film.

2. Strong bases—NaOH or KOH—precipitate, from solutions containing Ag^+, Ag_2O (brown), insoluble in excess of OH^- but readily soluble in NH_3 solution.

3. Ammonia solution, if very dilute, precipitates from solutions containing Ag^+, AgOH (white), rapidly turning brown because of formation of Ag_2O, which is soluble in excess of the reagent with formation of $[Ag(NH_3)_2]^+$. AgOH is a very strong base. AgBr and AgNCS are sparingly soluble in NH_3. AgI is practically insoluble.

4. Hydrogen sulfide and alkali sulfides precipitate, from solutions containing Ag^+, Ag_2S (black), insoluble in cold dilute acids, in alkali hydroxides and alkali sulfides and in dilute CN^- because of its extremely small solubility in water. The $K_{s.p.}$ of Ag_2S is reported to be 1×10^{-51}. All compounds of complex ions of Ag^+ can be converted into Ag_2S. Ag_2S dissolves in hot moderately concentrated nitric acid with formation of S and NO.

$$3\underline{Ag_2S} + 2NO_3^- + 8H^+ = 6Ag^+ + 3\underline{S} + 2\overline{NO} + 4H_2O$$

Ag_2S also dissolves in very concentrated CN^-,

$$\underline{Ag_2S} + 6CN^- \rightleftarrows 2[Ag(CN)_3]^- + S^-,$$

because $\dfrac{C_{Ag^+} \times C^3_{CN^-}}{C_{Ag(CN)_3^-}} = 8 \times 10^{-23}$. If C_{CN^-} in the solution is sufficiently great, $C^2_{Ag^+} \times C_{S^-}$ may become actually less than 1×10^{-51} and the extremely insoluble Ag_2S is forced to dissolve.

5. Metals which stand above silver in the electromotive series will reduce Ag^+ to Ag^0. In analysis this fact is utilized to bring the extremely insoluble halides into solution so that Ag^+ and the anion of the salt can be detected.

$$2\underline{AgCl} + 2\underline{Zn^0} + 2H^+ \rightleftarrows 2\underline{Ag^0} + 2Zn^{++} + 2Cl^- + \overline{H_2}$$

PRACTICE EXERCISE

Balance the following equations for important reactions of Ag^+ (consult Chapter 5).

1. $\underline{Ag} + H^+ + NO_3^- = Ag^+ + \overline{NO} + H_2O$
2. $\underline{AgCl} + Cl^- \rightleftarrows [AgCl_3]^-$
3. $\underline{AgCl} + NH_3 \rightleftarrows [Ag(NH_3)_2]^+$
4. $\underline{AgCl} + S_2O_3^- \rightleftarrows [Ag(S_2O_3)_2]^{-3}$
5. $\underline{AgCl} + CN^- \rightleftarrows [Ag(CN)_2]^-$
6. $\underline{Ag_2S} + CN^- \rightleftarrows [Ag(CN)_3]^- + S^-$
7. $\underline{Ag_2S} + H^+ + NO_3^- = \underline{S} + \overline{NO} + H_2O + Ag^+$
8. $\underline{AgCl} + \underline{Hg^0} \rightleftarrows \underline{Ag^0} + \underline{Hg_2Cl_2}$
9. $Ag^+ + \underline{Fe}\ (\underline{Cu}, \underline{Zn}) \rightarrow \underline{Ag} + Fe^{++}\ (Cu^{++}, Zn^{++})$
10. $2\underline{AgOH} \rightarrow \underline{Ag_2O}$

Mercury

For occurrence and dissolution of metal see page 219.

Reactions of Mercurous Ion

The mercurous ion, Hg_2^{++}, is complex, $[Hg : Hg]^{++}$, each Hg^+ furnishing one electron of the bond. Characteristic of the mercurous salts is the readiness with which they spontaneously decompose into Hg^{++} and Hg^0. Mercurous salts greatly resemble in solubility those of silver. Only the nitrate and chlorate are largely soluble in water. All mercurous salts are readily changed into mercuric salts by oxidants.

1. Chloride ion from HCl or soluble chlorides precipitates from $Hg_2(NO_3)_2$ solution Hg_2Cl_2 (white), insoluble in water and in cold dilute HNO_3. Hg_2Br_2 and Hg_2I_2 are even more insoluble than the chloride.

2. Strong bases—NaOH or KOH—precipitate from solutions of $Hg_2(NO_3)_2$ black Hg_2O, insoluble in excess of the reagent.

3. Ammonia solution instantly changes Hg_2Cl_2 into a mixture of white ammonobasic mercuric chloride, $HgNH_2Cl$, and Hg^0. The finely divided Hg^0 causes the mixture to appear black. This reaction is so sensitive that no further confirmation of Hg_2^{++} is necessary than the insolubility of its chloride in dilute H^+ and the blackening of the latter by NH_3.

$$Hg_2^{++} + 2Cl^- = \underline{Hg_2Cl_2}$$

$$\underline{Hg_2Cl_2} + 2NH_3 \rightleftarrows \underline{HgNH_2Cl} + \underline{Hg^0} + NH_4^+ + Cl^-$$

(For a discussion of ammonobasic salts, see "Reactions of Mercuric Ion," page 220.)

4. Hydrogen sulfide gives with solutions containing Hg_2^{++} a black mixture of HgS and Hg^0. Presumably Hg_2S is formed first but quickly decomposes.

PRACTICE EXERCISE

Balance the following equations for important reactions of Hg_2^{++}.

1. $Hg_2^{++} \rightarrow Hg^0 + Hg^{++}$
2. $Hg_2^{++} + NO_3^- + H_2O \rightarrow \underline{Hg_2OHNO_3} + H^+$

3. $\underline{Hg_2Cl_2} + NH_3 \rightarrow \underline{HgNH_2Cl} + Hg^0 + NH_4^+$

4. $\underline{HgNH_2Cl} + NH_4^+ \rightleftarrows HgCl_2 + NH_3$

5. $Hg^0 + HCl + NO_3^- \rightarrow [HgCl_3]^- + \overline{NO} + H_2O$

6. $Hg_2^{++} + OH^- \rightarrow \underline{Hg_2O} +$

7. $\underline{Hg_2Cl_2} + [SnCl_4]^= \rightarrow Hg^0 + [SnCl_6]^=$

8. $Hg_2^{++} + NO_3^- + NH_3 + H_2O \rightarrow \underset{\substack{\text{(Aquobasic ammonobasic}\\ \text{mercuric nitrate)}}}{\underline{H_2NHgOHgNO_3}} + NH_4^+ + Hg^0$

Lead

For reactions of lead ion see Group II.

THE IONS OF CATION GROUP II

(Pb^{++}, BiO^+, Cu^{++}, Cd^{++}; $HAsO_2$, SbO^+, Sn^{+4}, and Hg^{++})

Group reagent, H_2S in 0.3 *N* H^+. This group includes all those cations except Ag^+ and Hg_2^{++} which are precipitated (probably as hydrosulfides) in 0.3 *N* H^+.

In the periodic arrangement of the elements the members of the Analytical Group II are rather widely scattered: Cu in Group I-B, Cd and Hg in Group II-B, Sn and Pb in Group IV-B, As, Sb and Bi in Group V-B.

The sulfides of As, Sb, and Sn^{+4} are amphoteric like the oxides and soluble in alkali sulfide solution. Hg^{++} forms a stable complex anion with $S^=$ of sufficient concentration. For that reason it dissolves in Na_2S solution but not in $(NH_4)_2S$ (see Chapter 9). The sulfides of the other ions of the group are insoluble in alkali sulfide solution except that a little Bi_2S_3 occasionally dissolves.[4] On this basis of solubility or nonsolubility in alkali sulfide, the group will be divided into two subgroups: II-A, including Pb^{++}, BiO^+, Cu^{++}, and Cd^{++}; and II-B, including Hg^{++}, As^{+3}, SbO^+, and Sn^{+4}.

Stannous ion is not included for two reasons. (1) While chlorostannous acid, H_2SnCl_4, is a frequently used reagent, tin occurs usually in quadrivalent condition in materials actually analyzed. This is because

[4] The cause of the occasional, but not invariable, slight dissolution of Bi_2S_3 has not been found. In some cases insufficient washing of the H_2S precipitate ($Bi(SH)_3 \rightarrow Bi_2S_3$?) was clearly responsible. In other cases only modification of physical state, due to presence of other ions or to conditions of precipitation, seemed probable.

strong oxidants like HNO_3 or aqua regia are usually used to bring the metal or its compounds into solution. For this reason Sn^{++} is infrequently encountered except as it may be put into student unknown solutions. Moreover, even in acid solution, Sn^{++} is rapidly oxidized by air. (2) The mixture of NaHS and NaOH used to separate the "B" subgroup from the "A" subgroup always becomes somewhat yellow during the process of separation, because of oxidation by air. The persulfide ions so formed suffice to sulfurize any SnS present and dissolve it as $[SnS_3]^-$.

$$\underline{SnS} + S_2^- = [SnS_3]^-$$

Lead

Occurrence. Lead occurs in the earth's lithosphere chiefly as galena, PbS, but also as the weathered products cerussite, $PbCO_3$, and anglesite, $PbSO_4$. Occasionally it occurs as phosphate, arsenate, chromate, molybdate, or tungstate.

Dissolution of the metal. Like Al, the metal tarnishes in air because of the formation of a film of oxide. Hot dilute HNO_3 is the best solvent. Concentrated HNO_3 forms a protective film of $Pb(NO_3)_2$ insoluble in the concentrated acid.

In general, cold acids whose Pb salts are insoluble in water will form similar protective films. Lead vessels were formerly used for reactions with HF. The synthetic resin, bakelite, has largely replaced them.

Hot concentrated HCl and H_2SO_4 dissolve lead, the former by formation of $[PbCl_4]^-$, the latter because $Pb(HSO_4)_2$ is soluble.

Valences. Like the other elements of Periodic Group IV-B, lead shows valences of 2 and 4. In addition to the oxides litharge, PbO, and lead dioxide, PbO_2, it forms a so-called oxide, Pb_3O_4, minium, which is more probably a salt. Litharge is yellow; minium, bright red; lead dioxide, violet brown.

PbO_2 is the anhydride of a weak unstable plumbic acid. Because dilute HNO_3 dissolves $\frac{2}{3}$ of the Pb in Pb_3O_4 as Pb^{++} leaving $\frac{1}{3}$ as PbO_2, it has been suggested that this "oxide" may be a salt, Pb_2PbO_4, plumbous plumbate. Plumbates of Na, K, and Ca are formed only by fusion and are completely decomposed by water, with formation of PbO_2. The unstable plumbic acid might be formulated $[Pb(OH)_4(H_2O)_2]$ or $H_2Pb(OH)_6$, analogous to $[Sn(OH)_4(H_2O)_2]$ or $H_2Sn(OH)_6$. Both acids are gels insoluble in water. A yellow unstable chloroplumbate, $(NH_4)_2PbCl_6$, is not difficult to prepare. Since PbO_2 is the only compound of 4-valent lead

encountered in analysis, it is customary to speak of the ion Pb^{++} as lead ion and not as plumbous ion.

Reactions of Lead Ion

1. Chloride ion (Group I reagent) precipitates some $PbCl_2$ from solutions containing a large $C_{Pb^{++}}$. All lead halides except PbF_2 are much more soluble at 100° than at room temperature and crystallize out when hot saturated solutions are cooled.

SOLUBILITIES IN MG PER ML OF LEAD HALIDES

Temp.	PbF_2	$PbCl_2$	$PbBr_2$	PbI_2
25°	1.0	11	9.7	0.7
100°	...	33	45.5	4.2

Lead will therefore be precipitated in Group I as chloride if it is present in unusually large concentration. In semimicro analysis it usually will be found only in Group II.

A small excess of Cl^- decreases the solubility of $PbCl_2$ (common-ion effect) but a large excess renders it more soluble because of formation of complex anions such as $[PbCl_3]^-$ or $[PbCl_4]^=$.

2. Sulfate ion precipitates white $PbSO_4$, practically insoluble in water (0.04 mg/ml at 25°) and still less soluble in dilute $SO_4^=$ (common-ion effect) but soluble in concentrated H_2SO_4, because of formation of HSO_4^-. For the same reason $PbSO_4$ is distinctly soluble in dilute HNO_3.

$$\underline{PbSO_4} + H^+ \rightleftarrows Pb^{++} + HSO_4^- .$$

$PbSO_4$ dissolves in alkali acetate solution, probably because of both of the following reactions:

$$\underline{PbSO_4} + 2AcO^- \rightleftarrows (AcO)_2Pb + SO_4^=, \text{ and} \qquad (3)$$

$$\underline{PbSO_4} + 4AcO^- \rightleftarrows [Pb(AcO)_4]^= + SO_4^= \qquad (4)$$

These reactions are readily reversible. Addition of a small $C_{SO_4^=}$ to a solution of $(AcO)_2Pb$ causes precipitation of $PbSO_4$.

The dissolution of $PbSO_4$ in moderately concentrated alkali acetate solution apparently arises from two different causes: (1) $(AcO)_2Pb$ is much less ionized than other acetates of bivalent cations; (2) formation of complex anions such as $[Pb(AcO)_4]^=$. It is to be remembered that no very large amount of Pb^{++} enters Group II, since if originally large, it would have been partially precipitated as $PbCl_2$ in Group I. In equilibrium

(3) both of the right hand members are therefore rather small, while at the same time the C_{AcO^-} is relatively large. If $(AcO)_2Pb$ is ionized to an extent exceptionally small for a salt (25% in 0.1 N solution according to A. A. Noyes) the common-ion effect of the large C_{AcO^-} may force Pb^{++} into unionized $(AcO)_2Pb$ to such an extent that, considering the small $C_{SO_4^-}$ present, the ion product, $C_{Pb^{++}} \times C_{SO_4^-}$, becomes less than the solubility product of $PbSO_4$, and the salt dissolves. Addition of a little SO_4^- to the solution will cause $PbSO_4$ to reprecipitate. On the other hand there is evidence that reaction (4) also takes place to some extent.

3. Strong bases—KOH or NaOH—precipitate white $Pb(OH)_2$ or, more probably, a gel which might be formulated as $[Pb(OH)_2(H_2O)_4]$. The gel is soluble in excess of the reagent, forming solutions containing biplumbite ions such as $[HPb(OH)_4]^-$ analogous to $[HSn(OH)_4]^-$. The dissolution of the gel in alkali

$$\underline{[Pb(OH)_2(H_2O)_4]} + OH^- \rightleftarrows [HPb(OH)_4]^- + 3H_2O$$

would be precisely like that of aluminum oxide gel (see page 237).

4. Ammonia solution precipitates white basic salts, $PbOHX$, where X is the anion of the lead salt. Such basic salts may be mistaken in analysis for BiOOH unless a confirmation test is made.

5. Chromate or dichromate ion precipitates $PbCrO_4$ (yellow), more insoluble (7×10^{-5} mg/ml at 20°) than $PbSO_4$. It is insoluble in AcOH but soluble in mineral acids because of formation of $HCrO_4^-$ and $Cr_2O_7^=$. $PbCrO_4$ is also soluble in strong bases because of formation of anions such as $[HPb(OH)_4]^-$.

$$2PbCrO_4 + 2H^+ \rightleftarrows Cr_2O_7^= + H_2O + 2Pb^{++}$$
$$\underline{PbCrO_4} + 3OH^- + H_2O \rightleftarrows [HPb(OH)_4]^- + CrO_4^=$$

From ammonium acetate solution of lead sulfate, $CrO_4^=$ "quantitatively" precipitates $PbCrO_4$.

$$(AcO)_2Pb + CrO_4^= = \underline{PbCrO_4} + 2AcO^-$$

6. Hydrogen sulfide precipitates from solutions containing Pb^{++} or $[HPb(OH)_4]^-$, $Pb(HS)_2$ or PbS black.

$$Pb^{++} + 2H_2S \rightleftarrows \underline{Pb(HS)_2} + 2H^+$$
$$[HPb(OH)_4]^- + 3H_2S = \underline{Pb(HS)_2} + 4H_2O + HS^-$$

Infrequently, from solutions more concentrated in H^+ than 0.3 N, a brown-red chlorosulfide, $PbCl_2 \cdot PbS$, is obtained.

Lead sulfide is one of the most soluble of Group II sulfides. If C_{H^+} is much greater than 0.3 N, lead ion may be only partially

precipitated by H_2S or even escape precipitation altogether if the amount is very small. Lead sulfide is not attacked by alkali sulfide but dissolves readily in hot $3N$ HNO_3 with formation of sulfur and NO.

$$3PbS + 8H^+ + 2NO_3^- = 3Pb^{++} + S + 2NO + 4H_2O$$

Concentrated HNO_3 on PbS forms $PbSO_4$ and NO_2.

$$PbS + 8NO_3^- + 8H^+ = PbSO_4 + 8NO_2 + 4H_2O$$

The insolubility of $Pb(HS)_2$ makes H_2S one of the most sensitive reagents for the detection of Pb^{++}. It is said that in neutral solution 1 part of Pb^{++} in 100,000 parts of water can be detected by H_2S.

PRACTICE EXERCISE

Balance the following equations for important reactions of Pb^{++}.

1. $PbCl_2 + H_2O\ (100°) \rightleftarrows Pb^{++} + Cl^-$
2. $Pb^{++} + Cr_2O_7^= \rightleftarrows PbCrO_4$
3. $PbCrO_4 + OH^- \rightleftarrows [HPb(OH)_4]^- + CrO_4^=$
4. $Pb^{++} + SO_4^= \rightleftarrows PbSO_4$
5. $PbSO_4 + H_2SO_4\ (36N) \rightleftarrows HSO_4^- + Pb^{++}$
6. $PbSO_4 + AcO^- \rightleftarrows (AcO)_2Pb$
7. $PbSO_4 + AcO^- \rightleftarrows [Pb(AcO)_4]^=$
8. $PbSO_4 + H^+ + NO_3^- \rightleftarrows Pb^{++} + HSO_4^-$
9. $PbS + H^+ + NO_3^- = S + NO + Pb^{++}$
10. $PbS + H^+ + NO_3^- \rightarrow HSO_4^- + NO_2 + Pb^{++}$
11. $[HPb(OH)_4]^- + H_2S = Pb(HS)_2$
12. $Pb^{++} + HSO_4^- + NH_3 \rightarrow Pb_2(OH)_2SO_4$

Bismuth

Occurrence. Bismuth occurs in the earth's lithosphere occasionally as the metal but chiefly as the sulfide Bi_2S_3, bismuthinite. It is not a widely distributed element. The principal mines are in Bolivia and Tasmania.

Dissolution of the metal. Bismuth does not oxidize H^+ to H_2 and hence cannot dissolve in nonoxidizing solvents. It dissolves in hot $36N$ H_2SO_4 with evolution of SO_2. The best solvent is HNO_3.

Valences. Bismuth forms the oxide Bi_2O_3 (pale yellow) and a higher oxide, or mixture, of brown-red color varying between BiO_2 and Bi_2O_5. The so called "sodium bismuthate" is of variable composition and doubtfully a true salt. In most of its compounds the metal shows the valence three.

Bismuth is an important component of fusible alloys. An alloy of 15 parts of Bi, 8 parts Pb, 4 parts Sn, and 3 parts Cd melts at 60°. Bismuth is also used in the preparation of cosmetics and pharmaceuticals.

Aqueous solutions of bismuth salts contain the ion BiO^+ or, if strongly acid, anions such as $[BiCl_4]^-$, $[Bi(NO_3)_4]^-$, and the like. From aqueous solutions basic salts, such as BiOCl, $BiONO_3$, and $(BiO)_2SO_4$, are precipitated on dilution. Anhydrous $BiCl_3$ melts at 232°, fumes in moist air, and, like $AlCl_3$, is not a true salt but a coordination compound. $Bi(NO_3)_3 \cdot 5H_2O$ crystallizes from HNO_3 but on heating decomposes into $BiONO_3$. It is decomposed by water with precipitation of $BiONO_3$ or more probably $Bi(OH)_2NO_3$. Bismuth tends to form complex anions, such as $[BiCl_4]^-$. In all bismuth solutions, therefore, the following equilibria are present:

$$Bi^{+3} + H_2O \rightleftarrows BiO^+ + 2H^+, \text{ and}$$
$$Bi^{+3} + 4X^- \rightleftarrows [BiX_4]^-.$$

Reactions of Bismuthyl Ion

1. Strong bases—NaOH or KOH—and also ammonia solution precipitate BiOOH, or basic salts, insoluble in excess of either reagent but tending to become colloidal in high C_{OH^-}.

2. Alkali bistannite instantly reduces BiOOH to Bi^0 (black).

$$\underline{BiOOH} + H_2O + 3e^- \rightleftarrows \underline{Bi^0} + 3OH^-$$
$$[HSn(OH)_4]^- + 3OH^- \rightleftarrows [Sn(OH)_6]^{=} + 2e^- + H_2O$$

This constitutes a *sensitive test* for BiO^+.

3. Hydrogen sulfide precipitates, from solutions containing BiO^+ and not too great C_{H^+}, dark brown $Bi(HS)_3$ or Bi_2S_3 soluble in $3N$ HNO_3 with formation of sulfur and NO. The sulfide is insoluble in NaHS and NaOH. As stated on page 209, under certain conditions as much as 0.5 mg occasionally dissolves in this reagent.

4. Anhydrous $Bi_2(SO_4)_3$ is insoluble in concentrated H_2SO_4, more soluble in moderately dilute H_2SO_4 because of hydration and ionization but decomposed by much water into insoluble $(BiO)_2SO_4$. These facts are important in the analytical separation of Pb and Bi by H_2SO_4.

PRACTICE EXERCISE

Balance the following equations for important reactions of BiO^+.

1. $\underline{Bi(OH)_2Cl} + H_2S \rightleftarrows \underline{Bi(HS)_3}$
2. $\underline{Bi_2S_3} + H^+ + NO_3^- \rightleftarrows BiO^+ + \underline{S} + \overline{NO}$
3. $BiO^+ + HSO_4^- \rightarrow \underline{Bi_2(SO_4)_3}$
4. $BiO^+ + HSO_4^- + H_2O \rightarrow \underline{(BiO)_2SO_4}$
5. $BiO^+ + NH_3 + H_2O \rightleftarrows \underline{BiOOH}$
6. $\underline{BiOOH} + [HSn(OH)_4]^- \rightleftarrows \underline{Bi^0} + [Sn(OH)_6]^-$
7. $BiO^+ + H^+ + Cl^- \rightleftarrows [BiCl_4]^-$
8. $\underline{(BiO)_2SO_4} + AcO^- \rightleftarrows [Bi(AcO)_6]^{-3}$
9. $\underline{(BiO)_2Cr_2O_7} + OH^- \rightleftarrows \underline{BiOOH}$

Copper

Occurrence. Copper occurs in the earth's lithosphere as the metal; the oxide Cu_2O, cuprite; the sulfides Cu_2S, chalcocite, and $CuFeS_2$, chalcopyrite; and as basic carbonates, $Cu_2(OH)_2CO_3$, malachite, and $Cu_3(OH)_2(CO_3)_2$, azurite.

Dissolution of the metal. Since copper stands below hydrogen in the electromotive series it can not displace hydrogen from acid but it is readily dissolved by oxidizing acids such as HNO_3 or hot concentrated H_2SO_4.

$$\underline{Cu^0} \rightleftarrows Cu^{++} + 2e^-$$

$$NO_3^- + 4H^+ + 3e^- \rightleftarrows \overline{NO} + 2H_2O \text{ (dilute)}$$

$$NO_3^- + 2H^+ + e^- \rightleftarrows \overline{NO_2} + H_2O \text{ (12-16}N\text{)}$$

$$\underline{Cu^0} + 2H_2SO_4 \rightarrow \underline{CuSO_4} + \overline{SO_2} + 2H_2O$$

Valences. Copper forms two ions, Cu^+ (colorless) and Cu^{++} (in dilute aqueous solution $Cu(H_2O)_4^{++}$) blue green.

Cuprous salts, except in their instability toward oxygen, resemble very closely in appearance and in chemical properties the corresponding salts of silver. The halides, CuCl, CuBr, CuI, CuCN, CuNCS, like the silver halides, are all colorless and insoluble in water and dilute acids. Like them they tend strongly to formation of complex anions, such as $[CuCl_3]^=$, $[Cu(CN)_3]^=$, and the like. Cu_2S, CuS, and CuO are black. Cu_2O is red. Because cuprous salts are oxidized by air, the only cuprous compounds met in analysis are $[Cu(CN)_3]^=$ and possibly Cu_2S.

Reactions of Cupric Ion

1. Strong bases—NaOH or KOH—precipitate $Cu(OH)_2$ (pale blue), very slightly soluble in high C_{OH^-} because of formation of $[Cu(OH)_4]^=$ (deep blue).

2. Na_2CO_3 solutions, especially on boiling, dissolve more $Cu(OH)_2$ than does NaOH of the same normality. This is because of formation of complex anions such as $[Cu(CO_3)_2]^=$.

3. Ammonia solution, if very dilute, precipitates basic salts, CuOH*X* (pale blue), readily soluble in excess of NH_3, or in NH_4^+ salts, with formation of $[Cu(NH_3)_4]^{++}$ (deep blue).

$$\underline{CuOHX} + NH_4^+ + 3NH_3 \rightleftarrows [Cu(NH_3)_4]^{++} + H_2O + X^-$$

As little as 0.5 mg of Cu^{++} as $[Cu(NH_3)_4]^{++}$ in 1 ml of dilute NH_3 solution gives a clearly visible blue color. This constitutes a fairly sensitive test for Cu^{++}.

4. Hydrogen sulfide precipitates from solutions containing Cu^{++} a black precipitate said to be CuS but much more probably a mixture of $Cu(HS)_2$ and CuHS, since H_2S can reduce Cu^{++} to Cu^+.

Calculation from the molar potentials shows that at equilibrium

$$\frac{C^2_{Cu^+} \times C^2_{H^+}}{C^2_{Cu^{++}} \times C_{H_2S}} = 1.$$

In a solution 0.3*N* in H^+ and saturated with H_2S (C_{H_2S} = 0.1 molar), $C_{Cu^+}/C_{Cu^{++}} = 1$ approx., since 0.09/0.1 = 1 nearly. Since Cu_2S is nearly as insoluble as CuS, it appears that it should precipitate.

Evidence that the precipitate is a hydrosulfide rather than a sulfide is that the fresh unwashed precipitate is easily soluble in dilute CN^- but much less soluble after being repeatedly washed. The sulfide is insoluble in dilute OH^- and in NaHS. It is dissolved by hot 3*N* HNO_3 with formation of S and NO.

5. Alkali cyanide reduces blue $[Cu(NH_3)_4]^{++}$ to colorless $[Cu(CN)_3]^-$ (distinction from $Cd(NH_3)_4^{++}$).

$$[Cu(NH_3)_4]^{++} + 3CN^- + e^- \rightleftarrows [Cu(CN)_3]^- + 4NH_3$$
$$CN^- + 2OH^- \rightleftarrows NCO^- + H_2O + 2e^-$$

6. Coprecipitation of $Cu[Hg(NCS)_4]$ with $Zn[Hg(NCS)_4]$. If to a solution containing Cu^{++} in too minute concentration to show *any* blue color with NH_3, a drop of 1% $(AcO)_2Zn$ solution and a drop of $K_2[Hg(NCS)_4]$ is added and the mixture stirred with a glass rod for a few seconds, $Zn[Hg(NCS)_4]$, colored distinctly red-violet by coprecipitated $CuHg(NCS)_4$, is formed. This test is said to be capable of detecting 0.0001 mg of copper or 1 part in 500,000 parts of water. Cd^{++} does not interfere. This test is to be used for possible traces of Cu^{++} too small to give any blue color of $[Cu(NH_3)_4]^{++}$.

Coprecipitation. Many instances have been found of decided changes of physical properties of salts through inclusion or occlusion of foreign ions. This phenomenon has been extensively investigated by I. M. Kolthoff. The extraordinarily sensitive tests for traces of Cu^{++} below and for Zn^{++}, page 260, are interesting and valuable applications of this phenomenon. While $Zn[Hg(NCS)_4]$ tends strongly to form supersaturated solutions and can be made to crystallize only after prolonged vigorous stirring, in presence of a trace of either Cu^{++} or Co^{++} distinctively colored precipitates are formed within 15 seconds. In the detection of Zn the trace of Co^{++} used is but a minute fraction of that required to form the deep blue $Co[Hg(NCS)_4]$. The amount of Cu^{++} or of Co^{++} required to completely modify both the color and the crystallizing power of $Zn[Hg(NCS)_4]$ is unbelievably small. So far as we know this phenomenon is not yet adequately explained.

Detection of traces of Cu^{++}. In a depression of a spot plate place 1 drop of 6*N* acetic acid and 1 drop of the colorless ammonia solution which may contain a trace of $[Cu(NH_3)_4]^{++}$, along with $[Cd(NH_3)_4]^{++}$. Then add 1 drop of 1% $(AcO)_2Zn$ solution and 1 drop of $K_2[Hg(NCS)_4]$ reagent. Stir with a glass rod for a few seconds. Red-violet precipitate proves Cu^{++} present.

7. Flame color. $CuCl_2$ or, in general, cupric salts moistened with 12*N* HCl impart a blue and green color to a flame. This is not particularly sensitive as a test for Cu^{++}.

PRACTICE EXERCISE

Balance the following equations for important reactions of $Cu(H_2O)_4^{++}$.

1. $\underline{CuS} + H^+ + NO_3^- = \underline{S} + \overline{NO}$
2. $Cu^{++} + NH_3 \rightleftarrows [Cu(NH_3)_4]^{++}$
3. $[Cu(NH_3)_4]^{++} + CN^- + H_2O \rightleftarrows Cu(CN)_3^- + CNO^-$
4. $[CuCl_4]^- + \underline{Cu^0}$ (boiled) $\rightleftarrows [CuCl_3]^-$
5. $[CuCl_3]^- \rightleftarrows \underline{CuCl} + 2Cl^-$ } (Sandmeyer reaction)
6. $Cu^{++} + CO_3^=$ (conc. hot) $\rightleftarrows [Cu(CO_3)_2]^=$ (deep blue)
7. $\underline{Cu(OH)_2}$ (boiled) $\rightleftarrows \underline{CuO}$
8. $\underline{Cu(OH)_2} + OH^- \rightleftharpoons [Cu(OH)_4]^-$

Cadmium

Occurrence. The free metal is not found in the earth's lithosphere. Pure cadmium compounds are also extremely rare. The chief occurrence of cadmium is in the zinc ores, particularly the sulfide which almost always contains more or less cadmium. CdO is more volatile than ZnO and concentrates in the flue dust during the smelting of zinc ores.

Dissolution of the metal. Dilute HNO_3 is the best solvent. Dilute HCl or H_2SO_4 dissolves it slowly.

Valence. Cadmium is bivalent in all its compounds.

Reactions of Cadmium Ion

1. **Strong bases**—NaOH or KOH—precipitate $Cd(OH)_2$ (white), insoluble in excess of reagent (difference from Zn).

2. **Ammonia solution** precipitates basic $CdOHX$, soluble in large excess of NH_3, or in much smaller excess if NH_4^+ salts are present, due to formation of $[Cd(NH_3)_4]^{++}$. This ion appears to be much less stable than $[Zn(NH_3)_4]^{++}$. Its $K_{inst.}$ has been reported to be 1×10^{-7}.

3. **Hydrogen sulfide** precipitates from solutions containing not too great C_{H^+} bright yellow $Cd(HS)_2$ or CdS. According to the conditions of precipitation, temperature, C_{H^+}, rate of admission of H_2S, and so on, the color varies from pale yellow to orange red. It is completely precipitated in solutions in which C_{H^+} is $0.3\,N$. CdS is insoluble in NaHS solution. It dissolves readily in hot $3\,N$ HNO_3 with formation of S and NO.

4. Alkali cyanide with solutions containing $[Cd(NH_3)_4]^{++}$ forms $[Cd(CN)_4]^{=}$, much less stable than $[Cu(CN)_3]^{=}$. If to a mixture of the two ions which contains a small excess of CN^- a little HS^- is added, yellow $Cd(HS)_2$ precipitates but no black Cu_2S or CuHS results (detection of Cd^{++}).

PRACTICE EXERCISE

Balance the following equations for important reactions of Cd^{++}.

1. $\underline{CdS} + H^+ + NO_3^- = \underline{S} + \overline{NO} + H_2O + Cd^{++}$
2. $Cd^{++} + NH_3 \rightleftarrows [Cd(NH_3)_4]^{++}$
3. $[Cd(NH_3)_4]^{++} + CN^- \rightleftarrows [Cd(CN)_4]^{=}$
4. $[Cd(CN)_4]^{=} + HS^- \rightleftarrows \underline{CdS}$

Mercury

Occurrence. Mercury occurs in the earth's lithosphere usually as the sulfide HgS, cinnabar (dark red). It is unique among the metallic elements in its low melting point, −38.9°. In this respect it is approached only by the element gallium which melts at +29.75°.

Dissolution of the metal. The metal is scarcely attacked by dilute H_2SO_4 and HCl but is readily dissolved by oxidizing acids such as HNO_3 or hot 36 N H_2SO_4. Hot concentrated HNO_3 forms mercuric nitrate, $Hg(NO_3)_2$. Cold dilute HNO_3 with an excess of the metal forms mercurous nitrate, $Hg_2(NO_3)_2$.

Valences. Mercury forms mercurous ion Hg_2^{++}, and mercuric ion, Hg^{++}. The former is complex $[Hg \times Hg]^{++}$, each atom losing one electron and contributing one to the covalent bond. Hg_2Cl_2 is insoluble in water and Hg_2^{++} therefore belongs in analytical Group I of cations. $HgCl_2$ is soluble in water and in consequence Hg^{++} belongs in Group II.

Properties of the salts. Most mercuric salts are insoluble in water. The exceptions are $Hg(NO_3)_2$, $HgCl_2$, $HgBr_2$, $Hg(CN)_2$, $Hg(ClO_3)_2$, and $(AcO)_2Hg$. All the soluble salts of strong acids tend to take up OH^- from water with formation of insoluble basic salts. As a result their solutions are more or less acid.

$$HgX_2 + H_2O \rightleftarrows \underline{HgOHX} + H^+ + X^- \qquad (5)$$

Hg^{++} is a notable complex former. The following values of the instability constants of some of the complex ions have been determined.

$[HgCl_3]^-$ 1.1×10^{-16}, $[HgBr_4]^-$ 2.2×10^{-22}, $[Hg(NCS)_4]^-$ 1.0×10^{-22}, $[HgI_4]^-$ 5.3×10^{-31}, $[Hg(CN)_4]^-$ 4×10^{-42}.

Because of this complex formation most mercuric salt solutions are extremely poor conductors of electricity. $HgCl_2$ is less ionized in water than $(AcO)_2Pb$ or $CdCl_2$. It is soluble in water only to the extent of 67 mg per ml at 20°. In HCl or soluble chloride solution it is much more soluble because of the formation of $[HgCl_3]^-$. $HgCl_2$ is the extremely poisonous antiseptic commonly known as corrosive sublimate.

$Hg(CN)_2$ in water is almost a nonconductor. As a result it does not show many of the reactions of either Hg^{++} or CN^-. H_2S decomposes it with formation of HgS and HCN. $Hg(CN)_2$ is not decomposed by boiling $3N$ Na_2CO_3. It gives a test for CN^- only after it has been decomposed by H_2S.

Reactions of Mercuric Ion

1. Strong bases—KOH or NaOH—precipitate a reddish brown basic salt changing to HgO yellow, insoluble in OH^-.

2. Ammonia solution precipitates ammonobasic salts such as H_2NHgCl or aquobasic ammonobasic salts such as $H_2NHgOHgNO_3$.

$$HgCl_2 + 2NH_3 \rightleftarrows \underline{HgNH_2Cl} + NH_4^+ + Cl^- \quad (6)$$

$$2Hg^{++} + NO_3^- + 4NH_3 + H_2O \rightleftarrows \underline{H_2NHgOHgNO_3} + 3NH_4^+ \quad (7)$$

Ammonobasic salts appear in water solution only in the cases of Hg^{++} and Hg_2^{++}. Their formation in the case of mercury alone has been explained by E. C. Franklin as due to their extraordinary insolubility.

Like water NH_3 is slightly ionized.

$$2H_2O \rightleftarrows H_3O^+ + OH^-$$
$$2NH_3 \rightleftarrows NH_4^+ + NH_2^-$$

NH_2^- and NH_4^+ are therefore the OH^- and H^+ of an ammono system of chemistry in liquid NH_3 as solvent. Just as HgOHCl formed by *hydrolysis* is aquobasic mercuric chloride, so $HgNH_2Cl$ formed by *ammonolysis* is ammonobasic mercuric chloride. In liquid ammonia ammonobasic salts are formed by many cations but, with the exception of those of mercury, all are instantly decomposed by water. In the case of mercury the ammonobasic salts are so extremely insoluble that they can exist undecomposed in the presence of water. In aqueous ammonia solution it is not

surprising that mixed basic salts of mercury are known, such as the nitrate above and the precipitate, $H_2NHgOHgI$, formed with NH_3 by Nessler's reagent. It is to be noted that in such formulas —O— is the residue from 2 OH^- from which water has split off. Since $NH_4^+ + NH_2^- \rightleftarrows 2\ NH_3$, ammonobasic salts dissolve readily in excess of NH_4^+ salts (reverse of equation (6) above). This is completely analogous to the dissolution of aquobasic salts in acid $(H_3O)^+$ solution (reverse of equation (5) above).

3. Hydrogen sulfide may form, depending upon C_{H^+} precipitates which are first white, then yellow, then brown, and finally black. From cold 12*N* HCl solution about 50% of the Hg^{++} present is precipitated as white $HgCl_2 \cdot 2HgS$. From *hot* 12*N* HCl no precipitate is formed (difference from As). The black precipitate is HgS or, more probably when first formed, $Hg(HS)_2$. The white or yellowish precipitate appears to be a mixed salt whose composition corresponds to $2HgS \cdot HgX_2$ where X^- is the anion of the Hg salt. In the coordinated three-dimensional lattice the arrangement (looking along a line) probably is *X*—Hg—S—Hg—S—Hg—*X*. It is striking that the black HgS becomes nearly colorless when thus coordinated.

HgS is one of the most insoluble sulfides of Group II, being exceeded in this respect only by the sulfides of As. It is insoluble in HCl and in hot dilute HNO_3, an important difference from the sulfides of Pb^{++}, Bi^{+3}, Cu^{++}, and Cd^{++}. When black HgS is treated with hot *concentrated* HNO_3, white $Hg(NO_3)_2 \cdot 2HgS$ is formed. It is readily soluble in NaHS containing OH^-.

$$\underline{HgS} + HS^- + OH^- \rightleftarrows [HgS_2]^= + H_2O$$

The freshly precipitated and unwashed sulfide is readily soluble in NaOH, apparent evidence that it is $Hg(HS)_2$. After washing it becomes insoluble in NaOH alone. HgS is readily dissolved by aqua regia, Br_2, or Cl_2 because of the formation of complex ions such as $[HgCl_4]^=$ and because of oxidation of $S^=$ to S or $SO_4^=$.

$$3\underline{HgS} + 12Cl^- + 2NO_3^- + 8H^+ = 3[HgCl_4]^= + 2\overline{NO} + 3\underline{S} + 4H_2O$$

$$\underline{HgS} + 4Br_2 + 4H_2O = [HgBr_4]^= + SO_4^= + 4Br^- + 8H^+$$

4. Stannous chloride, probably for the most part $[SnCl_4]^=$, in HCl, reduces Hg^{++} to white Hg_2Cl_2 insoluble in water.

$$2HgCl_2 + [SnCl_4]^= \rightleftarrows \underline{Hg_2Cl_2} + [SnCl_6]^=$$

Excess of $[SnCl_4]^=$ further reduces Hg_2Cl_2 to black Hg^0.

$$\underline{Hg_2Cl_2} + [SnCl_4]^= \rightleftarrows 2Hg^0 + [SnCl_6]^=$$

This constitutes a fairly sensitive test for mercuric ion. Since the second of the above reactions can begin before the first is completed, a gray mixture of Hg_2Cl_2 and Hg^0 is usually obtained in the test.

5. Iodide ion precipitates scarlet HgI_2, soluble in excess of the reagent due to formation of the very stable $[HgI_4]^=$. A mixture of this complex ion and NaOH is the Nessler's reagent used for detection of traces of NH_4^+.

PRACTICE EXERCISE

Balance the following equations for important reactions of Hg^{++}.

1. $[HgCl_4]^=$ (in cold 12*N* HCl) + $H_2S \rightleftarrows$
2. $[HgCl_4]^=$ (in hot 12*N* HCl) + $H_2S \rightarrow$
3. $\underline{HgS} + H^+ + NO_3^- \rightarrow$
4. $\underline{HgS} + H^+ + Cl^- + NO_3^- = [HgCl_4]^= + \underline{S}$ (or $SO_4^=$) + $\overline{NO}$
5. $HgCl_2 + NH_3 \rightleftarrows \underline{HgNH_2Cl} + NH_4^+$
6. $HgCl_2 + OH^- \rightarrow \underline{HgO}$
7. $\underline{HgS} + OH^- + HS^- \rightleftarrows [HgS_2]^=$
8. $\underline{Hg(HS)_2} + OH^- \rightleftarrows [HgS_2]^=$
9. $Hg^{++} + I^- \rightleftarrows [HgI_4]^=$
10. $HgCl_2 + [SnCl_4]^= \rightleftarrows \underline{Hg_2Cl_2} + [SnCl_6]^=$
11. $NH_4^+ + [HgI_4]^= + OH^- \rightleftarrows \underline{H_2NHgOHgI}$

(Nessler reaction)

Arsenic

In the "B" family of Periodic Group V arsenic stands between phosphorus, an obvious nonmetal, and antimony which has distinctly metallic properties. On the whole, arsenic resembles phosphorus much more than it does antimony and should be considered a nonmetal or acid-forming element. Arsenic is usually steel-gray, brittle, and easily powdered; and when heated it sublimes without

melting. At 650° the density of the vapor indicates a molecular weight corresponding to As_4. In the neighborhood of 1800° dissociation, $As_4 \rightleftarrows 2As_2$, is nearly complete. The element burns in air when heated to 180°, forming As_4O_6.

Occurrence. In the earth's lithosphere arsenic is very widely distributed. It occurs combined with many metals, particularly Fe, Co, and Ni, as arsenides. Nearly all sulfide minerals contain a small amount of arsenic. Arsenic occurs combined with sulfur in two forms: realgar, As_4S_4 (red); and orpiment, As_2S_3 (yellow). Very probably the lattice unit is As_4S_6, since that of stibnite has been found to be Sb_4S_6. That As_4S_6 is yellow, although the ions of both elements are colorless, is probably because of deformation of the larger S atoms as compared with oxygen atoms in As_4O_6, which is colorless.

Dissolution of the metal. Arsenic is dissolved by oxidizing acids. Boiling $36N$ H_2SO_4 forms As_4O_6 and SO_2,

$$\underline{As_4} + 6H_2SO_4 = \underline{As_4O_6} + 6\overline{SO_2} + 6H_2O.$$

Hot dilute HNO_3 forms arsenious acid, $HAsO_2$,

$$\underline{As_4} + 4NO_3^- + 4H^+ \rightarrow 4HAsO_2 + 4\overline{NO}.$$

Hot $16N$ HNO_3 forms arsenic acid,

$$\underline{As_4} + 20NO_3^- + 20H^+ \rightarrow 4H_3AsO_4 + 20\overline{NO_2} + 4H_2O.$$

Hot concentrated KOH or NaOH dissolves arsenic,

$$\underline{As_4^0} + 2OH^- + 6H_2O \rightarrow 2As(OH)_4^- + 2\underline{AsH_3}.$$

Compare

$$\underline{P_4^0} + 3OH^- + 3H_2O \rightarrow 3H_2PO_2^- + \overline{PH_3}.$$
(hypophosphite)

HALIDES OF ARSENIC

COMPOUND	PHYSICAL STATE	M. P.	B. P.
AsF_3	Colorless liquid	−8.5°	+63°
AsF_5	Colorless gas	−80	−53
$AsCl_3$	Colorless liquid	−16.0	130.2
$AsBr_3$	Colorless prisms	+32.8	221
AsI_3	Red plates	146	ca. 400
AsI_5	Brown crystalline mass	70	decomps.

$AsCl_5$ and $AsBr_5$ have not been prepared.

The low melting and boiling points show that these halides are coordination compounds and not salts. The arsenic in them has no more the function of a cation than has C in CCl_4 or P in PCl_3 or PCl_5. All these halides are largely decomposed by water with formation of corresponding acids of arsenic. When $HAsO_2$ is evaporated with $12N$ HCl most of it will be volatilized as $AsCl_3$.

On account of the extremely small solubility of the sulfides, arsenites in dilute or concentrated acid solution (particularly HCl) are decomposed by H_2S with precipitation of As_2S_3. Arsenates in hot $12N$ HCl form with H_2S a mixture of As_2S_3, As_2S_5, and S. For this reason arsenic, although occurring almost entirely in anions, must be considered a member of Cation Group II. Compare in this respect chromates and permanganates, which because of reduction by H_2S cause Cr^{+3} and Mn^{++} to appear as cations in Group III. The properties of arsenious and arsenic acids and their salts are considered among the anions. In this place only the properties of the sulfides and halides need be considered.

X-ray examination shows that arsenious oxide consists of a molecular lattice of As_4O_6 units. Each As is covalently bound to three oxygen atoms and each oxygen to two arsenic atoms. At 25° crystalline As_4O_6 is soluble in water to the extent of 21.3 mg per ml. A saturated aqueous solution at 25° is therefore very nearly $0.1M$. As_4O_6 is much more soluble in HCl than in water, probably because of formation of anions such as $[AsCl_4]^-$.

Reactions of Arsenious and Arsenic Acids

1. Hydrogen sulfide. From solutions of arsenious acid containing a strong acid (best HCl), hydrogen sulfide precipitates yellow $As(HS)_3$. The color may vary with conditions of precipitation. When precipitated from cold $0.3N$ HCl the sulfide is buff yellow, from a hot solution perceptibly brighter yellow. From cold or hot $12N$ HCl the precipitate is bright canary yellow. Occasionally a red form is obtained. These variations may be due only to particle size, although two native sulfides occur, orpiment, As_4S_6 (yellow) and realgar $[As_2S_2]_x$ (red), suggesting that red precipitates may contain less sulfide.

Precipitation of the hydrosulfide (or sulfide) is most rapid in $12N$ HCl. That this may be due to increased concentration of AsO^+ in strongly acid solution appears from consideration of the equilibrium constants involved.

As an ampholyte $HAsO_2$ is said to have the following ionization constants:

$$K_a = \frac{C_{H^+} \times C_{AsO_2^-}}{C_{HAsO_2}} = 6 \times 10^{-10}, \quad (8)$$

$$K_b = \frac{C_{AsO^+} \times C_{OH^-}}{C_{HAsO_2}} = 5 \times 10^{-15}. \quad (9)$$

Dividing (8) by (9), and substituting $10^{-14}/C_{H^+}$ for C_{OH^-},

$$\frac{C_{AsO_2^-}}{C_{AsO^+}} = \frac{1.2 \times 10^{-9}}{C^2_{H^+}}. \quad (10)$$

Equation (10) indicates that a large C_{H^+} should favor rapid precipitation of $As(HS)_3$ by increasing C_{AsO^+}.

The freshly precipitated, centrifuged, but unwashed hydrosulfide dissolves readily and completely in hot $12N$ HCl containing no H_2S. After washing it becomes practically insoluble in this medium.

2. Action of hydrogen sulfide on arsenic acid. In hot $0.3N$ HCl H_3AsO_4 is decomposed by H_2S extremely slowly. In this system of analysis arsenate is detected as an anion. Its presence does not interfere with the analysis of Cation Groups III and IV. For these reasons no attempt is made to decompose it in Group II. However, the student should be familiar with its behavior to H_2S as given under "Arsenate Ion," page 358.

3. Bases, even weak ones, dissolve As_4S_6 and As_2S_5 to form various more or less sulfurized arsenite or arsenate ion. For example,

$$\underline{As_4S_6} + 12OH^- \rightleftarrows 2[AsOS_2]^{-3} + 2[AsO_2S]^{-3} + 6H_2O,$$

$$\underline{As_4S_6} + 6HS^- + 6OH^- \rightleftarrows 4[AsS_3]^{-3} + 6H_2O.$$

4. Decomposition of thioarsenite and thioarsenate by acids. All acids, even CO_2, cause reprecipitation of the sulfides from the thioanions. For example,

$$[AsS_3]^{-3} + 3H^+ \rightleftarrows \underline{As(SH)_3} \quad (11)$$

$$6[AsOS_2]^{-3} + 18H^+ \rightleftarrows \underline{4As(SH)_3} + 2HAsO_2 + 2H_2O \quad (12)$$

$$[AsO_2S]^{-3} + 2HS^- + 5H^+ \rightleftarrows \underline{As(SH)_3} + 2H_2O \quad (13)$$

Equation (12) shows why excess HS^- must be in the solution when Group II-B is reprecipitated after dissolution of the sulfides in NaSH and NaOH.

The sulfides of arsenic are separated from those of antimony and Sn^{+4} by their insolubility in $12\,N$ HCl saturated with H_2S. They are separated from HgS by their solubility in $15\,N$ NH_3 solution.

5. Detection of minute amounts of arsenic. This is a frequent problem of toxicologists. Many of the various methods devised are based on the so-called Marsh test, which involves the formation of gaseous AsH_3, analogous to NH_3, PH_3, SbH_3.

6. The Bettendorf test is based on the fact that in $12\,N$ HCl, $SnCl_2$ will reduce all arsenic compounds to As^0.

$$2[AsCl_4]^- + 3[SnCl_4]^= \rightleftarrows 2\underline{As^0} + 3[SnCl_6]^= + 2Cl^-$$

The test is carried out as follows. Half fill a micro test tube with $SnCl_2 \cdot 2H_2O$ crystals and cover with $12\,N$ HCl. Add a few drops of the solution to be tested for arsenic and heat moderately. A brown or black suspension of colloidal As^0 will be formed slowly and within times depending upon the amount present. The test is said to be able to detect 0.03 mg As in arsenites and 0.06 mg in arsenates. Compounds of Hg, Ag, and Bi are also reduced to the metals and must be absent. Sb does not interfere.

PRACTICE EXERCISE

Balance the following equations for important reactions of $HAsO_2$

1. $\underline{As_4O_6} + H_2O \rightarrow HAsO_2$
2. $HAsO_2 + H_2S \rightarrow \underline{As(SH)_3}$
3. $\underline{As_4S_6} + OH^- + HS^- \rightarrow [AsS_3]^{-3}$
4. $\underline{As_4S_6} + NH_3 + H_2O \rightarrow [AsOS_2]^{-3} + [AsO_2S]^{-3}$
5. $\underline{As_4S_6} + H^+ + NO_3^-\ (16\,N) \rightarrow H_3AsO_4 + \overline{NO_2} + \underline{S}$ (or $SO_4^=$)
6. $\underline{H_3AsO_4} + [SnCl_4]^= \rightarrow \underline{As_4^0}$
7. $HAsO_2 + [SnCl_4]^= \rightarrow \underline{As_4^0} + [SnCl_6]^=$
8. $[AsOS_2]^{-3} + HS + H^+ \rightarrow \underline{As(SH)_3}$

Antimony

Occurrence. Antimony occurs in the earth's lithosphere chiefly as stibnite, Sb_4S_6 (black) but also as thioantimonites of other metals, for example, pyrargyrite, Ag_3SbS_3, similar to proustite, Ag_3AsS_3. It occurs frequently in lead, copper, and silver ores along

with arsenic. Antimony is an important component of many alloys. It hardens soft metals such as tin and lead and hence is used in type metal. Antimony alloys expand on cooling and take the pattern of a mold very exactly. For this reason they are much used for cheap ornamental objects. Much Sb_4S_6 is now used in the processing of rubber.

Dissolution of the metal. Since antimony is below hydrogen in the electromotive series, it will not set free H_2 from reducing acids. Hence antimony will not dissolve in HCl or H_2SO_4.

Hot dilute HNO_3 forms Sb_4O_6, nearly insoluble in the acid. Sb_4O_6 dissolves in $12N$ HCl because of formation of anions such as $[SbCl_6]^{-3}$. Hot concentrated HNO_3 forms yellowish $(Sb_2O_5)_x$ which dissolves only slowly in $12N$ HCl.

The most rapidly acting solvent is $12N$ HCl to which a little $16N$ HNO_3 is added occasionally. Anions such as $[SbCl_6]^-$ or $[SbCl_6]^{-3}$ are formed. Probably when excess of Cl_2 is removed from such solutions nearly all $[SbCl_6]^-$ spontaneously decomposes to $[SbCl_6]^{-3}$ and Cl_2.

$$[SbCl_6]^- + 2Cl^- \rightleftarrows [SbCl_6]^{-3} + Cl_2$$

Halogen compounds. $SbCl_3$, sometimes called butter of antimony, is a soft, colorless, fuming semicrystalline substance which melts at 73.4°. $SbCl_5$, formed by chlorinating $SbCl_3$, is a colorless liquid which freezes at 2.8°. Like $AsCl_3$, these chlorides are coordination compounds and not true salts. Both are decomposed by water with precipitation of basic chlorides, and both dissolve in concentrated hydrochloric acid because of formation of complex anions such as $[SbCl_4]^-$, $[SbCl_6]^{-3}$, $[SbCl_6]^-$.

An equimolecular mixture of $SbCl_3$ and $SbCl_5$ forms a dark brown solution, although both components are colorless. Addition of the alkali chlorides to this mixture gives $Rb_2[SbCl_6]$ or $Cs_2[SbCl_6]$ (dark violet), isomorphous with the corresponding salts of $[PbCl_6]^=$, $[SnCl_6]^=$, $[PtCl_6]^=$. When either Sb_4O_6 or Sb_2O_5 is ignited in air, Sb_2O_4 (white), insoluble in water, is formed. The antimony in these compounds would seem to have a valence of 4.

Reactions of Antimonyl Ion

1. Water. Like the halides of Bi^{+3}, the halides of Sb^{+3} are largely decomposed by water with formation of insoluble basic salts, $SbOX$. The reaction is reversible.

$$SbX_3 + H_2O \rightleftarrows SbOX + 2H^+ + 2X^-$$

These insoluble basic salts are changed by H_2S into the corresponding sulfides. In hydrochloric acid solution it is to be assumed that various ions are in equilibrium, such as Sb^{+3}, SbO^+, $[SbCl_4]^-$, in proportions depending upon C_{H^+}.

2. Strong bases—NaOH or KOH—precipitate, from solutions of $SbCl_3$, $Sb(OH)_2Cl$, soluble in excess of reagent, forming $[Sb(OH)_4]^-$ or $[Sb(OH)_6]^{-3}$. As an acid $H[Sb(OH)_4]$ is extremely weak like $H[Al(OH)_4]$ and antimonites exist only in strongly basic solution.

3. Ammonia solution precipitates from $SbCl_3$ solution $Sb(OH)_2Cl$, insoluble in excess of the reagent.

4. Hydrogen sulfide precipitates from solutions containing Sb^{+3}, SbO^+, $[SbCl_4]^-$, or suspensions of basic salts, Sb_4S_6 (red-orange), soluble in $6N$ HCl. It is also soluble in alkali sulfides and hydrosulfides, including $(NH_4)_2S$, but distinctly less rapidly than As_2S_3. From such solutions H^+ in excess reprecipitates the sulfide. The mechanism of sulfide precipitation and dissolution is probably about like that suggested for As_4S_6.

5. Phosphomolybdic acid is reduced to molybdenum blue upon gentle warming by $[SbCl_4]^-$ salts. $[SnCl_6]^{=}$ does not interfere. For directions for carrying out the test see "Tin," page 297.

Reactions of Antimonic Compounds

Antimonates are very infrequently met in analysis. Best known is the so-called acid "pyroantimonate," $K_2H_2Sb_2O_7 \cdot 6H_2O$, used as a reagent for Na^+. It is prepared by fusing Sb_2O_5 with excess KOH and is rapidly decomposed by water with precipitation of yellowish $Sb_2O_5 \cdot xH_2O$. Various sodium antimonates, meta-, ortho-, and pyro- sodium antimonates, $NaSbO_3$, Na_3SbO_4, $Na_2H_2Sb_2O_7$, are described in the literature, but Linus Pauling has shown that all these have the same structure corresponding to $Na[Sb(OH)_6]$.

In the system of analysis used here 5-valent antimony need not be considered, since it is readily reduced by H_2S to Sb^{+3}. Reduction of Sb^{+3} to the metal is readily accomplished in acid solution by metals which stand above antimony in the electromotive series. Zn, Sn, Fe, and Al or Mg are frequently used for this purpose.

PRACTICE EXERCISE

Balance the following equations for important reactions of SbO^-

1. $[SbCl_4]^- + H_2O \rightleftarrows \underline{Sb(OH)_2Cl}$

2. $\underline{Sb^0} + H^+ + NO_3^- = \underline{Sb_4O_6}$

3. $\underline{Sb^0} + HNO_3\ (16N) = \underline{Sb_2O_5 \cdot xH_2O} + NO_2$

4. $SbO^+ + H_2S = \underline{Sb(HS)_3}$

5. $\underline{Sb(OH)_2Cl} + H_2S = \underline{Sb(HS)_3}$

6. $[SbCl_6]^- + I^- \rightleftarrows [SbCl_6]^{-3} + I_2$

7. $\underline{Sb_4S_6} + H^+ + Cl^- \rightleftarrows [SbCl_6]^{-3}$

8. $[SbCl_6]^{-3} + Mg = Sb^0 + Mg^{++}$

9. $[\underline{(H_2O)Sb(OH)_5}] + H^+ + Cl^- \rightleftarrows [SbCl_6]^-$

10. $\underline{Sb_4S_6} + HS^- + OH^- \rightleftarrows [Sb(HS)_6]^{-3}$

11. $[Sb(HS)_6]^{-3} + H^+ \rightleftarrows \underline{Sb(HS)_3}$

12. $[SbCl_6]^{-3} + H_2C_2O_4 \rightarrow [Sb(C_2O_4)_3]^{-3}$

13. $[Sb(C_2O_4)_3]^{-3} + H_2S \rightleftarrows \underline{Sb(HS)_3}$

Tin

Occurrence. Tin is found occasionally as the metal in the earth's lithosphere but most commonly as the oxide SnO_2, cassiterite.

Dissolution of the metal. The metal dissolves in HCl to form $SnCl_2$ and H_2. Dilute H_2SO_4 slowly dissolves it to form $SnSO_4$ and H_2. Hot concentrated H_2SO_4 rapidly dissolves it with formation of $Sn(SO_4)_2$ and SO_2. Cold $1N$ HNO_3 dissolves Sn slowly with formation of Sn^{++} and NH_4^+. Concentrated nitric acid oxidizes tin to white insoluble $SnO_2 \cdot xH_2O$ (similarity to antimony). With aqua regia tin forms chlorostannic acid, H_2SnCl_6.

Reactions of Stannous Ion

The only common commercial salt is $SnCl_2 \cdot 2H_2O$, colorless crystals decomposed by water to SnOHCl, which is redissolved only by large excess of HCl. A solution of $SnCl_2$ in HCl (H_2SnCl_4) is rapidly oxidized by air to H_2SnCl_6. The reaction is prevented by presence of the metal. For this reason the laboratory reagent must always be kept in contact with a considerable amount of tin in the form of foil or granules.

1. Strong bases, ammonia solution and Na_2CO_3 precipitate from solutions containing Sn^{++} white $Sn(OH)_2$ or basic salts soluble

in excess of OH^-, with formation of $[HSn(OH)_4]^-$ (resemblance to Pb^{++}).

2. Hydrogen sulfide precipitates from solutions 0.3 *N* in H^+ containing Sn^{++} dark brown SnS, insoluble in alkali sulfide or hydrosulfide (difference from SnS_2). Yellow persulfide ions $S_2^=$ oxidize and dissolve SnS.

$$\underline{SnS} + S_2^= \rightleftarrows [SnS_3]^=$$

3. Phosphomolybdic acid and ammonium phosphomolybdate are both reduced by Sn^{++} in HCl solution to molybdenum blue. The ammonium salt is not reduced by Sb^{+3}. The reduction of phosphomolybdic acid is said to be produced by 0.0003 mg of Sn^{++}.

4. Mercuric chloride in excess is reduced by $SnCl_2$ to white insoluble Hg_2Cl_2, Sn^{++} being oxidized to $[SnCl_6]^=$ (reverse of test for Hg^{++}).

Reactions of Stannic Compounds

1. Stannic acid, probably $[(H_2O)_2Sn(OH)_4]_x$, is formed when tin is treated with hot 8 *N* nitric acid (alloy analysis). This is frequently known as β-stannic acid or as metastannic acid. It is insoluble in acids but if boiled for a time with 12 *N* HCl passes into solution when water is added. The stannic acid known as α-stannic acid is a gel formed by the action of NaOH on H_2SnCl_6 solution. This form is readily soluble in both acids and bases for the same reason as is $[(H_2O)_3Al(OH)_3]_x$. It has been shown that α- and β-stannic acids differ only in size of particles. Those of β-acid are much larger and therefore less reactive. Laboratory solutions of H_2SnCl_6, unless recently prepared, contain colloidal stannic acid which does not react with H_2S. Freshly prepared solutions of H_2SnCl_6 appear to contain very little colloidal $SnO_2 \cdot xH_2O$.

2. Hydrogen sulfide precipitates, from solutions containing not much over 0.3 *N* HCl, buff yellow SnS_2, which may contain some $SnO_2 \cdot xH_2O$.

3. SnS_2 as an ampholyte dissolves in moderately concentrated solutions of both acids and bases,

$$\underline{SnS_2} + 4H^+ + 6Cl^- \rightleftarrows [SnCl_6]^= + 2\overline{H_2S},$$
$$\underline{SnS_2} + 2OH^- + 2H_2O \rightleftarrows [Sn(HS)_2(OH)_4]^=;$$

and in alkali sulfide or hydrosulfide solutions,

$$\underline{SnS_2} + S^{=} \rightleftarrows [SnS_3]^{=},$$
$$\underline{SnS_2} + HS^{-} + OH^{-} \rightleftarrows [SnS_3]^{=} + H_2O.$$

Aged $SnO_2 \cdot xH_2O$ is not dissolved by NaOH or NaHS and in analysis passes into Group II-A where it is troublesome.

4. Oxalic acid prevents precipitation of SnS_2 by H_2S probably due to formation of complex ions such as $[Sn(C_2O_4)_3]^{=}$. The solution must be saturated with $H_2C_2O_4$ (separation from Sb^{+3}).

5. Reduction of stannic compounds. In acid solution all compounds of Sn^{+4} are rapidly reduced to Sn^{++} by metals high in the electromotive series, such as Fe, Zn, Mg, Al.

PRACTICE EXERCISE

Balance the following equations for important reactions of Tin^{+4}.

1. $\underline{Sn} + H^{+} + NO_3^{-}\ (1N) = NH_4^{+} + Sn^{++}$
2. $\underline{Sn} + HNO_3\ (16N) = \underline{SnO_2 \cdot xH_2O} + \overline{NO_2}$
3. $\underline{Sn}\ (\text{excess}) + H^{+} + Cl^{-} = [SnCl_4]^{=} + \overline{H_2}$
4. $[\underline{(H_2O)_2Sn(OH)_2}] + OH^{-} \rightleftarrows [HSn(OH)_4]^{-}$
5. $[\underline{(H_2O)_2Sn(OH)_4}] + OH^{-} \rightleftarrows [Sn(OH)_6]^{=}$
6. $[SnCl_4]^{=} + O_2 + H^{+} + Cl^{-} \rightleftarrows [SnCl_6]^{=}$
7. $\underline{SnS_2} + H^{+} + Cl^{-}\ (6N) \rightleftarrows [SnCl_6]^{=}$
8. $[SnCl_6]^{=} + H_2S = \underline{Sn(HS)_4}$
9. $\underline{Sn(HS)_4} \rightleftarrows \underline{SnS_2} + H_2S$
10. $[SnCl_6]^{=} + H_2C_2O_4 \rightleftarrows [Sn(C_2O_4)_3]^{=}$

CATION GROUP III

$(Al^{+3}, Cr^{+3}, Fe^{+3}, Fe^{++}, Mn^{++}, Co^{++}, Ni^{++}, Zn^{++})$

This might well be called the Steel Group. All the elements except Zn are important in steel making. Vanadium, which immediately precedes chromium in the periodic arrangement of the elements, is equally important in steel making. Cr, Mn, Fe, Co, Ni, are "A"-family elements, "transition elements," of Period 4 (K to Kr) in Groups VI, VII, and VIII. These transition elements

are characterized by variable valence and by the strong colors of many of their ions.

All members of this third analytical group have sulfides (or hydrosulfides) too soluble to be precipitated by H_2S in $0.3N$ H^+. As a result they escape precipitation in Group II.

Actions of the group reagent. The following equations show that the group reagent may act in several different ways.

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^- \qquad K_b = 1.8 \times 10^{-5} \qquad (14)$$

$$NH_4^+ \rightleftarrows NH_3 + H^+ \qquad K_a = 5.6 \times 10^{-10} \qquad (15)$$

$$C_{H^+} \times C_{OH^-} = K_w = 1.10^{-14}\ (25°) \qquad (16)$$

$$H_2S \rightleftarrows H^+ + HS^- \qquad K_1 = 1.15 \times 10^{-8} \qquad (17)$$

$$HS^- \rightleftarrows H^+ + S^{=} \qquad K_2 = 1 \times 10^{-15} \qquad (18)$$

$$HS^- + H_2O \rightleftarrows H_2S + OH^- \qquad (19)$$

By combining algebraically the equilibrium ratios and constants of certain of the above equations, it is possible to calculate approximately the concentrations of the various ions in the group reagent.[5] For comparison the concentrations of certain of the ions in the Group II reagent are given.

	$1N$ NH_4HS	$0.3N$ H^+ saturated with H_2S
C_{HS^-}	0.92 M	4×10^{-7} M
$C_{S^=}$	9.2×10^{-8} "	1.3×10^{-22} "
C_{H_2S}	0.08 "	0.1 "
C_{OH^-}	1×10^{-6} "	
$C_{NH_4^+}$	0.95 "	
C_{NH_3}	0.05 "	

Whether hydroxides, hydrosulfides, or sulfides will be formed by this reagent with the ions of Group III will depend upon the relative solubility products of these compounds.

The hydroxides of the Group III ions are more insoluble than is $Mg(OH)_2$. Those of tervalent ions, Al^{+3}, Cr^{+3}, Fe^{+3}, are much more insoluble than those of the bivalent ions. The bivalent hydroxides are not precipitated by NH_3 in a solution which has been nearly saturated with NH_4Cl. The tervalent hydroxides are completely precipitated from such solution. The nonprecipitation of the bivalent hydroxides by NH_3 is due to two different causes.

1. Equations (14)–(16) show that in aqueous solutions containing ammonia and ammonium salts large $C_{NH_4^+}$ tends to reduce C_{OH^-}

[5] For method of calculation see Chapter 9, p. 134.

and to increase C_{H^+}, but always within the limit imposed by equation (16). The solubility products of the bivalent hydroxides of Group III, $C_{Me^{++}} \times C^2_{OH^-}$, may all be considered to be of the order 10^{-14} as compared with that of $Mg(OH)_2$, 10^{-11}. These hydroxides are therefore about one tenth as soluble as $Mg(OH)_2$ and experiment shows that a larger $C_{NH_4^+}$ will prevent their precipitation by NH_3, provided, in the cases of Fe^{++} and Mn^{++}, that oxidation by air to the much more insoluble FeOOH and MnOOH or $MnO(OH)_2$ is prevented.

2. A quite different cause also operates to prevent precipitation of the hydroxides of Co^{++}, Ni^{++}, and Zn^{++}. These ions, in contrast with Fe^{++} and Mn^{++}, form moderately stable complex ions with NH_3, such as $[Ni(NH_3)_4]^{++}$, $[Zn(NH_3)_4]^{++}$, $[Co(NH_3)_6]^{++}$. For $[Zn(NH_3)_4]^{++} \rightleftarrows Zn^{++} + 4NH_3$, the equilibrium constant,

$$\frac{C_{Zn^{++}} \times C^4_{NH_3}}{C_{Zn(NH_3)_4^{++}}} = 9.8 \times 10^{-10}$$

has been reported; for that of $[Co(NH_3)_6]^{++}$, 1.25×10^{-5}. Since ammonium salts tend to decrease the decomposition of water by NH_3 [equation (14)], they will favor strongly the formation of the complex ions rather than the hydroxides. Salts of the complex ions are *very* soluble in water.

It follows then that if to a solution containing all the ions of the group a large $C_{NH_4^+}$ then NH_3 in moderate excess were added, the hydroxides of Al^{+3}, Cr^{+3}, and Fe^{+3} should be completely precipitated, while the other ions should remain in solution as Fe^{++}, Mn^{++}, $[Ni(NH_3)_4]^{++}$, $[Co(NH_3)_6]^{++}$, $[Zn(NH_3)_4]^{++}$. In alkaline solution air rapidly oxidizes Fe^{++}, Mn^{++}, and $[Co(NH_3)_6]^{++}$ as will be discussed later.

The sulfides. The sulfides or hydrosulfides of all these ions are too soluble to be precipitated by the reagent of Group II, H_2S in $0.3N$ H^+. As already shown (page 232), NH_4HS contains a much higher C_{HS^-} and $C_{S^=}$ than does $0.3N$ H^+ saturated with H_2S, and so the larger solubility products of these sulfides or hydrosulfides can be exceeded.

Since the hydroxides of Al^{+3} and Cr^{+3} are much more insoluble than the sulfides, the OH^- of the reagent NH_4HS will precipitate the *hydroxides*. If prepared in absence of water the sulfides are rapidly and completely decomposed when thrown into water, for example,

$$\underline{Al_2S_3} + 4H_2O = \underline{2AlOOH} + 3\overline{H_2S}.$$

$Fe(HS)_3$ is more insoluble than $Fe(OH)_3$ and so NH_4HS precipitates the former.

Fe^{+3} in 0.3 N H^+ is completely reduced by H_2S in Group II,

$$2Fe^{+3} + H_2S = \underline{S} + 2Fe^{++} + 2H^+,$$

and therefore in *systematic* analysis always comes to Group III as Fe^{++} unless reoxidized by air.

$Zn(HS)_2$ is insoluble in dilute AcOH; $Fe(HS)_2$, $Co(HS)_2$, and $Ni(HS)_2$ are nearly insoluble in *buffered* AcOH. The pink sulfide of Mn^{++} (probably basic hydrosulfide, HO—Mn—SH) is soluble in buffered AcOH. This shows that $Zn(HS)_2$ is much more insoluble than the hydrosulfides of Fe^{++}, Co^{++}, Ni^{++}, which, in turn, are much more insoluble than HO—Mn—SH. The washed (aged) *sulfides* of Co^{++} and Ni^{++} are more insoluble than ZnS. A green sulfide of Mn^{++}, said to be MnS, is infrequently seen in analysis.

Valence. All the ions of Group III, except Al^{+3} and Zn^{++}, show variable valence. Manganese forms compounds in five different valences, chromium in three, iron and cobalt in at least three, and nickel in at least two. Knowing what reagents will change these ions from one valence to another is an important part of a chemist's equipment. Hence, special attention must be paid to oxidation-reduction equations in this group of cations.

Aluminum

Occurrence. Aluminum is one of the most abundant of the elements in the earth's lithosphere, being exceeded only by oxygen and silicon. It occurs in enormous quantity in aluminosilicates, such as feldspars and micas, and in the clays which result from these by the weathering action of water and CO_2.

It also occurs as the oxide corundum, Al_2O_3. The gems sapphire and ruby are corundums colored by minute amounts of Ti^{+3} in sapphire and Cr^{+3} in ruby. These gems are now made synthetically by fusing ammonium alum, $NH_4Al(SO_4)_2 \cdot 12H_2O$, in the oxyhydrogen flame. Emerald is a beryllium aluminosilicate (beryl) in which the green color is due to replacement of some of the Al atoms by Cr.

The important ores are bauxite, $Al_2O_3 \cdot xH_2O$ and cryolite Na_3AlF_6.

Dissolution of the metal. Hydrohalic acids dissolve the metal slowly when cold but rapidly when hot. Cold dilute H_2SO_4 has

little effect but the hot concentrated acid dissolves the metal readily with evolution of SO_2.

$$2Al + 3HSO_4^- + 9H^+ = 3\overline{SO_2} + 6H_2O + 2Al^{+3}$$

Nitric acid renders the metal "passive" and insoluble, a phenomenon observed with several other metals, notably Cr and Fe. Passivity has been explained as due to the outwardly directed valence forces of the surface layer of aluminum atoms attracting oxygen atoms furnished by strong oxidants but without actual compound formation that would detach these Al atoms from the others. In this way a protective layer only one atom thick would be formed.

In air the metal is quickly covered by a "skin" of AlOOH or Al_2O_3, which protects it from further oxidation. This is a case of compound formation and not related to "passivity." If the surface of Al foil is rubbed with $HgCl_2$, an amalgam is formed in which the oxide does not dissolve. The free atoms of Al are then able to release H_2 even from water.

The metal dissolves readily in strong bases with evolution of H_2. Water in this case acts as the acid after OH^- has removed the protective layer.

$$Al_2O_3 + 2OH^- + 3H_2O = 2[Al(OH)_4]^-$$

Then

$$2Al^0 + 6H^+ \rightleftarrows 3\overline{H_2} + 2Al^{+3} \qquad (20)$$

because, from the potentials

$$\frac{C_{Al^{+3}} \times C^{\frac{3}{2}}_{H_2}}{C^3_{H^+}} = 10^{87} = K_{equil.},$$

even the minute C_{H^+} in NaOH or KOH will be reduced.

Accumulation of Al^{+3} which would stop the reaction is prevented by the formation of the very stable $[Al(OH)_4]^-$.

$$2Al^{+3} + 8OH^- = [2Al(OH)_4]^- \qquad (21)$$

Adding (20) and (21) and considering that $6H^+ + 6OH^- = 6H_2O$ we obtain

$$2Al^0 + 6H_2O + 2OH^- \rightleftarrows 2[Al(OH)_4]^- + 3H_2$$

Reactions of Aluminum Ion[6]

1. Ammonia. From solutions of aluminum salts ammonia precipitates aluminum oxide gels of variable composition, depending on the temperature and concentration of the solution. They may be represented by the indefinite formula $Al_2O_3 \cdot xH_2O$. These gels are amphoteric and are dissolved by both H^+ and OH^-. The gels begin to precipitate at $C_{H^+} = 5 \times 10^{-3}$ and precipitation is complete at $C_{H^+} = 7 \times 10^{-7}$. The gel begins to dissolve at $C_{OH^-} = 2.5 \times 10^{-4}$. To simplify writing of equations we shall formulate the gel as AlOOH.

If the gel precipitated at room temperature is extracted with acetone as long as water is removed, the composition is reported to approximate $Al(OH)_3$ fairly closely. Gels precipitated from hot solution when similarly treated finally reach a composition approximating AlOOH. While the former, when examined by X rays, are entirely amorphous, the latter show to some extent the structure characteristic of the mineral bauxite, $Al_2O_3 \cdot xH_2O$. All these gels in contact with their saturated solutions undergo rearrangement of the atoms into crystalline forms. The end product of these rearrangements is reported to be AlOOH. Several months are required to reach the final structure.

2. Strong bases—NaOH or KOH—precipitate $Al_2O_3 \cdot xH_2O$ gel or, more simply, AlOOH. The gel is soluble in both strong acids and strong bases. It is a typical representative of the class of compounds called *ampholytes*. Its dissolution in both acids and bases has been accounted for in two ways:

1. The older theory assumes that the gel can furnish to water two sets of ions,

$$\underline{\text{AlOOH}}$$
$$\Downarrow\uparrow$$
$$AlO^+ + OH^- \rightleftarrows AlOOH \rightleftarrows AlO_2^- + H^+.$$

In water, "aluminum hydroxide" has very small solubility. Its saturated aqueous solution contains only a minute concentration of the molecules. If acid is added to the water, the reaction $H^+ + OH^- \rightleftarrows H_2O$, by removing OH^-, leaves AlO^+ in water; the water is no longer saturated with AlOOH; and more solid must dissolve. If a base is added to the water, AlOOH must give up H^+ to form water, leaving AlO_2^- in solution.

[6] Crystalline salts of Al appear to contain the ion $Al(H_2O)_6^{+3}$. It will be permissible in writing equations to represent this ion by Al^{+3} in solutions rather strongly acid with HNO_3 or H_2SO_4 (*not* halide acids with which it forms complex anions). In slightly acid solutions (including the halide acids) AlO^+ would be more probable.

A few known crystalline aluminates contain the anion AlO_2^-. As salts of the extremely weak acid $HAlO_2$, these salts are largely decomposed by water, for example,

$$KAlO_2 + H_2O \rightleftarrows HAlO_2 + K^+ + OH^-.$$

2. The more modern theory does not admit that aluminum hydroxide (aluminic acid) can ionize but ascribes the dissolution of the gel in both acids and bases to the presence in it of both OH^- and coordinated water molecules. For example, if we formulate[7] the gel as $[Al(OH)_3(H_2O)_3]$, in acid solution H^+ should extract OH^- to form H_2O which by coordination would replace the OH^- removed.

$$[Al(OH)_3(H_2O)_3] + H^+ \rightleftarrows [Al(OH)_2(H_2O)_4]^+$$
$$[Al(OH)_2(H_2O)_4]^+ + H^+ \rightleftarrows [Al(OH)(H_2O)_5]^{++}$$
$$[Al(OH)(H_2O)_5]^{++} + H^+ \rightleftarrows [Al(H_2O)_6]^{+3}$$

In basic solution OH^- should withdraw a H^+ from a water molecule, the coordination position of which would then be filled by OH^-.

$$[Al(OH)_3(H_2O)_3] + OH^- \rightleftarrows [Al(OH)_4(H_2O)_2]^- + H_2O$$
$$[Al(OH)_4(H_2O)_2]^- + OH^- \rightleftarrows [Al(OH)_5H_2O]^- + H_2O$$
$$[Al(OH)_5H_2O]^- + OH^- \rightleftarrows^{8} [Al(OH)_6]^{-3} + H_2O$$

Thus, either a sufficiently high C_{H^+} or a sufficiently high C_{OH^-} would cause the gel to dissolve.

Note that $[Al(OH)_3(H_2O)_3]$ is formally merely a more highly hydrated form of AlOOH or $HAlO_2$.

$$AlOOH + H_2O \rightleftarrows Al(OH)_3$$
$$Al(OH)_3 + 3H_2O \rightleftarrows [Al(OH)_3(H_2O)_3]$$

Thus, the decomposition of $KAlO_2$ by water could be written

$$KAlO_2 + 5H_2O \rightleftarrows [Al(OH)_3(H_2O)_3] + OH^- + K^+$$

3. Alkali sulfides and hydrosulfides precipitate from solutions of aluminum salts, $Al_2O_3 \cdot xH_2O$ gel. This is because the oxide gel is more insoluble in water than is the sulfide. As the salt of an extremely weak acid, H_2S, and an extremely weak and also insoluble base, AlOOH, Al_2S_3 will be completely hydrolyzed.

$$AlO^+ + S^= + H_2O \rightleftarrows AlOOH + HS^-$$
$$AlO^+ + HS^- + H_2O \rightleftarrows AlOOH + H_2S$$
$$Al_2S_3 + 4H_2O = 2AlOOH + 3H_2S$$

[7] Wildman, J. Chem. Ed., **12**, 11 (1935).

[8] Whether Al^{+3} coordinates in this case 4 or 6 OH^- is uncertain. Neither $Al(OH)_4^-$ nor $Al(OH)_6^{-3}$ is improbable.

For the same reason alkali salts of all very weak acids such as HCN, H_2CO_3, precipitate $Al_2O_3 \cdot xH_2O$ rather than cyanide or carbonate.

4. Alkali phosphate precipitates from solutions of aluminum salts gelatinous $AlPO_4 \cdot xH_2O$, soluble in mineral acids and in NaOH but insoluble in buffered AcOH.

$$AlO^+ + HPO_4^{=} \rightleftarrows \underline{AlPO_4 \cdot xH_2O} + OH^-$$
$$\underline{AlPO_4} + 2H^+ \rightleftarrows Al^{+3} + H_2PO_4^-$$
$$\underline{AlPO_4} + 4OH^- \rightleftarrows [Al(OH)_4]^- + PO_4^{-3}$$

5. Alkali acetate. If alkali acetate is added to a neutral or slightly acid solution of aluminum salt, and the solution then largely diluted and boiled, $Al_2O_3 \cdot xH_2O$ is precipitated.

$$AlO^+ + AcO^- + H_2O \rightleftarrows \underline{AlOOH} + AcOH$$

The high C_{AcO^-} prevents the AcOH from giving up H^+ which would reverse the reaction.

6. Aluminon, the trade name for the dye ammonium aurin tricarboxylate, forms a brilliant scarlet lake[9] with aluminum hydroxide, which is not decomposed by $(NH_4)_2CO_3$. $Be(OH)_2$ behaves similarly. Some other white hydroxides, such as $ZrO(OH)_2$ and $SiO(OH)_2$, form lakes with the dye, which are decolorized if warmed with $(NH_4)_2CO_3$ solution. FeOOH and CrOOH form lakes, but not in the presence of $(NH_4)_2CO_3$. Aluminon is thus as valuable in distinguishing AlOOH from other white hydroxides (except $Be(OH)_2$) as S and O reagent is for $Mg(OH)_2$.

PRACTICE EXERCISE

Balance the following equations for important reactions of Al^{+3}.

1. Al^{+3} (or AlO^+) + OH^- (strong bases) $\rightleftarrows$ $\underline{AlOOH}$ + H_2O

2. $\underline{HAlO_2}$ + OH^- (excess) $\rightleftarrows$ $[Al(OH)_4]^-$

3. $[Al(OH)_4]^-$ + $NH_4^+ \rightleftarrows$ $\underline{AlOOH}$ + $\overline{NH_3}$

4. $[Al(OH)_4]^-$ + $\overline{CO_2} \rightleftarrows$ $\underline{AlOOH}$ + HCO_3^- + H_2O

5. Al^{+3} + NH_3 + $H_2O \rightleftarrows$ $\underline{AlOOH}$ + NH_4^+

[9] For definition of "lake," see under Magnesium, p. 268.

6. $Al^{+3} + HS^- + H_2O \rightleftarrows \underline{AlOOH} + H_2S$

7. $Al^{+3} + AcO^- + H_2O \rightleftarrows \underline{AlOOH} + AcOH$

8. $Al^{+3} + HCO_3^- + H_2O \rightleftarrows \underline{AlOOH} + \overline{CO}_2 + H_2O$

9. $Al^{+3} + CN^- + H_2O \rightleftarrows \underline{AlOOH} + HCN$

Chromium

Occurrence. The principal ore is chromite, Cr_2FeO_4. Considerable deposits occur in Canada, the United States, Sweden, and Russia. Crocoite, $PbCrO_4$, occurs in moderate quantity in some localities. Cr^{+3} replaces Al^{+3} to a small extent in aluminosilicates; and, hence, traces of it occur in many minerals.

Dissolution of the Metal. Chromium dissolves in the hydrohalic acids, and in dilute H_2SO_4. Like aluminum it is made "passive" and not dissolved by HNO_3.

Valences. Chromium forms chromous ion, Cr^{++}, and chromic ion, Cr^{+3}. The former is blue like Cu^{++}, the latter green. In its highest valence of 6, chromium is always in anions, for example, $CrO_4^=$, $Cr_2O_7^=$, $Cr_3O_{10}^=$, $Cr_4O_{13}^=$. The colors of these ions shift toward longer wave lengths at each successive polymerization in accordance with what appears to be a general phenomenon. $CrO_4^=$ is yellow, $Cr_2O_7^=$ orange, $Cr_3O_{10}^=$ red, $Cr_4O_{13}^=$ brown. The last two exist only under special conditions and require no consideration analytically.

Chromous ion, Cr^{++} (blue), is obtained by reducing Cr^{+3} by means of zinc and HCl with exclusion of air. It is an extremely powerful reductant and rapidly reduces atmospheric oxygen, changing into Cr^{+3}.

$$4Cr^{++} + O_2 + 4H^+ = 4Cr^{+3} + 2H_2O$$

In consequence of this property it is not met in analysis.

Complex ions. Chromic ion, like Co^{+3} and Rh^{+3}, is a notable former of complexes, both cations with NH_3 and water, and anions with halides. Typical examples are $[Cr(NH_3)_6]^{+3}$ (yellow), $[Cr(H_2O)_6]^{+3}$ (violet), and $[Cr(NCS)_6]^{-3}$ (red). Many of the complex salts are very stable. The colors depend more on the structure of the complex than on the nature of the metal, salts of $[Co(NH_3)_6]^{+3}$ having nearly the same yellow tint as those of $[Cr(NH_3)_6]^{+3}$. The chrome alums are violet because they contain $[Cr(H_2O)_6]^{+3}$.

There are three different chromic chlorides all having the formula $CrCl_3 \cdot 6H_2O$. One is violet, two are green. The structures have been proved to be (1) $[Cr(H_2O)_6]Cl_3$; (2) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$; and (3) $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$. From freshly made solutions Ag^+ precipitates all the chloride from the first, $\frac{2}{3}$ from the second, and only $\frac{1}{3}$ from the third. In a dessicator over conc. H_2SO_4 the first loses no water, the second $\frac{1}{6}$ of its water, the third $\frac{1}{3}$. Accordingly the structures given above were assigned to the three salts. This kind of isomerism is known as *hydrate isomerism*. Moderately dilute chromic chloride solutions frequently show a mixture of violet and green because

$$\underset{\text{(violet)}}{[Cr(H_2O)_6]Cl_3} \rightleftarrows \underset{\text{(green)}}{[Cr(H_2O)_4Cl_2]Cl} + 2H_2O.$$

More concentrated solutions show more green color, more dilute solutions appear more violet. The partial dissolution of chromic "hydroxide" in large C_{NH_3} is due to formation of $[Cr(NH_3)_5H_2O]^{+3}$ (rose color).

The chromate-dichromate equilibrium. All chromate solutions contain *three* ions in proportions determined by the C_{H^+} as shown by the reactions

$$\underset{\text{(orange)}}{Cr_2O_7^{=}} + H_2O \rightleftarrows 2HCrO_4^- \rightleftarrows \underset{\text{(yellow)}}{2CrO_4^{=}} + 2H^+$$

The constants involved and method for calculating equilibrium concentrations in $CrO_4^{=} \rightleftarrows Cr_2O_7^{=}$ solutions can be found in Chapter 7, page 93.

All dichromates except $(BiO)_2Cr_2O_7$ are largely soluble in water. Hence alkali dichromate solutions can precipitate only *chromates*. Whether or not a given chromate is precipitated depends chiefly on the C_{H^+} in the solution.

Valence changes—oxidation of Cr^{+3},—reduction of $Cr_2O_7^{=}$. Study thoroughly the rules for balancing redox equations, Chapter 5, pages 56–58.

It should be noted that in general H^+ (acid solution) favors reduction (gain of electrons) while OH^- (basic solution) favors oxidation (loss of electrons).

Reactions of Chromic Ion[10]

1. Ammonia forms a gel, $Cr_2O_3 \cdot xH_2O$, or more simply CrOOH. The gel is bluish violet when precipitated from violet solutions containing chiefly $[Cr(H_2O)_6]^{+3}$, grayish green when precipitated from green solutions containing chiefly $[Cr(H_2O)_4Cl_2]^+$. In pres-

[10] $Cr(H_2O)_6^{+3}$, and the like may be represented in writing equations by Cr^{+3} or CrO^+ as stated for $Al(H_2O)_6^{+3}$ (footnote, p. 236).

ence of very large excess of NH_3 precipitation is incomplete, owing to formation of $[Cr(NH_3)_5H_2O]^{+3}$ (rose colored). Very long boiling is required to decompose this ion and to precipitate CrOOH. Ammonia does not precipitate chromic ion in the presence of a large C_{AcO^-}.

2. Strong bases precipitate CrOOH, soluble in excess of OH^-. It is not yet settled whether the CrOOH is merely dispersed to a colloidal suspension or whether ions such as $Cr(OH)_4^-$ are formed. When the solution or dispersion is boiled, CrOOH precipitates. This difference in the behavior of aluminate solutions and "chromite" solutions is an argument for the dispersion view. On the whole the evidence seems to indicate that both chemical reaction and dispersion take place.

3. Alkali sulfides and hydrosulfides, carbonates, and the like, precipitate CrOOH for the reasons stated under "Aluminum ion" (page 237).

4. Sodium peroxide or H_2O_2 in alkaline solution oxidizes CrOOH to $CrO_4^=$.[11]

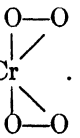
$$Na_2O_2 + H_2O \rightarrow HO_2^- + OH^- + 2Na^+ \text{ (at 0°)}$$
$$2CrOOH + 3HO_2^- + OH^- = 2CrO_4^= + 3H_2O$$

5. Alkali phosphate precipitates green $CrPO_4 \cdot xH_2O$, insoluble in buffered AcOH but readily soluble in mineral acids and moderately concentrated AcOH.

6. Alkali acetate. If alkali acetate is added to a neutral or slightly acid solution of a chromic salt, and the solution then largely diluted and boiled, CrOOH is not precipitated. If, however, a large amount of Fe^{+3} is present, the precipitate of FeOOH carries down with it most of the chromic ion probably as CrOOH.

7. Reaction of $Cr_2O_7^=$ with H_2O_2. If to a solution containing even a trace of $CrO_4^=$ a little H_2O_2 is added and the solution acidified, a flash of blue color is momentarily seen which disappears almost instantly. If the solution has been previously shaken with enough ether so that an ether layer and a water layer separate, on acidifying and immediately shaking, the blue color passes into the ether layer, having been stabilized by forming an etherate. The blue compound is usually considered to be peroxochromic acid,

[11] At higher temperatures HO_2^- decomposes considerably:
$$2HO_2^- \leftrightarrows \overline{O_2} + 2OH^-.$$

H_3CrO_8. According to R. Schwarz,[12] however, it is diperoxochromic anhydride,  .

PRACTICE EXERCISE

Balance the following equations for important reactions of Cr^{+3}.

1. $Cr^{+3} + OH^- \text{ (small concentration)} \rightleftarrows \underset{\text{(gray green)}}{\underline{CrOOH}}$
2. $\underline{CrOOH}$ + large $OH^- \rightarrow$ colloidal CrOOH and probably also $[Cr(OH)_4]^-$
3. $Cr^{+3} + NH_3 + H_2O \rightleftarrows \underline{CrOOH} + NH_4^+$
4. $\underline{CrOOH}$ or $[Cr(OH)_4]^- + Na_2O_2 + H_2O = CrO_4^= + OH^-$
5. $\underset{\text{(yellow)}}{CrO_4^=} + H^+ \rightleftarrows HCrO_4^- \rightleftarrows \underset{\text{(orange)}}{Cr_2O_7^=} + H_2O$
6. $Cr_2O_7^= + H_2O_2 + H^+ \rightarrow O^=\underset{\text{(blue)}}{Cr(O_2)_2} + H_2O$ (CrO_5 forms an etherate)
7. $\underset{\text{(blue)}}{OCr(O_2)_2} + H_2O_2 + H^+ \rightleftarrows Cr^{+3} + \overline{O_2} + H_2O$
8. Cr^{+3} + excess $NH_3 + H_2O \rightarrow [Cr(NH_3)_5H_2O]^{+3}$ (pink soln.)
9. $Cr_2O_7^= + H_2S + H^+ \rightleftarrows Cr^{+3} + \underline{S} + H_2O$
10. $Cr^{+3} + HS^- + OH^- \rightleftarrows$

Iron

Occurrence. In order of abundance iron is fourth among the elements. The core of the earth is presumed to consist of an Fe-Ni alloy. The principal ores are the oxides, Fe_2O_3 (hematite), FeOOH (limonite), and Fe_3O_4 (magnetite), and the carbonate, $FeCO_3$ (siderite). The most widely distributed compounds are the sulfides, pyrite and marcasite, FeS_2, and pyrrhotite, approximately FeS.

Dissolution of the metal. Dilute HCl and H_2SO_4 dissolve iron readily, forming Fe^{++} and H_2. Cold concentrated H_2SO_4 does not attack it but the hot acid forms Fe^{+3} and SO_2. Cold very dilute HNO_3 forms Fe^{++} and NH_4^+ or N_2O according to conditions. Hot dilute HNO_3 forms Fe^{+3} and NO.

[12] Ber., 65, 871 (1932).

Valence. Fe^{++} and Fe^{+3} both form many salts. Fe^{+3} is *slightly* amphoteric. The freshly precipitated "hydroxide" dissolves somewhat in hot concentrated NaOH and KOH; and crystalline $NaFeO_2$ and $KFeO_2$, *ferrites*, have been obtained from such solutions. Neither "hydroxide" is perceptibly peptized or dissolved by moderate C_{OH^-} (difference from Al^{+3} and Cr^{+3}). If iron filings are heated with solid KNO_3 to red heat, the cooled melt dissolves in water to a bright violet solution from which Ba^{++} precipitates unstable $BaFeO_4 \cdot H_2O$ (crimson red). This *barium ferrate* contains 6-valent iron and is analogous to $BaCrO_4$ and $BaSO_4$. It is an even stronger oxidant than $KMnO_4$.

$$FeO_4^{=} + 8H^+ + 3e^- \rightleftarrows Fe^{+3} + 4H_2O \qquad +1.7 \text{ v.}$$
$$MnO_4^- + 8H^+ + 5e^- \rightleftarrows Mn^{++} + 4H_2O \qquad +1.52 \text{ v.}$$

Reactions of Ferrous Ion

$FeSO_4 \cdot 7H_2O$, iron vitriol,[13] and $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, Mohr's salt, are the commonest compounds.

1. Ammonia in absence of a large $C_{NH_4^+}$ precipitates incompletely white gelatinous $Fe(OH)_2$.

$$Fe^{++} + 2NH_3 + 2H_2O \rightleftarrows \underline{Fe(OH)_2} + 2NH_4^+$$

If a sufficient $C_{NH_4^+}$ is present, a precipitate may not form immediately. The solubility product of ferrous hydroxide is of the order 10^{-15} and the common-ion effect of a large $C_{NH_4^+}$ can reduce the concentration of hydroxyl ion to so small a value that $C_{Fe^{++}} \times C^2_{OH^-}$ remains less than the $K_{s.p.}$ For the same reason NH_3 cannot precipitate Fe^{++} completely, since the increasing $C_{NH_4^+}$ constantly decreases C_{OH^-} and the product

$$C_{Fe^{++}} \times C^2_{OH^-}$$

becomes equal to the $K_{s.p.}$ before all the Fe^{++} has precipitated.

2. Atmospheric oxygen rapidly oxidizes Fe^{++} to Fe^{+3} in alkaline solution. In consequence, precipitated $Fe(OH)_2$ is rarely pure white. It usually is pale green. On exposure to the air it becomes darker green, then black and, when it will absorb no more O_2, shows the red-brown color of FeOOH. The black stage is said to show the X-ray pattern of *magnetite*, a spinel, $Fe_2[FeO_4]$.

The electrode potential of the reaction $Fe^{++} \rightleftarrows Fe^{+3} + e^-$ requires that the $C_{Fe^{++}}$ in ferric solutions and the $C_{Fe^{+3}}$ in ferrous solutions should be greater than *zero*.

[13] The structure of iron vitriol is described on p. 37.

3. Strong bases precipitate completely $Fe(OH)_2$, insoluble in excess of the reagent.

4. Hydrogen sulfide in $0.3N$ H^+ forms no precipitate. When the gas is passed into a solution of $FeSO_4 \cdot 7H_2O$ (green vitriol), a minute amount of black FeS is visible. In buffered AcOH solution a considerable, although far from complete, precipitation takes place. The precipitation is complete in alkaline solution.

5. Alkali hydrosulfide or sulfide precipitates ferrous ion completely, probably as $Fe(HS)_2$ which during washing becomes less soluble, presumably due to change into FeS.

$$Fe^{++} + 2HS^- = \underline{Fe(HS)_2}$$

$$\underline{Fe(HS)_2} \rightarrow \underline{FeS} + \overline{H_2S}$$

FeS dissolves readily in cold $1N$ HCl. FeS when moist oxidizes in air rather rapidly to basic ferric sulfate. Alkali sulfide solutions are sometimes green owing to colloidal FeS. Such green solutions are occasionally seen in Group II. The trace of ferrous ion may have entered the acid solutions from Fe^{++} in some reagent.

6. Sodium carbonate precipitates white $FeCO_3$, which may be more or less yellow because of FeOOH if the Fe^{++} solution contains Fe^{+3}. $FeCO_3$ is soluble in H_2CO_3 (water containing CO_2).

$$\underline{FeCO_3} + H_2CO_3 \rightleftarrows Fe^{++} + 2(HCO_3)^-$$

This reaction accounts for the presence of iron in ground water.

7. Potassium cyanoferroate (ferrocyanide) forms either

$$K_2Fe[Fe(CN)_6] \text{ or } Fe_2[Fe(CN)_6]$$

according to the relative proportions of Fe^{++} and reagent.

$$Fe^{++} + 2K^+ + [Fe(CN)_6]^{-4} \rightleftarrows \underline{K_2Fe[Fe(CN)_6]}$$

Both precipitates, if perfectly pure, are white but they usually appear more or less blue because of the presence of some Fe^{+3}, which forms Prussian blue. The white or light blue precipitates, on standing in air, are completely oxidized to dark blue Prussian blue. The precipitates are insoluble in dilute HCl but are decomposed by solutions of strong bases, with formation of $Fe(OH)_2$.

8. Potassium cyanoferriate (ferricyanide) forms a dark blue precipitate which is usually formulated as $Fe_3[Fe(CN)_6]_2$ and known as Turnbull's blue.

$$3Fe^{++} + 2[Fe(CN)_6]^{-3} \rightleftarrows \underline{Fe_3[Fe(CN)_6]_2}$$

The precipitate is insoluble in HCl but is decomposed by alkali with formation of $Fe(OH)_2$.

For a more probable formulation of Turnbull's blue as ferrous "berlinate" see Chapter 10 (page 152).

9. Thiocyanate ion, NCS^-, does not react with Fe^{++}, but ferrous solutions usually give at least a faint pink tint due to $[Fe(NCS)_6]^{-3}$

10. Oxidants. In alkaline solution Fe^{++} is oxidized to Fe^{+3} by even mild oxidants such as atmospheric oxygen. In acid solution stronger oxidants such as HNO_3, $KClO_3$, or Br_2 are required.

PRACTICE EXERCISE

Balance the following equations for important reactions of Fe^{++}.

1. Fe^{++} + large OH^- = $\underline{Fe(OH)_2}$
2. $\underline{Fe(OH)_2} + O_2 + H_2O \rightarrow$ black $\underline{Fe_3O_4 \cdot xH_2O}$ $\rightarrow \underline{FeOOH}$ (red brown)
3. $Fe^{++} + H_2O + NH_3 \rightarrow$ (Similarity to Mn^{++} and Mg^{++})
4. $Fe^{++} + [Fe(CN)_6]^{-3} + K^+ \rightarrow \underline{KFe[Fe(CN)_6Fe]_3}$ (Turnbull's blue or K ferrous berlinate).
5. $Fe^{++} + [Fe(CN)_6]^{-4} \rightarrow \underline{Fe_2[Fe(CN)_6]}$
6. $Fe^{++} + K^+ + [Fe(CN)_6]^{-4} \rightarrow \underline{K_2Fe[Fe(CN)_6]}$
7. $Fe^{++} + Br_2 \rightleftarrows Fe^{+3} + Br^-$
8. $Fe^{++} + H^+ + NO_3^- \rightarrow Fe^{+3} + \underline{NO} + H_2O$
9. $\underline{Fe(OH)_2} + \underline{Na_2O_2} \rightleftarrows \underline{FeOOH} + OH^- + Na^+$

Reactions of Ferric Ion[14]

1. Ammonia, even in solutions saturated with NH_4^+ salts, precipitates completely red-brown $Fe_2O_3 \cdot xH_2O$ gel. The precipitate is insoluble in excess of NH_3.

2. Strong bases precipitate $Fe_2O_3 \cdot xH_2O$ gel, insoluble in excess of OH^-. The gel dissolves somewhat in hot extremely concentrated KOH or NaOH and from such solutions crystalline ferrites such as $NaFeO_2$ and $KFeO_2$ have been obtained. This indicates that the

[14] For $Fe(H_2O)_6^{+3}$ it is permissible to write Fe^{+3} or FeO^+. Solutions of ferric chloride contain colloidal FeOOH, $[FeCl_6]^{-3}$ and H^+.

gel has a very small ability to give up protons and form anions. However, compared with the amphoteric properties of the gels of Al^{+3} and Cr^{+3}, ability to dissolve in hydroxyl ion is negligible.

3. Hydrogen sulfide reduces Fe^{+3} to Fe^{++}, but no FeS is precipitated in $0.3\,N$ H^+.

$$2Fe^{+3} + H_2S \rightleftarrows 2Fe^{++} + \underline{S} + 2H^+$$

4. Alkali hydrosulfide or sulfide precipitates probably $Fe(HS)_3$ (black) which changes into Fe_2S_3 on washing. The sulfide is soluble in $1\,N$ HCl.

$$\underline{Fe_2S_3} + 4H^+ = 2Fe^{++} + 2H_2S + \underline{S}$$

(See, however, note 2, page 321.)

5. Sodium carbonate precipitates $Fe_2O_3 \cdot xH_2O$ gel and not a carbonate for the reason stated for Aluminum (page 238).

6. Potassium cyanoferroate precipitates dark blue ferric cyanoferroate, usually formulated $Fe_4[Fe(CN)_6]_3$, but more probably a high polymer of ferric "berlinate" $(Fe[Fe(CN)_6Fe]_3)_x$, Prussian blue (see Chapter 10, page 152). A colloidal suspension of this blue is obtained when the cyanoferroate is in very large excess. This may be a polymer of potassium "berlinate" $(K[Fe(CN)_6Fe])_x$. Prussian blue is insoluble in dilute HCl but is decomposed by strong bases.

$$\underline{Fe_4[Fe(CN)_6]_3} + 12OH^- \rightleftarrows \underline{4Fe(OH)_3} + 3[Fe(CN)_6]^{-4}$$

$[Fe(CN)_6]^{-4}$ is a sensitive reagent for Fe^{+3}. When very small Fe^{+3} is present and an excess of $[Fe(CN)_6]^{-4}$ is used, a green solution may be obtained, which results from the small amount of blue in the presence of the yellow of the reagent ion.

7. Potassium cyanoferriate does not precipitate Fe^{+3}, but a dark brown solution is formed, probably because of unionized $Fe[Fe(CN)_6]$.

8. Thiocyanate ion, NCS^-, forms a deep red solution, because of $[Fe(NCS)_6]^{-3}$. The color is more intense in the presence of moderately concentrated HCl. The red compound is more soluble in ether or a mixture of ether and amyl alcohol than in water, presumably because of etherate formation with $H_3[Fe(NCS)_6]$.

9. Action of hydrohalic acids. HF instantly decolorizes ferric solutions because of formation of the very stable $[FeF_6]^{-3}$. Solutions of $FeCl_3 \cdot 6H_2O$ vary in color from red-brown to yellow, according

to the amount of Fe^{+3} and the concentration of HCl in the solution. In solutions high in HCl only such ions as $[FeCl_4]^-$, $[FeCl_5]^=$, and $[FeCl_6]^{-3}$ can exist. In solutions only slightly acid the reddish brown color is due mostly to $Fe_2O_3 \cdot xH_2O$ dispersed in a solution containing $[FeCl_4]^-$, and the like. HBr and bromide ions form complex ions similar to those with Cl^-. HI and soluble iodides reduce Fe^{+3} practically completely to Fe^{++}. For this reason no ferric iodides or iodoferriates are possible.

10. Alkali secondary phosphates precipitate $FePO_4$ or $Fe_2(HPO_4)_3$, but incompletely unless ionization of $H_2PO_4^-$ is repressed by buffering the solution.

$$Fe^{+3} + 2HPO_4^= \rightleftarrows \underline{FePO_4} + H_2PO_4^-$$

$FePO_4$ is insoluble in buffered AcOH. One method of removing the interference in cation analysis caused by $HPO_4^=$ is to precipitate it as $FePO_4$ or $Fe_2(HPO_4)_3$ before precipitating Group III cations.

11. Alkali acetate, if very concentrated, forms with ferric ion red solutions somewhat resembling those containing $[Fe(NCS)_6]^{-3}$. The color is probably due to formation of a complex anion such as $[Fe(AcO)_6]^{-3}$. This complex is little stable. If a known solution containing it is buffered with alkali acetate and then largely diluted and boiled all the iron precipitates as $Fe_2O_3 \cdot xH_2O$ gel.

12. Alkali cyanides precipitate $Fe_2O_3 \cdot xH_2O$ gel soluble in excess of the reagent to form $[Fe(CN)_6]^{-3}$.

$$Fe^{+3} + 3CN^- + 2H_2O \rightleftarrows \underline{FeOOH} + 3HCN$$
$$\underline{FeOOH} + 6CN^- + H_2O \rightleftarrows [Fe(CN)_6]^{-3} + 3OH^-$$

13. Oxalate ion forms a very stable complex anion, $[Fe(C_2O_4)_3]^{-3}$.

PRACTICE EXERCISE

Balance the following equations for important reactions of Fe^{+3}

1. $Fe^{+3} + H_2S = Fe^{++} + \underline{S} + H^+$
2. $Fe^{+3} + \text{(large) } C_{OH^-} = \underline{FeOOH}$
3. $Fe^{+3} + \text{(small) } C_{OH^-}\ (NH_4^+ + NH_3) \rightleftarrows \underline{FeOOH}$
4. $\underline{FeOOH} + \underline{Na_2O_2} + H_2O \rightarrow \underline{FeOOH} + HO_2^- + OH^- + Na^+$
5. $Fe^{+3} + NCS^- \rightleftarrows [Fe(NCS)_6]^{-3}$ (difference from Fe^{++})
   (red)

6. $Fe^{+3} + AcO^- \rightleftarrows [Fe(AcO)_6]^{-3}$ (difference from Fe^{++})

7. $Fe^{+3} + [Fe(CN)_6]^{-4} \rightarrow \underset{\text{(Prussian blue or ferric berlinate)}}{Fe[Fe(CN)_6Fe]_3}$

8. $[Fe(NCS)_6]^{-3} + H_2SO_3$ (Na_2SO_3 in HCl) $+ H_2O = HSO_4^- + H^+ + NCS^- + Fe^{++}$

9. $Fe^{+3} + HS^- = \underset{\text{(black)}}{Fe(HS)_3}$

10. $Fe_4[Fe(CN)_6]_3 + OH^- \rightleftarrows FeOOH + [Fe(CN)_6]^{-4}$

Manganese

Occurrence. Manganese occurs in the earth's lithosphere chiefly as pyrolusite, MnO_2, less abundantly as the carbonate, $MnCO_3$ (rhodochrosite), bright pink and as the silicate $MnSiO_3$, rhodonite, dull pink. Manganese and iron are close companions. Nearly all iron ores contain manganese; nearly all manganese ores contain iron.

Preparation and dissolution of the metal. The metal is usually obtained by reduction of MnO_2 by aluminum (Goldschmidt).

$$3MnO_2 + 4Al^0 \rightarrow 3Mn^0 + 2Al_2O_3$$

The metal dissolves readily in the hydrohalic acids with evolution of H_2. Cold 36*N* H_2SO_4 scarcely attacks it. Above 100° solution is rapid with evolution of SO_2. HNO_3 dissolves it with evolution of NO.

Valence. Manganese forms compounds in the valences 1, 2, 3, 4, 6, and 7. Compounds in which manganese has a valence of 1 or 3 have, for the most part, little stability and the element is usually in a complex anion. Some of the more stable of these are the following.

Mn^+ $K_5Mn(CN)_6$, white powder.

Mn^{+3} $[MnCl_6]^{-3}$ (dark brown), $[Mn(PO_4)_2]^{-3}$ (violet), $CsMn(SO_4)_2 \cdot 12H_2O$ (dark red), $[Mn(CN)_6]^{-3}$ (dark red), $[Mn(C_2O_4)_3]^{-3}$ (dark red–black), $[MnF_5]^{=}$ (dark red), $(AcO)_3Mn \cdot 2H_2O$ (brown).

Mn^{+4} $MnO_2 \cdot xH_2O$ appears to be the only definite stable compound. A very few salts containing Mn^{+4}, such as $Mn(SO_4)_2$ (black), K_2MnCl_6 (dark red), K_2MnF_6 (yellow) have been made but only under special conditions. None of them are very stable. So-called "manganites," for example,

$CaMnO_3$, $MnMnO_3$, are decidedly variable in composition. They are best regarded as adsorption compounds and not true salts.

$MnO_4^=$ is stable only in a high concentration of OH^-. Even CO_2 decomposes it into MnO_2 and MnO_4^-.

MnO_4^- is very easily reduced to MnO_2 in neutral or alkaline solution and to Mn^{++} in acid solution.

For analytical purposes the three important stable valences of manganese are 2, 4, and 7 in Mn^{++}, $MnO_2 \cdot xH_2O$, and MnO_4^-.

Reactions of Manganous Ion

1. Strong bases, NaOH or KOH, precipitate $Mn(OH)_2$ (white), rapidly oxidized by air to $MnO_2 \cdot xH_2O$ (dark brown). Very probably $Mn(OH)_3$, also brown, is formed as an intermediate state. $Mn(OH)_2$ is soluble in concentrated NH_4^+ salt solution. $MnO_2 \cdot xH_2O$ and $Mn(OH)_3$, which are much more insoluble in water than is $Mn(OH)_2$, are insoluble in NH_4^+.

2. Ammonia incompletely precipitates Mn^{++} from solutions containing not too much NH_4^+ as white $Mn(OH)_2$.

$$Mn^{++} + 2NH_3 + 2H_2O \rightleftarrows \underline{Mn(OH)_2} + 2NH_4^+$$

As discussed on page 233, $Mn(OH)_2$ is not precipitated by NH_3 from a solution nearly saturated with NH_4^+ salt. On standing, $MnO_2 \cdot xH_2O$ and $Mn(OH)_3$ gradually precipitate, since these compounds are much more insoluble than $Mn(OH)_2$. A yellow modification of $Mn(OH)_3$ occasionally is formed.

3. Ammonium hydrosulfide or sulfide precipitates salmon pink hydrated manganese sulfide which may be a basic hydrosulfide, HS—Mn—OH. This sulfide is soluble in acetic acid (difference from ZnS) and is not precipitated by H_2S even in strongly buffered acetic acid. It is slowly oxidized by air to $MnO_2 \cdot xH_2O$.

A green manganese sulfide, said to be $(MnS)_3 \cdot H_2O$, is infrequently met in analysis.

4. Sodium bismuthate (frequently formulated as $NaBiO_3$ but more probably a mixture of Bi_2O_4 and Bi_2O_5, containing much adsorbed Na^+) in *cold* dilute HNO_3 oxidizes Mn^{++} to permanganate ion MnO_4^- (purple red). PbO_2 in hot dilute H_2SO_4 acts similarly.

5. Potassium chlorate, $KClO_3$, in hot *concentrated* nitric acid oxidizes Mn^{++} to MnO_2. This reaction separates manganese from

nearly all other cations. In alkaline solution Na_2O_2, H_2O_2, BrO^-, and ClO^- oxidize Mn^{++} to $MnO_2 \cdot xH_2O$.

6. $MnO_2 \cdot xH_2O$ is the most important compound of manganese in its valence of 4. It is often said to be amphoteric. On *fusion* with a strong base, NaOH or $Ca(OH)_2$, it *may* form manganites, for example, Na_2MnO_3, $CaMnO_3$, and the like. These, however, are immediately decomposed by water with precipitation of $MnO_2 \cdot xH_2O$ and are not formed in presence of water.

When MnO_2 is treated with concentrated HCl, $[MnCl_6]^{=}$ brown probably forms but quickly decomposes to $[MnCl_6]^{-3}$, also brown.

$$2[MnCl_6]^{=} + 2Cl^- \rightleftarrows 2[MnCl_6]^{-3} + \overline{Cl_2}$$

7. Manganate ion (green) is stable only in basic solutions. It is formed in the dry way by fusion of a Mn^{++} salt with NaOH or Na_2CO_3 with an oxidant such as $NaNO_3$ or $KClO_3$. It is decomposed to $MnO_2 \cdot xH_2O$ and $MnO_4^{=}$ by even very weak acids such as H_2CO_3.

Formation of green $MnO_4^{=}$ in a Na_2CO_3 bead is a sensitive test for Mn. In a small loop of the platinum wire a bead of fused Na_2CO_3 is formed. If a *very minute* quantity of any Mn compound is taken up in the bead and the latter reheated in the oxidizing Bunsen flame, the bead takes on a distinct green tint. Too much Mn spoils the test since only brown MnO_2 is formed.

$$Mn^{++} + 4CO_3^{=} \rightleftarrows MnO_4^{=} + 4CO_2 + 4e^-$$
$$O_2 + 2CO_2 + 4e^- \rightleftarrows 2CO_3^{=}$$
$$\overline{Mn^{++} + O_2 + 2CO_3^{=} = MnO_4^{=} + 2\overline{CO_2}}$$

8. Permanganate ion (purple) is one of the strongest oxidants and is reduced by nearly all reductants. In neutral or alkaline solution it is reduced to $MnO_2 \cdot xH_2O$. In acid solution it is reduced to Mn^{++}.

In *strongly* basic solution MnO_4^- is reduced to green $MnO_4^{=}$. This is probably caused by presence of a little colloidal MnO_2 in permanganate solutions.

9. Potassium cyanoferroate with Mn^{++} forms white, or very slightly pink, $Mn_2[Fe(CN)_6]$, insoluble in dilute HCl.

Reactions of Manganous Ion as Reductant

$$Mn^{++} + 3OH^- \rightleftarrows \underline{Mn(OH)_3} + e^-$$
$$Mn^{++} + 4OH^- \rightleftarrows \underline{MnO_2 \cdot xH_2O} + 2e^-$$

$$Mn^{++} + 2H_2O \rightleftarrows \underline{MnO_2} + 4H^+ + 2e^-$$
$$Mn^{++} + 8OH^- \rightleftarrows \underline{MnO_4^=} \text{ (green)} + 4H_2O + 4e^-$$
$$Mn^{++} + 4H_2O \rightleftarrows \underline{MnO_4^-} \text{ (purple)} + 8H^+ + 5e^-$$
$$Mn^{++} + 4CO_3^= \rightleftarrows \underline{MnO_4^=} + 4CO_2 + 4e^- \text{ (fusion)}$$

Reduction of Oxidants Commonly Used with Mn^{++}

$$\underline{NaBiO_3} + 6H^+ + 2e^- \rightleftarrows Bi^{+3} + 3H_2O + Na^+$$

or possibly

$$\underline{BiO_2} + 4H^+ + e^- \rightleftarrows Bi^{+3} + 2H_2O,$$
$$\underline{PbO_2} + HSO_4^- + 3H^+ + 2e^- \rightleftarrows \underline{PbSO_4} + 2H_2O,$$
$$HO_2^- \text{ (}\underline{Na_2O_2}\text{, or } H_2O_2 + OH^-\text{)} + H_2O + 2e^- \rightleftarrows 3OH^-,$$
$$ClO_3^- \text{ in } 16\,N\ HNO_3\text{: } HClO_3 + H^+ + e^- \rightleftarrows \underline{ClO_2} + H_2O.$$

PRACTICE EXERCISE

Balance the following equations for important reactions of manganese.

1. Mn^{++} + large OH^- = $\underline{Mn(OH)_2}$
2. $\underline{Mn(OH)_2} + O_2 + H_2O = \underline{MnO_2 \cdot H_2O}$
3. Mn^{++} + (small) OH^- $(NH_4^+ + NH_3) \rightarrow$
4. $Mn^{++} + HO_2^- + OH^- = \underline{MnO_2 \cdot H_2O}$
5. $Mn^{++} + HS^- = \underline{HO—Mn—SH}$ (pink)
6. $Mn^{++} + \underline{Na_2O_2} + H_2O = \underline{MnO_2 \cdot H_2O}$
7. $\underline{MnO_2 \cdot H_2O} + H_2O_2 + H^+ = Mn^{++} + \overline{O_2}$
8. $Mn^{++} + \underline{NaBiO_3} + H^+ + (NO_3^-) \rightarrow MnO_4^- + Bi^{+3}$
9. $MnO_4^- + NO_2^- + OH^- \rightarrow MnO_4^= + NO_3^-$
10. $MnO_4^= + H^+ \rightleftarrows \underline{MnO_2 \cdot xH_2O} + MnO_4^-$

See electron partial equations above. Follow rules for balancing redox reactions, page 56.

Cobalt and Nickel

Occurrence. Both elements occur as the metal in iron meteorites. In the earth's lithosphere they are usually associated with

Fe and S or As. Some minerals are smaltite, $CoAs_2$; cobaltite, CoAsS; Co-Ni pyrite, (Co, Fe, Ni,)S_2; millerite, NiS; pentlandite, $NiS(FeS)_2$; gersdorffite, NiAsS.

These two elements stand in the periodic arrangement between iron and copper. They always accompany each other in ores. Most commercial cobalt salts contain some nickel. Nickel salts usually are much freer from cobalt.

The ions of cobalt resemble in their reactions those of iron. Ni^{++} resembles Cu^{++} in its reactions rather more than it does Co^{++} and Fe^{++}.

Dissolution of the metals. Both cobalt and nickel, if pure, dissolve more slowly in dilute hydrohalic and sulfuric acids than does iron. They dissolve readily in dilute HNO_3 but are made "passive" by the concentrated acid. They are not dissolved by strong bases in aqueous solution.

Valences. Cobalt forms both Co^{++} and Co^{+3}. Co^{++} forms a vitriol, $[Co(H_2O)_6]SO_4 \cdot H_2O$. Co^{+3} forms alums, K_2(Rb, Cs) $Co(SO_4)_2 \cdot 12H_2O$, all dark blue.

Nickel forms ordinarily only $[Ni(H_2O)_4]^{++}$ (for brevity, Ni^{++}). A black dioxide, $NiO_2 \cdot xH_2O$ is formed by powerful oxidants in alkaline solution.

Most hydrated Co^{++} salts are red because of $[Co(H_2O)_6]^{++}$. When dehydrated, they become blue. "Sympathetic ink" is $CoCl_2$ solution. The writing is ordinarily invisible but turns blue when the paper is warmed.

All simple salts of Co^{+3} decompose water with liberation of O_2. Very insoluble compounds such as $Co(OH)_3$ can exist in presence of water.

$Co(OH)_3$, unlike $Fe(OH)_3$, dissolves in dilute HCl to form Co^{++} and Cl_2; in dilute HNO_3 or H_2SO_4 to form Co^{++} and O_2. In the latter acids probably H_2O_2 is formed first.

$$2H_2O + 2Co^{+3} \rightarrow H_2O_2 + 2Co^{++} + 2H^+$$
$$2Co^{+3} + H_2O_2 \rightarrow 2Co^{++} + O_2 + 2H^+$$

Very powerful oxidants such as BrO^- in alkaline solution oxidize Co^{++} and Ni^{++} to $CoO_2 \cdot xH_2O$ and $NiO_2 \cdot xH_2O$ (both black), resembling MnO_2 in their properties.

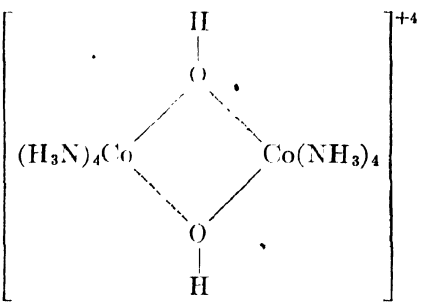
Reactions of Cobaltous Ion

1. Strong bases, NaOH or KOH, precipitate from cold solutions of Co^{++} a blue basic salt which is changed, by excess of alkali and by

warming, to pink $Co(OH)_2$. In contact with air $Co(OH)_2$ becomes green and then brown. The green form is stated to be a hydrate of Co_3O_4, analogous to Fe_3O_4. The brown form is $Co(OH)_3$ or CoOOH. Note in these reactions the resemblance of $Co(OH)_2$ to $Fe(OH)_2$ and $Mn(OH)_2$ and its difference from $Ni(OH)_2$, which is not oxidized by air. Both $Co(OH)_2$ and $Co(OH)_3$ are soluble in concentrated solutions of ammonium salts containing NH_3.

$$Co(OH)_2 + 2NH_4^+ + 4NH_3 \rightleftarrows [Co(NH_3)_6]^{++} + 2H_2O$$
$$2Co(OH)_3 + 4NH_4^+ + 4NH_3 \rightleftarrows [Co_2(NH_3)_8(OH)_2]^{+4} + 4H_2O$$

2. Ammonia in the absence of NH_4^+ salt precipitates blue basic salts which do not change to $Co(OH)_2$ (difference from fixed alkali). In the presence of sufficient NH_4^+, ammonia forms no precipitate but the pink solution of $Co(NH_3)_6^{++}$ is rapidly oxidized by air to a brown solution because of the formation of



The broken bond-lines indicate coordination through an electron-pair donated by the oxygen atom.

On standing, this brown solution slowly decomposes with formation of a red ion such as $[Co(NH_3)_5Cl]^{++}$ if NH_4Cl was used.

$$[Co_2(NH_3)_8(OH)_2]^{+4} + 2NH_4^+ + 2Cl^- \rightarrow 2[Co(NH_3)_5Cl]^{++} + 2H_2O$$

3. Hydrogen sulfide forms no precipitate either in $0.3\,N$ H^+ or in acetic acid solution. In strongly buffered acetic acid Co^{++} is partially precipitated, probably as $Co(HS)_2$.

4. Ammonium hydrosulfide or sulfide with neutral solutions of Co^{++}, or with basic solutions containing complex ions such as $[Co(NH_3)_6]^{++}$, $[Co_2(NH_3)_8(OH)_2]^{+4}$, forms probably black $Co(HS)_2$. The fresh unwashed precipitate is somewhat soluble in $1\,N$ HCl but becomes nearly insoluble after repeated washing. This may be due

to change of $Co(HS)_2$ into CoS. CoS is readily soluble in hot HNO_3, in HCl + HNO_3 or in HCl + $KClO_3$.

5. Cyanide ion. From a neutral solution of Co^{++} cyanide ion precipitates $Co(CN)_2$ red-brown, readily soluble in excess of CN^- with formation of brown cyanocobaltoate ion, $[Co(CN)_6]^{-4}$, analogous to cyanoferroate ion. Unlike the latter, cyanocobaltoate ion is rapidly oxidized by air in warm solution to form the much more stable yellow cyanocobaltiate ion $[Co(CN)_6]^{-3}$. This is so stable that neither cobalt nor cyanide can be detected in it until the complex has been destroyed by powerful reagents (Difference from $[Ni(CN)_4]^=$).

6. Potassium nitrite, in excess, precipitates from concentrated solutions of cobaltous ion in acetic acid yellow crystalline potassium hexanitrocobaltiate, commonly called potassium cobaltinitrite, $K_3[Co(NO_2)_6]3H_2O$ (difference from nickel).

7. Alpha-nitroso beta-naphthol in 50% acetic acid forms a bright brick-red precipitate containing Co^{+3}. This is an extremely sensitive test for Co^{++} in the absence of Fe^{+3} which forms a black precipitate with the reagent. Nickel gives no precipitate.

8. Alkali thiocyanates in moderately concentrated HCl form $[Co(NCS)_4]^=$ (deep blue). (Compare $[Fe(NCS)_6]^{-3}$, deep red.) The free acid of the complex ion is much more soluble in ether (better, a mixture of one part of ether and two parts amyl alcohol) than in water. A little Co^{++} is added to a solution of any alkali thiocyanate (K^+, Na^+, NH_4^+), and then 1 ml of a mixture of amyl alcohol and ether added and the solution shaken to saturate mutually the two solutions. If the mixture is now made strongly acid with HCl and vigorously shaken, a blue color will be seen in the ether-alcohol layer, the depth of color depending upon the amount of Co^{++} in the solution.

If Fe^{+3} is present, the ether-alcohol will be purple red instead of blue. In this case if a tiny crystal of $Na_2S_2O_3$ is added and the mixture again shaken vigorously, Fe^{+3} is reduced to Fe^{++} and the blue color can be seen. This is an extremely delicate test for Co^{++}.

This test was proposed by Treadwell in 1901.[15] Neither he nor certain authors who have recommended the test seem to have understood it entirely since they state that the test must be made in neutral solution. Treadwell used NH_4NCS. $(NH_4)_2Co(NCS)_4$ is somewhat soluble in ether.

[15] Z. anorg. Chem., **26**, 105.

The corresponding K^+ and Na^+ salts are entirely insoluble in ether. When ammonium thiocyanate is used in neutral or only slightly acid solution, sufficiently large concentrations of Co^{++} will indeed give a blue color in the ether layer, but small amounts of cobalt can not be detected in this way because most of the cobalt remains in the water layer. If the solution used is made strongly acid with HCl and again shaken, nearly all the cobalt passes into the ether layer. This is probably due to formation of a covalent etherate by the unionized complex acid. The test is capable of detecting minute amounts of Co^{++} only when a *high* concentration of HCl is present to form $H_2[Co(NCS)_4]$. With this high C_{H^+} present, KNCS, NaNCS, and NH_4NCS behave identically.

9. Thiocyanatomercurate ion precipitates deep blue crystalline $Co[Hg(NCS)_4]$. Two drops of a 0.05 mg/ml solution (0.005 mg Co^{++}) on a spot plate with 1 drop of 0.3 formal $K_2[Hg(NCS)_4]$ solution give a distinct precipitate after stirring about one minute.

10. Cyanoferroate ion precipitates green $Co_2[Fe(CN)_6]$ nearly insoluble in dilute HCl.

PRACTICE EXERCISE

Balance the following equations for important reactions of Co^{++}.

1. $Co^{++} + OH^- + X^- \rightarrow \underset{\text{(blue)}}{CoOHX}$ (cold soln.) $\rightarrow \underset{\text{(pink)}}{Co(OH)_2}$
2. $CoOHX + O_2 + OH^- \rightarrow \underset{\text{(brown)}}{Co(OH)_3}$ (cf. Fe^{++}, Mn^{++})
3. $Co^{++} + NH_3 + H_2O + X^- \rightarrow\!\!\!\!\rightarrow \underset{\text{(blue)}}{CoOHX}$
4. $CoOHX + NH_4^+ + NH_3 \rightleftarrows \underset{\text{(pink)}}{Co(NH_3)_6^{++}}$
5. $Co^{++} + NH_4^+$ (large) $+ NH_3 \rightleftarrows Co(NH_3)_6^{++}$
6. $Co^{++} + Na_2O_2 + H_2O = Co(OH)_3$ (cf. Fe^{++})
7. $Co^{++} + HS^- = Co(HS)_2$ (cf. Fe^{++}) $\rightarrow CoS + H_2S$
8. $Co^{++} + CN^- \rightarrow [Co(CN)_6]^{-4}$ (cf. Fe^{++})
9. $[Co(CN)_6]^{-4} + O_2 + H_2O = [Co(CN)_6]^{-3}$ (difference from Fe, Ni).
10. $Co^{++} + NCS^- + H^+ \rightleftarrows \underset{\text{(blue)}}{H_2[Co(NCS)_4]}$ (cf. $\underset{\text{(red)}}{H_3[Fe(NCS)_6]}$

Reactions of Nickel Ion

1. Strong Bases, depending on their concentration, precipitate either a basic salt or $Ni(OH)_2$, both light green and readily soluble in NH_4^+ and NH_3, forming probably $[Ni(NH_3)_4(H_2O)_2]^{++}$ blue.

$Ni(OH)_2$ is not oxidized by air [difference from $Cr(OH)_2$, $Mn(OH)_2$, $Fe(OH)_2$ and $Co(OH)_2$. Resemblance to $Cu(OH)_2$].

2. Ammonia solution, if quite dilute, precipitates green basic salts such as Ni(OH)Cl, which, like $Ni(OH)_2$, are readily soluble in excess of NH_3 or in NH_4^+. More concentrated solutions of NH_3 form the complex ion at once.

3. Hydrogen sulfide forms no precipitate in solutions of Ni^{++} in $0.3N$ H^+. From strongly buffered acetic acid solution Ni^{++} is partially precipitated, probably as $Ni(HS)_2$ (black).

4. Ammonium hydrosulfide or sulfide, from neutral solutions of Ni^{++} or basic solutions containing $[Ni(NH_3)_4]^{++}$, precipitates probably $Ni(HS)_2$. Like $Co(HS)_2$ the fresh unwashed precipitate is somewhat soluble in cold $1N$ HCl. After repeated washing it dissolves only very slowly (separation of Co^{++} and Ni^{++} from Zn^{++}). This decrease of solubility is probably owing in part at least to $\underline{Ni(HS)_2} \rightarrow \underline{NiS} + H_2S$. However NiS has several different forms, change from one of which into another is accompanied by decrease of solubility. $Ni(HS)_2$ very readily forms brown colloidal suspensions. Their formation seems to be favored by (1) large concentration of NH_3 and (2) yellow persulfide ions such as $S_2^=$, $S_3^=$, and the like. To prevent formation of colloidal $Ni(HS)_2$ the NH_4HS reagent should always be *colorless*. Like CoS, NiS is readily dissolved by hot nitric acid or by HCl and $KClO_3$ with formation of sulfur.

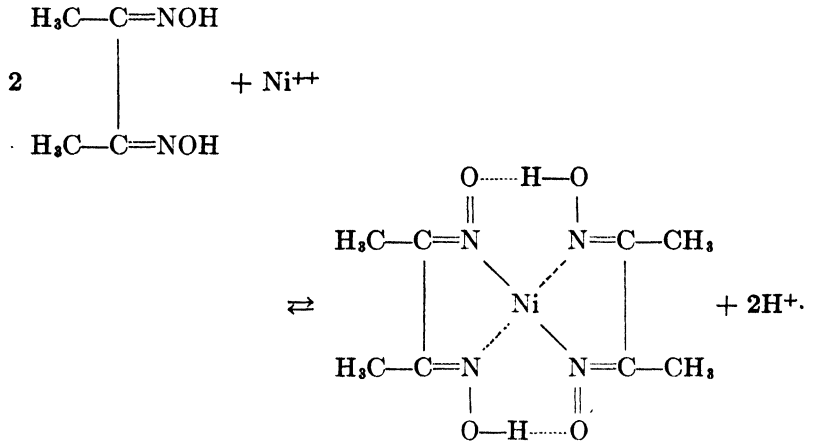
Moist sulfides of cobalt, nickel, and zinc are rapidly oxidized by air to sulfates and for this reason should always be dissolved as soon as washed.

5. Cyanide ion forms a green precipitate of $Ni(CN)_2$, readily soluble in excess of CN^- with formation of $[Ni(CN)_4]^=$ (compare with $[Co(CN)_6]^{-4}$). Tetracyanonickeloate ion is not oxidized by air and is much less stable than is $[Co(CN)_6]^{-3}$.

6. Nitrous acid (NO_2^- and AcOH) does not oxidize Ni^{++} and forms no precipitate with it except in very concentrated solutions of Ni^{++} (difference from Co^{++}).

7. Dimethylglyoxime in alcoholic solution forms with Ni^{++} a voluminous brilliant scarlet precipitate of nickel glyoximine, an "inner complex" salt:[16]

[16] Structure according to P. Pfeiffer, Ber. **63**, 1811–1816 (1930); C. A., **24**, 5723 (1930); and Brady and Muers, J. Chem. Soc. (1930), 1599; C. A., **24**, 5296 (1930).



Nickel glyoximine (frequently written $Ni(Dn)_2$) is amphoteric and should be precipitated in buffered acetic acid or buffered ammonia to prevent accumulation of H^+ which would reverse the reaction. It is also soluble in OH^-.

The reagent is said to be capable of detecting 1 part of Ni^{++} in 400,000 parts of water. Co^{++} forms brown solutions with this reagent. When it is present, more reagent must be added than is equivalent to the Co^{++} present before Ni^{++} begins to precipitate.

Unbelievably small amounts of nickel in cobalt salts can be detected with dimethyglyoxime by the following procedure.

To 1 ml of cobaltous salt solution CN^- is added until the precipitate of $Co(CN)_2$ just redissolves. The solution is warmed and stirred for two or three minutes. It now contains the extremely stable $[Co(CN)_6]^{-3}$ and the much less stable $[Ni(CN)_4]^-$. The solution is diluted with two or three volumes of water. To about 1 ml of the diluted solution a drop of dimethylglyoxime solution is added and then $AgNO_3$ dropwise with constant stirring until a permanent precipitate of $Ag[Ag(CN)_2]$ or $Ag_3[Co(CN)_6]$ forms. The white precipitate is colored more or less deeply pink if any nickel is present. The silver precipitate evidently adsorbs the colloidal nickel glyoximine.

The solution contains a large $C_{Co(CN)_6^{-3}}$, a very minute $C_{Ni(CN)_4^-}$ and a moderate C_{CN^-}. $Ni(Dn)_2$ cannot form in spite of its great insolubility because $\dfrac{C_{Ni^{++}} \times C^4_{CN^-}}{C_{Ni(CN)_4^-}} = K_{equil.}$ the relatively large C_{CN^-} and the minute $C_{Ni(CN)_4^-}$ make $C_{Ni^{++}}$ vanishing small so that even the extremely small $K_{s.p.}$ of $Ni(Dn)_2$ is not reached. The ion $Ag(CN)_2^-$ is very stable and its silver salt $Ag[Ag(CN)_2]$ is very slightly soluble. When Ag^+ is added to the mixture of CN^- and cyano-anions, it reacts with CN^- to form AgCN,

which redissolves on stirring or shaking due to formation of $[Ag(CN)_2]^-$. When C_{CN^-} in this way becomes sufficiently small, the moderately stable $[Ni(CN)_4]^-$ decomposes into Ni^{++} and CN^- and the latter forms $[Ag(CN)_2]^-$ which, when C_{Ag^+} is made large enough, precipitates as $Ag[Ag(CN)_2]$. Even when all the Ni^{++} is released from $[Ni(CN)_4]^-$, its concentration may be far too small to form flocculent $Ni(Dm)_2$. Adsorption of the red colloid on the white surface of $Ag[Ag(CN)_2]$ or $Ag_3[Co(CN)_6]$, causes these precipitates to appear pink or scarlet according to the amount of Ni^{++} present. However, this may be another instance of coprecipitation.

TABLE 9

COMPARISON OF THE BEHAVIOR OF Co^{++} AND Ni^{++} TOWARD VARIOUS REAGENTS

REAGENT	Co^{++}	Ni^{++}
OH^- (KOH, NaOH)	Blue $CoOHX$ (X-anion of salt)	Green $NiOHX$
OH^- (excess)	Pink $Co(OH)_2$ + air → $Co(OH)_3$ (brown)	Green $Ni(OH)_2$ stable to air
OH^- ($NH_3 + H_2O$)	Blue $CoOHX$ + air → green $Co_3O_4 \cdot xH_2O$? → $Co(OH)_3$ (brown)	Green $NiOHX$ Blue $[Ni(NH_3)_4]^{++}$ stable to air
OH^- ($NH_4^+ + NH_3$)	$Co(NH_3)_6^{++}$ (pink) + air → brown complex ion	Blue $[Ni(NH_3)_4]^{++}$
HS^-	$Co(HS)_2$ (black) → CoS (on washing)	Black $Ni(HS)_2$ → NiS (on washing)
HO_2^- [Na_2O_2 (or $NH_2 + H_2O_2$)]	$Co(OH)_3$ (brown)	$Ni(OH)_2$ (green)
$OH^- + Br_2$ or Cl_2 (BrO^- or ClO^-)	CoO_2 (black)	NiO_2 (black)
CN^-	Brown $Co(CN)_2$ → brown $[Co(CN)_6]^{-4}$ + air → $[Co(CN)_6]^{-3}$ yellow	$Ni(CN)_2$ (green) → $[Ni(CN)_4]^-$ (green) stable to air
$HNO_2 + NO_2^-$	$K_3[Co(NO_2)_6]$ (yellow)	No reaction
Dimethylglyoxime	Brown solution	$Ni(Dn)_2$ (scarlet)
NCS^- + large H^+	$H_2[Co(NCS)_4]$ blue forms etherate	No reaction
α-Nitroso β-naphthol	Brown-crimson precipitate	No reaction

PRACTICE EXERCISE

Balance the following equations for important reactions of Ni^{++}.

1. $Ni^{++} + OH^- = Ni(OH)_2$ (insoluble in excess)
2. $Ni^{++} + NH_4^+ + NH_3 \rightleftarrows [Ni(NH_3)_4]^{++}$ (cf. Zn^{++})

3. $Ni^{++} + HS^- = \underline{Ni(HS)_2}$

4. $Ni^{++} + \underline{Na_2O_2} + H_2O = \underline{Ni(OH)_2} + HO_2^- + Na^+$
(difference from Co^{++})

5. $Ni^{++} + CN^- \rightleftarrows Ni(CN)_4^=$ (difference from Co^{++})

6. $Ni^{++} + HDn$ (dimethylglyoxime) $\rightleftarrows \underline{Ni(Dn)_2} + H^+$

Zinc

Occurrence. Zinc occurs in the earth's lithosphere chiefly as ZnS, sphalerite. It also occurs as smithsonite, $ZnCO_3$; willemite, Zn_2SiO_4; and zincite, ZnO. In the periodic arrangement of the elements it constitutes, together with cadmium and mercury, the II-B family.

Dissolution of the metal. Commercial zinc dissolves readily in dilute mineral acids, but very pure zinc does not because of "hydrogen overvoltage." Zinc reduces HNO_3 to NH_4^+, N_2O, NO, or NO_2 according to the concentration of acid. Zinc dissolves also in strong bases with liberation of H_2.

Reactions of Zinc Ion

1. Strong bases precipitate white $Zn(OH)_2$ gel, possibly $[Zn(OH)_2(H_2O)_2]$, soluble in excess of base forming $[HZn(OH)_4]^-$. The amphoterism of zinc hydroxide is explainable on the same grounds as that of $[Al(OH)_3(H_2O)_3]$.

$$\underline{[Zn(OH)_2(H_2O)_2]} + OH^- \rightleftarrows [HZn(OH)_4]^- + H_2O$$

2. Ammonia, if dilute, precipitates incompletely $Zn(OH)_2$ gel, readily soluble in excess of the reagent or in NH_4^+ salts with formation of $[Zn(NH_3)_4]^{++}$ (similarity to Ni^{++}; difference from aluminum, chromium, iron, manganese). Hydrogen sulfide does not precipitate $Zn(HS)_2$ from solutions $0.3N$ in H^+. $Zn(HS)_2$ is completely precipitated by H_2S from AcOH solutions. In this respect it differs from all the elements of Cation Group III.

3. Ammonium hydrosulfide or sulfide precipitates white $Zn(HS)_2$ from solutions containing Zn^{++}, $[HZn(OH)_4]^-$ or $[Zn(NH_3)_4]^{++}$. Like $Ni(HS)_2$ it has a considerable tendency to form colloidal suspensions. To prevent this, precipitates which may contain $Zn(HS)_2$ should be washed with hot water containing $AcONH_4$ or NH_4NO_3.

4. Rinmann's green. Zn^{++} is distinguished in analysis by its white sulfide precipitated by H_2S from $6N$ AcOH solution. One

confirmatory test formerly much used consists of formation of a green compound, $CoZnO_2$, or a solid solution of CoO and ZnO, known as Rinmann's green. To obtain the green color, neither oxide may be in large excess over the other. The test is most delicate when a piece of filter paper impregnated with $K_3[Co(CN)_6]$ is spotted with a drop containing not too high concentration of Zn^{++} and the paper then gently heated to charring in a crucible. A green color will appear on the spotted portion.

5. Coprecipitation of cobalt thiocyanatomercurate with zinc thiocyanatomercurate. $Zn[Hg(NCS)_4]$ white, crystalline, is only very slowly precipitated because of super-saturation. In presence of a trace of Co^{++}, however, pale blue mixed crystals of $Zn[Hg(NCS)_4]$ and $Co[Hg(NCS)_4]$ are rather quickly precipitated (usually within 15 seconds).

The test is performed as follows. In a depression of a spot plate place 1 drop of the solution to be tested for Zn^{++} and 1 drop of 0.02% Co^{++} in 0.5*N* HCl. Place a drop of the Co^{++} solution in an adjacent depression. To each add 1 drop of 0.3 formal $K_2[Hg(NCS)_4]$. Stir each with a glass rod for 15 seconds. If the test solution contains Zn^{++}, a blue precipitate will appear in less than 2 minutes, usually in less than 30 seconds. In the solution containing only Co^{++} a blue precipitate will not appear within 3 minutes. This test is said to detect 0.5γ (= 0.0005 mg) per drop, or 1 part of Zn^{++} in 100,000 parts of water. Fe^{+3} if present would form red $[Fe(NCS)_6]^{-3}$. Addition of 1 to 2 mg of an alkali fluoride removes the interference by forming colorless $[FeF_6]^{-3}$.

PRACTICE EXERCISE

Balance the following equations for important reactions of Zn^{++}.

1. $Zn^{++} + OH^-$ (small) $\rightarrow \underline{Zn(OH)_2}$
2. $\underline{Zn(OH)_2} + OH^-$ (large) $= [HZn(OH)_4]^-$ (cf. Al^{+3}, Cr^{+3})
3. $Zn^{++} + NH_3 \rightleftarrows [Zn(NH_3)_4]^{++}$
4. $Zn^{++} + H_2S$ (in AcOH) $= \underline{Zn(HS)_2} \rightarrow \underline{ZnS} + H_2S$
5. $[Zn(NH_3)_4]^{++} + HS^- = \underline{Zn(HS)_2} + NH_3$

CATION GROUP IV

(Ba^{++}, Sr^{++}, Ca^{++}, and Mg^{++})

Barium

Occurrence. Barium occurs most commonly as barite, $BaSO_4$,

and witherite, $BaCO_3$. It is much less abundant than calcium and magnesium but it is considerably more abundant than strontium.

Dissolution of the metal. Until recently the metal was almost unknown, but its use in alloys and in vacuum tubes has produced a demand. In the form of an alloy with nickel, it is also used in ignition systems of gasoline engines. It closely resembles the alkali metals in appearance and like them decomposes water.

Reactions of Barium Ion

1. Strong bases—KOH and NaOH—if free from carbonate, give no precipitate. These reagents have usually absorbed CO_2 from the air and give a turbidity of $BaCO_3$. Alkaline solutions containing Ba^{++} rapidly absorb CO_2 and become turbid. Consult the table on page 264 and note the large solubility of $Ba(OH)_2$ as indicated there.

2. Ammonia solution, if free from carbonate, gives no precipitate.

3. Ammonium sulfide, $(NH_4)HS$, if free from carbonate, gives no precipitate because BaS, like the sulfides of Al and Cr, is completely hydrolyzed in aqueous solution.

4. Alkali carbonates precipitate white, flocculent $BaCO_3$, which becomes crystalline on standing or heating. Precipitation by $(NH_4)_2CO_3$ is somewhat incomplete because NH_4^+ is an acid ($K_{ion} = 5.6 \times 10^{-10}$) and forces the reaction

$$NH_4^+ + CO_3^= \rightleftarrows NH_3 + HCO_3^-$$

to the right. Bicarbonates of alkaline earth ions are soluble in water. In consequence of the above reaction $C_{CO_3^=}$ becomes too small to precipitate the last of the Ba^{++}. Since H_2CO_3 ($K_1 = 10^{-7}$; $K_2 = 10^{-11}$) is a weaker acid than AcOH, $BaCO_3$ is readily soluble in mineral acid and in AcOH.

$$\underline{BaCO_3} + H^+ \rightleftarrows Ba^{++} + HCO_3^-$$

$$HCO_3^- + H^+ \rightleftarrows H_2CO_3 \rightleftarrows H_2O + \overline{CO_2}$$

5. Sulfate ion, from dilute H_2SO_4 or any soluble sulfate, precipitates white, powdery $BaSO_4$, the most insoluble compound of Ba^{++}. It is practically insoluble in water and in dilute HCl and HNO_3. It is less soluble in dilute H_2SO_4 than in water due to the common ion effect. It dissolves somewhat in concentrated HCl or HNO_3, because of formation of HSO_4^- (bisulfates are soluble), and to a considerable extent in hot concentrated H_2SO_4 for the same reason. When boiled with Na_2CO_3 solution (3 *N* or more) barium

sulfate is sufficiently transposed into $BaCO_3$ so that $SO_4^{=}$ can be detected in the solution. The transposition is much more complete when $BaSO_4$ is fused with Na_2CO_3 in a crucible.

6. Chromate ion forms pale yellow $BaCrO_4$, practically insoluble in water and in strongly buffered AcOH but soluble in mineral acids and slightly soluble in unbuffered AcOH. The different behavior of $BaSO_4$ and $BaCrO_4$ toward H^+ is due to the large difference in the ionization of HSO_4^- ($K_{ion} = 1.2 \times 10^{-2}$) and $HCrO_4^-$ ($K_{ion} = 3.2 \times 10^{-7}$). Furthermore for

$$2HCrO_4^- \rightleftarrows Cr_2O_7^{=} + H_2O$$

$$K_{equil.} = \frac{C_{Cr_2O_7^{=}}}{C^2_{HCrO_4^-}} = 44$$

The values of the constants show that even a small C_{H^+} must dissolve some $BaCrO_4$ by forming $HCrO_4^-$ and $Cr_2O_7^{=}$. Both barium chromate and barium sulfate should be precipitated in boiling solution so as to obtain a crystalline precipitate which is more rapidly washed free from contaminating ions.

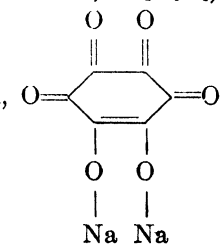
7. Oxalate ion forms white $BaC_2O_4 \cdot H_2O$ slightly soluble in water and soluble in hot AcOH (difference from CaC_2O_4).

8. Secondary phosphate ion, $HPO_4^{=}$, precipitates from neutral solutions white flocculent $BaHPO_4$. In strongly alkaline solutions mostly $Ba_3(PO_4)_2$ probably is formed. Both are readily soluble in mineral acids and even in AcOH because of formation of $H_2PO_4^-$ ($K_{ion} = 6.2 \times 10^{-8}$), the alkaline earth salts of which are soluble.

9. Flame color. Barium salts impart to the Bunsen flame a yellow-green color.

$BaCl_2$ is the most volatile of the salts. Even $BaSO_4$ and $BaCrO_4$, if moistened with concentrated HCl, color the flame. It has been observed that, upon heating, Ba compounds tend to creep up a platinum wire more rapidly than compounds of Sr. This facilitates detection of Sr^{++} and Ba^{++} by flame tests in presence of each other.

10. Sodium rhodizonate, $Na_2C_6O_6$, the Na salt of 3, 4, 5, 6-tetraketocyclohexenediol,



forms with Ba^{++} in neutral

solution red-brown BaC_6O_6, which becomes bright red when treated with very dilute HCl. Because many heavy-metal ions interfere, the reaction may be used only after removal of these ions. The reaction is best used as a spot test as follows:

On a strip of filter paper place 1 drop of barium ion test solution, then add a small drop of an aqueous solution of sodium rhodizonate. If barium ion is present, a red-brown spot forms. The color is darker the more Ba^{++} is present. If the spot is touched with a drop of $0.3N$ HCl the spot becomes bright red. Feigl claims that this test will detect 0.5γ of Ba^{++} in presence of fifty times as much Sr^{++}. The latter forms a precipitate of the same color which, however, dissolves instantly to a colorless compound when touched with $0.3N$ HCl.

Strontium

Occurrence. Except radium, strontium is the least abundant of the alkaline earth elements. The principal minerals are celestite, $SrSO_4$, and strontianite, $SrCO_3$. Small amounts occur in some calcium minerals.

Dissolution of the metal. The metal at present is little more than a curiosity. It decomposes water less vigorously than barium but much more vigorously than calcium. Practically the only use of this element is that of its salts for production of red light as in fireworks, signal flares, and the like.

Reactions of Strontium Ion

1. **Strong bases.** Same as with barium ion.
2. **Ammonia solution.** Same as with barium ion.
3. **Ammonium hydrosulfide.** Same as with barium ion.
4. **Alkali carbonates** precipitate white $SrCO_3$, the most insoluble compound of strontium. NH_4 salts tend to prevent precipitation for the reason given in 4, barium ion, page 261.
5. **Sulfate ion.** Same as with barium ion. However, $SrSO_4$ is more soluble than $BaSO_4$ but much less soluble than $CaSO_4$. Consult the table on page 264. Because of its greater solubility, $SrSO_4$ is almost completely transposed by boiling with $3N$ Na_2CO_3.
6. **Chromate ion** precipitates $SrCrO_4$ only from rather concentrated neutral solutions. AcOH prevents the precipitation for the reason given in 6, barium ion. $SrCrO_4$ is a deeper yellow than $BaCrO_4$.
7. **Oxalate ion.** Same as with barium ion.
8. **Secondary phosphate ion.** Same as with barium ion.

9. Flame color. Strontium salts impart to the Bunsen flame a carmine-red color. $SrCl_2$ is the most volatile salt. $SrSO_4$ moistened with $12N$ HCl gives the color readily. Unlike barium salts strontium salts do not tend to creep up a platinum wire and the strontium flame persists at the tip of the wire after a barium flame is no longer visible there.

10. Sodium rhodizonate gives with Sr^{++} in neutral solution the same red-brown precipitate, SrC_6O_6, as with Ba^{++}. The precipitate is readily soluble in $0.3N$ HCl (difference from BaC_6O_6).

Feigl states that if a test paper is used which has been impregnated with saturated K_2CrO_4 solution and then dried, 4γ of Sr^{++} can be detected

TABLE 10
APPROXIMATE SOLUBILITIES IN WATER OF ALKALINE EARTH SALTS

Solid Phase	Temp.	mg salt / 1000 mg water	Solid Phase	Temp.	mg salt / 1000 mg water
$Mg(OH)_2$	18°	0.009	$MgC_2O_4 \cdot 2H_2O$	18°	0.151
$Ca(OH)_2$	20°	1.61	$CaC_2O_4 \cdot H_2O$	25°	0.0071
$Sr(OH)_2 \cdot 8H_2O$	20°	17.4	$SrC_2O_4 \cdot H_2O$	25°	0.057
$Ba(OH)_2 \cdot 8H_2O$	25°	87.0	$BaC_2O_4 \cdot H_2O$	25°	0.087
			MgF_2	18°	0.087
$MgSO_4 \cdot 7H_2O$	20°	710.	CaF_2	18°	0.016
$CaSO_4$	25°	2.09	SrF_2	27°	0.12
$CaSO_4 \cdot 2H_2O$	25°	2.65	BaF_2	10°	1.7
$SrSO_4$	30°	0.141			
$BaSO_4$	25°	0.0025	$MgSO_3 \cdot 6H_2O$	15°	12.5
			$CaSO_3 \cdot 2H_2O$	18°	0.043
$MgCrO_4 \cdot 7H_2O$	18°	1280.	$SrSO_3$	17°	0.33
α-$CaCrO_4 \cdot 2H_2O$	20°	186.	$BaSO_3$	20°	0.2
β-$CaCrO_4 \cdot 2H_2O$	20°	130.			
$SrCrO_4$	15°	1.2	$Mg_3(PO_4)_2 \cdot 4H_2O$	cold	0.2
$BaCrO_4$	16°	0.0034	$Ca_3(PO_4)_2$	"	0.02
			$Sr_3(PO_4)_2$	"	insol.
$MgCO_3$	19°	0.9	$Ba_3(PO_4)_2$	"	insol.
$CaCO_3$	25°	0.015			
$SrCO_3$	18°	0.011	$MgNH_4PO_4 \cdot 6H_2O$	0°	0.23
$BaCO_3$	18°	0.02			

NOTE: It must not be taken for granted that the solubilities of the *freshly precipitated* salts are, even with close approximation, those listed in the table. The latter were determined in pure water. When the salts are precipitated in analysis, rather large concentrations of soluble electrolytes are usually present, and this "salt effect" may considerably change the solubilities of precipitated salts. It will usually be safe to assume that the *order* of solubility is correct and that the salt effect will influence the solubility of similar salts, for example, the four oxalates, to about the same extent.

in presence of 84 times its weight of Ba^{++}. We have never succeeded in precipitating semimicro amounts of Ba^{++} upon this paper so completely that it did not react with $Na_2C_6O_6$.

Calcium

Occurrence. Calcium ranks fifth among all the elements and third among the metallic elements in order of abundance. It is believed to constitute about 3.5% of the lithosphere. The most important of the minerals are $CaCO_3$ in many different forms, fluorspar, CaF_2, gypsum, $CaSO_4 \cdot 2H_2O$, apatite, $Ca_5(PO_4)_3(F,Cl)$, and dolomite, $(Ca,Mg)CO_3$. It occurs in many silicates and aluminosilicates.

Dissolution of the metal. The metal is now made in large quantities by electrolysis and has many uses. It does not decompose water very rapidly at room temperature. Like magnesium it becomes coated with a protective film of oxide or basic carbonate and thereafter unites with oxygen only when heated. As with magnesium, the nitride, Ca_3N_2, as well as oxide, CaO, is formed as a combustion product. The metal dissolves readily in dilute highly ionized acids.

Reactions of Calcium Ion

1. Strong bases. Same as with barium ion.

2. Ammonia solution. Same as with barium ion.

3. Ammonium hydrosulfide. Same as with barium ion.

4. Alkali carbonates. Same as with barium ion.

5. Sulfate ion precipitates white $CaSO_4 \cdot 2H_2O$ only from concentrated solutions. The solubility of $CaSO_4$ is increased by large concentration of NH_4^+ more than is that of $SrSO_4$.

6. Potassium chromate does not precipitate $CaCrO_4$ except from very concentrated solutions.

7. Oxalate ion precipitates from neutral or alkaline solutions white crystalline $CaC_2O_4 \cdot H_2O$, the most insoluble compound of Ca^{++}. Unlike the oxalates of Ba^{++} and Sr^{++}, CaC_2O_4 is insoluble in AcOH. It dissolves readily in mineral acids.

8. Secondary phosphate ion. Same as with barium ion.

9. Flame color. Calcium salts impart to the Bunsen flame a color which is yellow-red at first but which becomes brick-red. This flame is difficult for beginners to distinguish readily from the carmine-red flame of Sr^{++}. If reliance is to be placed on the flame tests for Ca^{++} and Sr^{++} the flame given by the unknown must be

compared with that given by known solutions of both a Ca^{++} salt and a Sr^{++} salt.

10. Sodium rhodizonate gives no reaction with Ca^{++}.

Magnesium

Occurrence. Magnesium is believed to constitute about 2% of the earth's lithosphere. It is as widely distributed as calcium. Important minerals are magnesite, $MgCO_3$, dolomite, $(Mg,Ca)CO_3$, spinel, Al_2MgO_4, kieserite, $Mg(H_2O)_6SO_4 \cdot H_2O$ (in the salt beds), and a great number of silicates.

Dissolution of the metal. The metal dissolves readily in dilute acids with liberation of H_2. Like Al it is superficially oxidized by air and thus acquires a protective coating. When this coating has been removed, the metal liberates H_2 from hot water. Like Ca it burns readily in air when heated. The products of combustion are MgO and Mg_3N_2.

Reactions of Magnesium Ion

1. Strong bases, in absence of NH_4^+, precipitate white, gelatinous $Mg(OH)_2$, insoluble in excess of the base. $Mg(OH)_2$ is readily soluble in ammonium salt solutions.

$$\underline{Mg(OH)_2} + 2NH_4^+ \rightleftarrows Mg^{++} + 2NH_3 + 2H_2O$$

2. Ammonia precipitates from neutral solutions of Mg^{++} white, gelatinous $Mg(OH)_2$. This reaction is only partial because formation of NH_4^+ soon produces equilibrium.

$$Mg^{++} + 2NH_3 + 2H_2O \rightleftarrows \underline{Mg(OH)_2} + 2NH_4^+$$

At equilibrium,

$$C_{Mg^{++}} \times C^2_{OH^-} = 3.4 \times 10^{-11} \text{ and} \tag{22}$$

$$\frac{C_{NH_4^+} \times C_{OH^-}}{C_{NH_3}} = 1.8 \times 10^{-5}. \tag{23}$$

Combining (22) and (23) and eliminating C_{OH^-},

$$\frac{C^2_{NH_4^+}}{C^2_{NH_3} \times C_{Mg^{++}}} = \frac{(1.8 \times 10^{-5})^2}{3.4 \times 10^{-11}} = 9.53. \tag{24}$$

If NH_3 is added to a 0.1 *M* solution of Mg^{++} until C_{NH_3} is 0.1 *M* when

$Mg(OH)_2$ ceases to precipitate, we shall have in equation (24)

$$\frac{(2x)^2}{(0.1)^2 \times (0.1 - x)} = 9.53,$$

whence $x = 0.03833$. $C_{Mg^{++}}$ still unprecipitated, $(0.1 - x) = 0.06167\,M$. $C_{NH_4^+}$ $(= 2x)$ will be $0.07666\,M$. That is, when equilibrium has been attained, less than 40% of the Mg^{++} originally present will have been precipitated.[17]

3. Ammonium hydrosulfide, in absence of considerable other NH_4^+ salt, may precipitate some $Mg(OH)_2$. For this as well as other reasons partial precipitation of Mg^{++} in Group III must always be expected (compare page 320). MgS is completely decomposed by water,

$$\underline{MgS} + 2H_2O = \underline{Mg(OH)_2} + \overline{H_2S}$$

4. Ammonium carbonate does *not* precipitate $MgCO_3$ which is much more soluble than the carbonates of Ba^{++}, Sr^{++}, and Ca^{++}. In the presence of sufficient NH_4^+ the reagent precipitates no $Mg(OH)_2$.

5. Sulfate ion produces no precipitate.

6. Chromate ion produces no precipitate. $MgCrO_4$ is deliquescent. It is more orange-yellow than $CaCrO_4$. The yellow color of the alkaline earth chromates becomes paler in the order Mg, Ca, Sr, Ba.

7. Oxalate ion precipitates white crystalline $MgC_2O_4 \cdot 2H_2O$, but it does so very slowly. This salt forms strongly supersaturated solutions.

8. Secondary phosphate ion precipitates from neutral solutions flocculent $MgHPO_4$. From a solution which contains much NH_3 and some NH_4^+ crystalline $MgNH_4PO_4 \cdot 6H_2O$ is precipitated. This is the most insoluble compound of Mg^{++}. The precipitate is soluble in mineral acids and in acetic acid due to formation of $H_2PO_4^-$. In the formation of $MgNH_4PO_4$ the following equilibria are involved:

$$HPO_4^= + OH^- \rightleftarrows H_2O + PO_4^{-3}$$
$$PO_4^{-3} + Mg^{++} + NH_4^+ \rightleftarrows \underline{MgNH_4PO_4}$$

In the absence of NH_3 the reaction would be

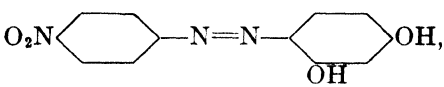
$$HPO_4^= + Mg^{++} + NH_4^+ \rightleftarrows \underline{MgNH_4PO_4} + H^+,$$

[17] Fredholm, Z. anorg. Chem., **217**, 203; **218**, 169, 225, 235 (1934) has shown that an ion $[Mg(NH_3)]^{++}$, more probably $[MgNH_3(H_2O)_5]^{++}$, is formed to the extent of about 8% in a solution in which $C_{Mg} = C_{NH_3} = 0.1\,M$.

and precipitation would be incomplete because H^+ would reverse the reaction. The presence of NH_4^+ salts serves two purposes: (1) to prevent precipitation of $Mg(OH)_2$ when the solution is made alkaline; (2) by the common-ion effect to make the precipitate more insoluble. However, too large $C_{NH_4^+}$ should prevent formation of the crystalline precipitate because of the reaction

$$NH_4^+ + PO_4^{-3} \rightleftarrows NH_3 + HPO_4^{=}.$$

9. **Flame color.** Mg salts impart no color to the Bunsen flame.
10. **Sodium rhodizonate** does not react with Mg^{++}.
11. **O-p-dihydroxymonazo-p-nitrobenzene,**



commonly called S. and O. reagent from Suitsu and Okuma who first (1926) proposed its use, forms[18] with $Mg(OH)_2$ a sky-blue lake.[19] The dye is yellow in acid solution, even when the acidity is due to NH_4^+. In basic solution it is violet. Ammonium salts are said to interfere with the formation of the lake. Probably the "interference" is due only to the necessity of adding an unusually large quantity of sodium hydroxide to convert the NH_4^+ to NH_3. Feigl states that the reagent will detect 0.5γ of Mg^{++} when used as a spot test. The dye forms a pale violet lake with Ni^{++} and Co^{++}.

[18] Traces of other cations which had escaped precipitation in Groups I to III may precipitate here when the solution is made basic. For this reason the solution should always be centrifuged and any precipitate washed. Washing once or twice will not decompose the blue lake formed by $Mg(OH)_2$, $MgHAsO_4$, and $MgHPO_4$.

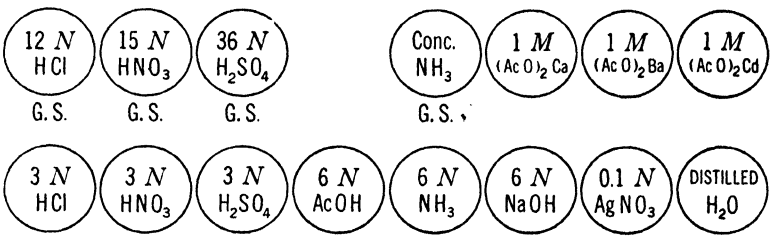
[19] A term used by dyers. Cotton fibers will not "take up" or absorb certain dyes. They are then coated with a "mordant," usually a metal oxide-hydrate which will adsorb, or form a compound with, the dye. The combination of mordant and dye is called a *lake*. $Mg(OH)_2$ here would be a mordant.

CHAPTER 14

PREPARATION FOR THE LABORATORY WORK

Apparatus and reagents. Check on an apparatus list (a form list is included in the appendix) the apparatus found in the locker. Any cracked or missing articles should be called to the attention of an instructor.

Thoroughly clean the bottles in the reagent kit (consult page 182). Also clean the fifteen small dropper pipets and cap the flanged ends with the rubber bottle-nipples. Label as below. Half fill each bottle with the proper reagent and insert the pipet stopper. The Ca, Ba, and Cd acetates will not be needed for some time. A suggested order for arranging bottles in the reagent block is that below.



G.S. = Glass Stoppered. Do Not Use Dropper Pipets in These Bottles.

Make at least four capillary pipets for removing centrifugates from precipitates. These are made by holding in both hands a piece of 7-mm soft glass tubing about 20 cm (8 inches) long and heating with micro burner the middle of the tubing. While the tubing is being heated it should be constantly rotated slowly with the fingers so that the middle is heated uniformly. When the glass is soft enough that it appears ready to collapse, the tube is withdrawn from the flame and while held in a horizontal position the two ends are pulled apart to make a long capillary. After cutting at the middle of the capillary, the wide end of each tube is expanded to a flange by heating to red heat and pressing the hot glass firmly on a metal surface. The capillary end can be cut off at any length to give an orifice having a diameter of 0.1–0.2 mm. Too large an

orifice is likely to draw up precipitates. Cap the flanged end with a rubber nipple.

Calibration of dropper pipets. Calibrate in the following manner the two dropper pipets not required for the reagent kit. Partly fill a *clean* 10 ml graduated cylinder with distilled water so that the bottom of the meniscus is *exactly* at any milliliter mark. Take up some distilled water in the pipet and, *holding it vertically*, let the drops fall freely, counting the number of drops required to bring the miniscus to the next milliliter mark. Repeat until two trials agree within one drop. Each pipet should deliver 18–22 drops per ml. If outside these limits, widen or narrow slightly the tip after softening in flame. Place an identifying mark on each pipet and record the number of drops per milliliter delivered by each. You will use them frequently for *exact* work. Keep each one inserted in a clean one-dram vial.

A preliminary experiment. Experience has shown that the troubles and uncertainties of beginners in analysis arise chiefly from two sources. These are (1) failure to test for complete precipitation, and (2) insufficient washing of precipitates.

After the equipment has been prepared and cleaned as directed, carefully perform the following experiment. Its purpose is to demonstrate the importance of the two operations mentioned above and also to teach the student the correct technique of washing precipitates.

Place in a small centrifuge tube 4 drops of chromic chloride ($CrCl_3$) test solution (2 mg Cr^{+3}), 4 drops of barium chloride test solution (2 mg Ba^{++}), and 12 drops of distilled water. Stir vigorously with a glass rod. Add 1 drop of $6N$ NH_3 solution and again stir. (After *each* addition of a reagent the solution should be vigorously stirred.) Centrifuge and test *for complete precipitation* by adding another drop of $6N$ NH_3 solution. Centrifuge out any additional precipitate. Repeat the test for complete precipitation until the addition of a drop of $6N$ NH_3 produces no further precipitate. The precipitate is hydrated chromic oxide, $Cr_2O_3 \cdot xH_2O$, often written as $Cr(OH)_3$. The solution (hereafter called the centrifugate) contains barium ions, Ba^{++} ($Ba(OH)_2$ is soluble); chloride ions, Cl^-; ammonium ions, NH_4^+; hydroxide ions, OH^-; and ammonia, NH_3.

Pipet off and discard the clear centrifugate. The precipitated $Cr_2O_3 \cdot xH_2O$ in the centrifuge tube is washed by adding 4 drops of distilled H_2O and 1 drop $6N$ NH_3 and stirring up the precipitate

very thoroughly. Centrifuge and pipet off the centrifugate to a clean test tube. To the clear centrifugate, made *acid* with HCl, add one drop potassium sulfate solution. A white precipitate of barium sulfate ($BaSO_4$) proves that Ba^{++} ion is being extracted from the precipitate. Note its amount.

Repeat the washing operation, each time using fresh wash solution and centrifuging and adding K_2SO_4 to the centrifugate until the washings give no precipitate or cloudiness upon addition of sulfate ion. Record the number of times the precipitate has to be washed until barium ion can no longer be detected in the washings. Note and record the relative amount of $BaSO_4$ precipitated in *each* successive portion of wash liquid. Finally dissolve the chromium precipitate in $3N$ HCl, dilute with an equal volume of water, and add a drop of K_2SO_4. Did a detectable amount of Ba^{++} remain in the washed precipitate? Is it conceivable that, if the chromium precipitate had been insufficiently washed, the Ba^{++} in it might have interfered with some subsequent test?

Remember this experiment throughout your later work.

CHAPTER 15

INTRODUCTORY STUDY OF THE CATIONS

While the student is familiarizing himself with the characteristic reactions of the individual cations, he should be looking forward to the use which later will be made of most of these reactions in the systematic separation and detection of these ions. To aid him in discovering the various points of application, this chapter is accompanied by flow sheets (Tables 11 to 14) which show what reagents each cation encounters in the systematic analysis, and how it behaves toward each reagent encountered.

ALKALI METAL IONS

Read pages 190–198 on "notebook records."

Sodium Ion (Na^+)

Study pages 201, 202.

***Experiment 1.**[1] **Action of zinc uranyl acetate reagent.** Place 2 drops of Na^+ test solution in a test tube, add 2 drops of zinc uranyl acetate, and stir vigorously to start crystallization. If a precipitate forms, add more reagent, a drop at a time, as long as precipitate seems to form. Write equation for the reaction.

For detection of very small amounts of Na^+ by this reagent the following procedure is recommended. Place in a test tube 2 drops of the unknown solution from which all ions of Groups I to IV have been removed. Add 10 drops of zinc uranyl acetate reagent and stir vigorously. A precipitate will form with as little as 0.001 mg (1γ) of Na^+. This test should *not* be applied directly to the water-soluble portion of a solid unknown.

Experiment 2. Flame tests. Carefully clean the platinum wire as directed on page 190. Take up a very little solid sodium carbonate (Na_2CO_3) and bring into the flame as directed. Note color and then reexamine the flame through a *double* thickness of blue glass. Is the color absorbed?

[1] Experiments marked * may be omitted in shorter courses. The reactions involved are not used in the system of analysis.

TABLE 11
SEPARATION OF CATIONS INTO GROUPS

Original unknown tested for Na^+, K^+, and NH_4^+.

Ag^+		$\overline{AgCl}$					
Hg_2^{++}		$\overline{Hg_2Cl_2}$	Group I Chlorides				
Pb^{++} (large concn.)		$\overline{(PbCl_2)}$					
Pb^{++}		Pb^{++}		$\overline{Pb(HS)_2}$			
BiO^+		BiO^+		$\overline{Bi(HS)_3}$			
Cu^{++}		Cu^{++}		$\overline{Cu(HS)_2}$			
Cd^{++}		Cd^{++}		$\overline{Cd(HS)_2}$	Group II Hydrosulfides		
Hg^{++}		Hg^{++}		$\overline{Hg(HS)_2}$			
As^{+3}		As^{+3}		$\overline{As(HS)_3}$			
SbO^+		SbO^+		$\overline{Sb(HS)_3}$			
Sn^{+4}	HCl	Sn^{+4}		$\overline{Sn(HS)_4}$			
Co^{++}		Co^{++}		$\overline{Co^{++}}$		$\overline{Co(HS)_2}$	
Ni^{++}		Ni^{++}	0.3 N H^+	Ni^{++}		$\overline{Ni(HS)_2}$	
Fe^{+3}		Fe^{+3}	H_2S	Fe^{++}		$\overline{Fe(HS)_{2-3}}$	
Mn^{++}		Mn^{++}		Mn^{++}		$\overline{MnOHHS}$	Group III Hydrosulfides and Hydroxides
Cr^{+3}		Cr^{+3}		Cr^{+3}		$\overline{CrOOH}$	
Al^{+3}		Al^{+3}		Al^{+3}	NH_3 NH_4HS	$\overline{AlOOH}$	
Zn^{++}		Zn^{++}		Zn^{++}		$\overline{Zn(HS)_2}$	
Ba^{++}		Ba^{++}		Ba^{++}		$\overline{Ba^{++}}$	
Sr^{++}		Sr^{++}		Sr^{++}		Sr^{++}	
Ca^{++}		Ca^{++}		Ca^{++}		Ca^{++}	
Mg^{++}		Mg^{++}		Mg^{++}		Mg^{++}	

Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++} $\xrightarrow{K_2SO_4}$ $\overline{BaSO_4}$, $\overline{SrSO_4}$, $\overline{Ca^{++}}$, Mg^{++}

Group IV

$\overline{Ca^{++}}$, Mg^{++} $\xrightarrow{C_2O_4^-}$ $\overline{CaC_2O_4}$, Mg^{++} $\xrightarrow[\text{reagent}]{\text{S. \& O.}}$ $\overline{Mg(OH)_2}$ (dyed blue)

Potassium Ion (K^+)

Study pages 202, 203.

***Experiment 1. Action of hexanitrocobaltiate ion.** Place 2 drops of K^+ test solution in a test tube and dilute to 1 ml with distilled water. Add 2 drops of sodium hexanitrocobaltiate reagent, $Na_3[Co(NO_2)_6]$. Stir thoroughly and record result.

Experiment 2. Flame tests. On a *clean* platinum wire bring a little K_2CO_3 into the flame. Observe and record flame color, then observe again through a *double* thickness of blue glass. Observe carefully the changed appearance of the flame. Note that potassium salts volatilize *much* more rapidly than sodium salts. When present as KCl, K^+ is rather easily missed. Be looking through the blue glass *at the instant* the wire enters the flame.

Experiment 3. Repeat experiment 2, using a mixture of Na_2CO_3 and K_2CO_3. State the function of the blue glass.

Ammonium Ion (NH_4^+)

Study pages 203–205.

***Experiment 1. Action of hexanitrocobaltiate ion.** Place 2 drops of NH_4^+ test solution in a test tube and dilute to 1 ml with distilled water. Add 2 drops of sodium hexanitrocobaltiate reagent, $Na_3[Co(NO_2)_6]$. Stir thoroughly and record result.

Experiment 2. Flame tests. On a *clean* platinum wire bring a little NH_4Cl into the flame. Observe and record flame color, then observe again through a *double* thickness of blue glass.

Experiment 3. Action of Nessler's reagent. Place 1 drop of NH_4^+ test solution in a test tube and dilute to 1 ml. Dilute one drop of this solution to 1 ml and to the latter add one drop of $K_2[HgI_4]$ reagent and 1 drop of NaOH. Stir thoroughly and record results. Write equation for the reaction.

Experiment 4. Test for ammonium. Place 10 drops of NaOH reagent in the Erlenmeyer flask. Do not let the solution or dropper touch the walls of the flask. Insert a "wedge-point" pin into the bottom of a No. 6 cork, which should fit the flask. In the loop of the pin place a piece of red litmus paper about $\frac{1}{4}$ inch long. Moisten the paper and insert the cork. Carefully warm the flask preferably on a steam plate. *The liquid must not be allowed to boil.* Even a trace of NH_3 will affect the test paper within 5 minutes. Paper turning blue proves NH_4^+ *in the reagent.* If NH_4^+ is present,

remove the cork and heat the NaOH until a test with a fresh piece of paper proves the NaOH free from NH_4^+.

To the NaOH free from NH_4^+ add the tiniest possible fragment of NH_4Cl and proceed as directed above. Why was a "blank test" made on the NaOH? Write equations: (1) for the action of OH^- on NH_4^+ in the solution, (2) for the reaction (of the gas with the water on the paper) which causes the litmus to change color.

Experiment 5. Volatility of ammonium salts. Place two or three grains of solid NH_4Cl in a 100 ml beaker and heat with the free flame. Is *all* the salt volatilized? Similarly heat a small crystal of $(NH_4)_2SO_4$ and then one of NH_4NO_3. Are both salts completely volatilized? Does it appear that NH_3 can be driven out of ammonium salts by heating strongly?

Questions To Be Answered in the Notebook

1. How would you proceed to detect by flame test a little K^+ in a large amount of Na^+?

2. Outline a procedure to detect by precipitation a little K^+ in a large amount of NH_4^+ salt. (*Hint:* Consider Experiment 1, K^+; Experiments 1 and 5, NH_4^+.)

3. Using only the flame test, how would you distinguish between a *trace* (less than 0.5 mg) of Na^+ and a *medium amount* (2–3 mg) of that ion?

Analysis of a Practice Unknown Solid Mixture

Procure from the instructor a solid unknown mixture containing only alkali-metal ions. Analyze it as directed on page 308.

As soon as each ion is *proved* absent or present, check result with laboratory instructor to learn whether you have correctly followed and interpreted the systematic procedure. No grade will be given on this exercise.

Analysis of Unknown Mixtures

Read pages 197–199.

Procure from the instructor three unknown solid mixtures which may contain any or all of the three alkali metal ions. (*Note:* Other ions giving colored flames may be present.) Analyze for alkali metals only as directed on page 308. Report ions found and amount

of each estimated to be in 20 mg of the unknown mixture. See pages 199, 200 for directions for filling out unknown reports.

IONS OF CATION GROUP IV

Barium Ion (Ba^{++})

Study pages 261–263.

Calculate the molar and normal concentration of the Ba^{++} test solution.

Experiment 1. Action of sulfate ion. In a centrifuge tube place 2 drops (how many mg of the ion?) of Ba^{++} test solution. Add 1 drop $3N$ HCl and 16 drops of distilled water. Mix thoroughly; warm to a temperature of about 80°. Add dropwise, with stirring, potassium sulfate (K_2SO_4) reagent until precipitation is complete. Centrifuge and test for complete precipitation. Remove centrifugate, wash precipitate twice with 4 drops of water each time, removing washings as completely as possible. Use the precipitate for the following experiment.

Experiment 2. Flame test. Moisten the $BaSO_4$ from experiment 1 with 1 drop of $12N$ HCl. Stir vigorously. Dip a *clean* platinum wire into the mixture and bring into the flame. Observe *very carefully* the first and final color. *Important.* When flame is no longer colored add a drop of $12N$ HCl to the wire and again bring into the flame. Does the color reappear? Observe whether Ba seems to creep up the wire.

***Experiment 3. Action of oxalate ion.** In a centrifuge tube place 2 drops of Ba^{++} test solution. Add 18 drops of water. Stir thoroughly, then add ammonium oxalate reagent until precipitation is complete. Centrifuge and pipet off the clear liquid (centrifugate) into a test tube. Add 1 drop of ammonium oxalate to the clear solution to test for complete precipitation. Centrifuge out any additional precipitate. To the solution from the Ba precipitate add 1 drop potassium sulfate and stir vigorously. Any precipitate? Explain if one is visible. Consult Table 10, page 264.

Experiment 4. Action of sodium rhodizonate. On a strip of filter paper place a capillary drop of sodium rhodizonate ($Na_2C_6O_6$) solution. To the spot add a drop of a solution made by diluting one drop Ba^{++} test solution to 1 ml. Note the color of the precipitate. Place on it 1 drop of ethyl alcohol. Let stand for 1 minute. Now touch the spot with 1 drop of $0.3N$ HCl. Note that the

precipitate turns bright red. What fraction of a mg gave the test? The red spot may disappear when no more than a trace of Ba^{++} is present but not so rapidly that it cannot be seen. Sr rhodizonate dissolves *instantly* when touched with HCl.

Strontium Ion (Sr^{++})

Study pages 263–265.

Experiments 1–4. Repeat experiments 1–4, barium, using Sr^{++} test solution. Note that SrC_6O_6 has the same color as BaC_6O_6 and that (unlike Ba) it dissolves instantly when touched with 0.3 *N* HCl.

Calcium Ion (Ca^{++})

Study pages 265, 266.

Repeat experiment 1, barium, using 2 drops of Ca^{++} test solution but use no more than 2 drops of potassium sulfate reagent. If no precipitate forms, add at once to the hot solution 1 drop of 6 *N* NH_3 and then $(NH_4)_2C_2O_4$ reagent as long as precipitate continues to form. Centrifuge. Wash precipitate twice with 4 drops of water, each time removing washings as completely as possible. Treat the washed CaC_2O_4 with 1 drop of 12 *N* HCl and apply flame test, after making sure that the wire is *clean*.

Magnesium Ion (Mg^{++})

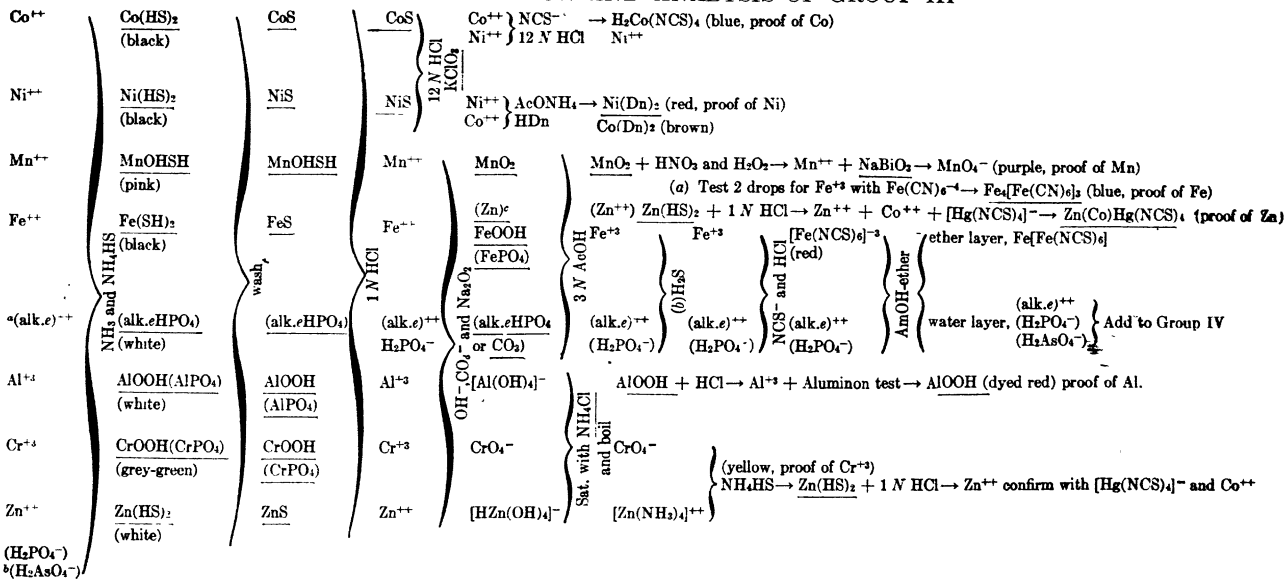
Study page 266.

***Experiment 1. Action of sulfate ion.** To 2 drops of the test solution of Mg^{++} and 18 drops of water add 1 drop K_2SO_4 reagent. Mix thoroughly. Does any precipitate form? Use solution for experiment 2.

***Experiment 2. Action of oxalate ion.** To the solution from experiment 1 add 1 drop of $(NH_4)_2C_2O_4$ reagent. Does a precipitate form? Use solution for experiment 3.

Experiment 3. S. and O. lake test. Make the solution from experiment 2 acid to litmus with HCl and add 2 drops of S. and O. reagent. What is the color of the solution? Now add NaOH dropwise with constant stirring until the dye changes to violet or blue. Stir vigorously. Centrifuge and note that the $Mg(OH)_2$ has formed a lake and is now deep blue. Note for future comparisons the volume occupied by 1 mg of Mg^{++} as $Mg(OH)_2$. See footnotes 18, 19, page 268.

TABLE 12
PRECIPITATION AND ANALYSIS OF GROUP III



[a] alk.e = Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}.

[b] $HAsO_4^-$ will react exactly as does HPO_4^- throughout the analysis and will pass into Group IV.

[c] (Zn) indicates that Zn^{++} *may* precipitate here. All compounds or ions in parentheses are to be understood as merely possibilities.

Practice on Flame Tests

Make up the following mixtures:

(*a*) 4 drops of Ba^{++} test solution and 1 drop of Sr^{++} test solution.

(*b*) 1 drop of Ba^{++} test solution and 4 drops of Sr^{++} test solution.

Precipitate the mixture with K_2SO_4 at 80°. Centrifuge, wash twice. Moisten the residue with 1 drop of $12N$ HCl. Conduct flame test as directed on page 189. Be sure that you can detect Sr^{++} in (*a*) and Ba^{++} in (*b*).

Notice that a yellow-green color appears first, quickly followed by a deeper green which disappears and is followed by the red of Sr. If, after Sr red appears at the tip of the wire, a higher portion of the wire is brought into the flame, Ba green will appear.

Practice Analysis of an Unknown Solution Containing only Alkaline Earth Ions

Procure a practice unknown solution from the instructor. Make 1 ml of it acid to litmus with HCl and proceed as directed in Table 19, (page 325).

As soon as each ion is *proved* absent or present, check result with laboratory instructor to determine whether you have correctly followed and interpreted the systematic procedure.

Analyses of Unknown Solutions

Procure 2 unknown solutions which may contain any of the four alkaline earth ions. Analyze and report results and amounts on report forms.

IONS OF CATION GROUP III, THE AMMONIUM SULFIDE GROUP

Before performing the following experiments, the student should read pages 231 to 234 in connection with the flow sheet, Table 12.

Ions of Aluminum

$([Al(H_2O)_6]^{+3}$ (for brevity Al^{+3}), AlO^+, $[Al(OH)_6]^{-3}$, $[AlCl_4]^-$, and the like)

Study pages 234–239.

Experiment 1. Action of NH_3. In a small centrifuge tube place 2 drops of aluminum ion (Al^{+3}) test solution and 18 drops of water. Stir the solution thoroughly. Add dropwise, with thorough stirring after each drop, 3 drops of $6N$ NH_3. Centrifuge. Test

for complete precipitation by adding 1 drop $6N$ NH_3. If more precipitate is formed, add 1 drop $6N$ NH_3 stir thoroughly and centrifuge again. Pipet off the centrifugate and discard. Use the precipitate for experiment 2.

Experiment 2. Action of NaOH. To the precipitate[2] AlOOH from experiment 1, add 3 drops of water and 3 drops of $6N$ NaOH and stir thoroughly until precipitate dissolves. Why did the AlOOH dissolve? Heat the mixture to boiling. Does any precipitate form? (Difference from "chromite" solution.) Use the solution for experiment 3.

Experiment 3. Action of NH_4^+ on aluminate ion. To the solution (experiment 2) add solid NH_4Cl until the solution is saturated. Boil until the solution does not smell very strongly of NH_3. What happens? Explain, considering that NH_4^+ is an acid. Write equations for all reactions. Centrifuge, wash and use the precipitate for experiment 4.

Experiment 4. Aluminon test. Dissolve the AlOOH (experiment 3) in the least number of drops of warm $1N$ HCl, add 3 drops of $3N$ ammonium acetate solution ($AcONH_4$), 2 drops of aluminon solution and stir. Then add NH_3 solution until, after stirring, the mixture smells of it. Stir vigorously and add 3 drops of ammonium carbonate ($(NH_4)_2CO_3$) solution and stir. Centrifuge and wash the precipitate with $(NH_4)_2CO_3$ solution. The AlOOH should have formed a brilliant red lake which did not change color when washed with $(NH_4)_2CO_3$ solution.

***Experiment 5. Action of hydrosulfide ion.** Place 2 drops of aluminum ion test solution in a test tube. Dilute to 1 ml with distilled water. Now add ammonium hydrosulfide (NH_4HS) solution. Explain why the precipitate is not a hydrosulfide. Write all equations.

Ions of Chromium

$[Cr(H_2O)_6^{++}$, $Cr(H_2O)_6^{+3}$ (for brevity Cr^{+3}), CrO^+, $Cr(OH)_6^{-3}$, $CrCl_6^{-3}$ and the like, CrO_4^-, $Cr_2O_7^-]$

Study pages 239–242.

Experiment 1. Action of NH_3. To a mixture of 2 drops of chromic ion test solution and 18 drops of water add $6N$ NH_3 as

[2] The chemical properties of the gels formed with NH_3 by AlO^+, CrO^+, FeO^+, BiO^+, and so on, are probably best shown by an ideal formula such as $[Al(OH)_x(H_2O)_{6-x}]_y$. For simplification these gels may be formulated in equations as AlOOH, and so on, which appears to be the composition they

directed in experiment 1, aluminum. Formulate the gel as CrOOH. Use the gel in experiment 2.

Experiment 2. Action of NaOH. To the precipitate from experiment 1 add 3 drops of water and 3 drops of sodium hydroxide and stir thoroughly until precipitate dissolves. Boil the solution. What is the precipitate formed? Compare result with that in experiment 2, aluminum. Centrifuge and use the precipitate in experiment 3.

Experiment 3. Action of Na_2O_2. To the precipitate from experiment 2 add a few grains of solid sodium peroxide (Na_2O_2), warm and stir until the precipitate dissolves. What color is the solution?

Experiment 4. Confirmatory test for chromium. To 1 ml of water add 1 drop of $CrO_4^=$ test solution and 5 or 6 drops of ether. Shake vigorously to mutually saturate the two layers. Cool the tube in a stream of tap water as much as possible. Then add 1 drop of hydrogen peroxide (H_2O_2) and 1 to 3 drops of $3N$ H_2SO_4. Shake quickly. A brilliant blue color in the ether layer is due to diperoxochromic anhydride, $OCr(O_2)_2$, moderately stable in ether but almost instantly decomposed in water.

Experiment 5. Action of H^+ on $CrO_4^=$. Acidify with $3N$ H_2SO_4 2 drops of $CrO_4^=$ test solution. Note the change of color. Make the acid solution alkaline again with NaOH. Is the original color restored? Is the reaction perfectly reversible? Study the equilibrium relations of $CrO_4^= \leftrightharpoons Cr_2O_7^=$, Chapter 7, page 93.

***Experiment 6. Action of hydrosulfide ion.** To a mixture of 2 drops of Cr^{+3} test solution and 18 drops of water, add NH_4HS reagent as directed in experiment 5, aluminum.

Ions of Iron

$[Fe(H_2O)_6]^{++}$ (for brevity, Fe^{++}); $Fe(H_2O)_6^{+3}$ (for brevity, Fe^{+3}), FeO^+, $[FeCl_6]^{-3}$, and the like]

Study pages 242–248.

Under different conditions iron can lose either two electrons to form ferrous ion (Fe^{++}) or three electrons to form ferric ion (Fe^{+3}). In analysis either ion may be encountered. The behavior of the two ions with respect to the same reagent should be compared.

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ultimately reach when equilibrium is finally established (usually after months). The subscript y, which in case of Al appears to be not smaller than 8 [Jander, Kolloid Beihefte, **43**, 312 (1936)], indicates polymerization.

Prepare a fresh solution of Fe^{++} by dissolving in a test tube a little Mohr's salt, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, in a few drops of water. In each of the following experiments place in a depression of the spot plate 1 drop of this solution of Fe^{++} and in the adjacent depression 1 drop of the test solution of Fe^{+3}. Conduct all the experiments by adding a drop of the reagent to the Fe^{++} solution and immediately thereafter another drop to the Fe^{+3} solution. Record carefully all observed differences in the behaviour of the two ions. Observe and record colors *carefully*. Write balanced ionic equations for *all* reactions.

Experiment 1. Action of NH_3. To each solution add 1 drop of $6N$ NH_3. Stir thoroughly until the two precipitates have the same appearance. Account for the various color changes of the Fe^{++} precipitate. To each then add 3 drops of $6N$ NH_3. Does Fe^{+3} appear to form a complex ion such as $[Fe(NH_3)_6]^{+3}$?

Experiment 2. Action of NaOH. To other drops of the Fe^{++} and the Fe^{+3} solutions add 1 drop of NaOH solution. Stir thoroughly. Do the same color changes as in experiment 1 take place in the Fe^{++} precipitate? Is the rate of change slower or faster? To the precipitates add 3 drops more of NaOH and stir. Does "ferric hydroxide" appear to be amphoteric like the "hydroxides" of Al and Cr?

Experiment 3. Action of hydrosulfide ion. In each of 3 test tubes place 2 drops of *colorless*[3] NH_4HS. To one tube add a drop of Fe^{++} test solution, to a second tube add a drop of Fe^{+3} test solution. Is there any difference in the appearance of the two precipitates? Would you expect them to have the same formula? Acidify the contents of each of the *three* tubes with a few drops of $1N$ HCl and stir. Is there distinctly more turbidity in one of the iron solutions than in the "blank"?

By writing equations show that (assuming the absence of persulfide ions in the NH_4HS) one of the sulfides should dissolve in acid without residue while the other should leave a turbidity. What would a small turbidity in the "blank" indicate about the composition of the NH_4HS?

Experiment 4. Action of thiocyanate ion. To adjacent drops of the two test solutions add 1 drop of $3N$ HCl and 1 drop of KNCS reagent. Account for what is seen. Stir the Fe^{++} solution vigorously and see whether the color deepens. Explain. Place 1 drop

[3] For the reasons stated on page 353, it is absolutely essential that the reagent be colorless.

of $3N$ HCl on the spot plate and add a drop of KNCS reagent. Any tinge of color?

Experiment 5. Action of cyanoferroate ion. To each of the test solutions add 1 drop of $3N$ HCl and 1 drop of $K_4Fe(CN)_6$ reagent. Note the difference of color. Stir the Fe^{++} precipitate for some time and see whether the color becomes like that of the Fe^{+3} precipitate. Explain.

Experiment 6. Action of cyanoferriate ion. Repeat experiment 5, using as reagent a solution prepared by dissolving a small crystal of $K_3Fe(CN)_6$ in 3 or 4 drops of water. Read pages 150–152.

Tabulate in 3 columns, reagent, Fe^{++}, Fe^{+3}, the formulas and colors of the compounds and ions observed in experiments 1 to 6. Underline precipitates.

From your observations in experiments 4, 5, and 6 state how you would proceed to find out whether an unknown solution contained Fe^{++} or Fe^{+3}. Do the results indicate that solutions of ferrous salts are likely to be entirely free from Fe^{+3}?

Ions of Manganese

[$Mn(H_2O)_6^{++}$ (for brevity, Mn^{++}), $MnCl_4^{=}$, $MnCl_6^{-3}$, $MnO_4^{=}$, MnO_4^{-}, and the like]

Study pages 248–251.

***Experiment 1. Valences of manganese.** On the spot plate place a drop of $0.1N$ potassium permanganate ($KMnO_4$) solution. What is the valence of Mn in MnO_4^{-}? Add drops of $6N$ NaOH and stir until the solution becomes green. What ion is in the green solution? What is the valence of Mn in the green ion? To the green solution add 1 drop Mn^{++} test solution. What is the black-brown precipitate formed? What is the valence of Mn in this compound? Again take 1 drop of $0.1N$ $KMnO_4$ solution and add to it NaOH till it becomes green. Stir the green solution with a rod which has been dipped into H_2O_2 solution (1 *drop* of H_2O_2 would cause a different reaction to take place). What color does the solution become? Does HO_2^{-} appear to have acted as reductant in this experiment? In these experiments you have seen Mn in how many different valences?

Manganous Ion

***Experiment 2. Action of NH_3.** On each of two adjacent depressions of a spot plate place 1 drop of Mn^{++} test solution. To

one of the drops add a drop of saturated NH_4Cl solution and stir. To both drops add a drop of $6N$ NH_3 and stir vigorously for some time. Do the two mixtures behave differently? Explain the difference.

***Experiment 3. Action of NaOH.** To 1 drop of Mn^{++} add 1 drop of $6N$ NaOH. Is the precipitate apparently different from either one obtained in experiment 2? Account for any difference.

Experiment 4. Action of hydrosulfide ion. To a drop of Mn^{++} test solution add a drop of NH_4HS reagent. The salmon-pink precipitate is very probably MnHSOH. Will the precipitate dissolve in AcOH?

Experiment 5. Action of "sodium bismuthate." To 2 drops of Mn^{++} test solution on the spot plate add 3 drops of $6N$ HNO_3 and a little solid $NaBiO_3$. Stir vigorously. Note that a purple solution forms. What ion does it contain?

Experiment 6. Action of sodium peroxide. To 2 drops of Mn^{++} test solution on the spot plate add 1 or 2 grains of Na_2O_2.

Cobalt and Nickel Ions

($[Co(H_2O)_6]^{++}$ (for brevity, Co^{++}), $[Co(NH_3)_6]^{++}$, $[CoCl_4]^{=}$, and the like; $[Co(NCS)_4]^{=}$, $[Co(CN)_6]^{-4}$, $[Co(CN)_6]^{-3}$, $[Co(NO_2)_6]^{-3}$, and many others; $[Ni(H_2O)_4]^{++}$ (for brevity Ni^{++}), $[Ni(NH_3)_4]^{++}$, $[Ni(CN)_4]^{=}$)

Study pages 251–259.

Experiment 1*a*. Action of NH_3. In each of two adjacent depressions of the spot plate place 1 drop of Co^{++} test solution. To one add a drop of saturated NH_4Cl solution and stir. Then add to each solution 1 drop of $6N$ NH_3. Note and explain (using balanced ionic equations) observed differences in the behavior of the two solutions. After one minute stir both solutions vigorously to introduce atmospheric oxygen. Do both solutions behave alike with respect to this reagent? Let the mixtures remain on the spot plate for comparison with Ni^{++} in the following experiment.

Experiment 1*b*. Repeat experiment 1*a*, using Ni^{++} test solution instead of Co^{++} solution. Does atmospheric oxygen have any effect on the products of the reactions? In what respects does the behavior of Ni^{++} toward NH_3 resemble and in what respects does it differ from that of Co^{++}?

***Experiment 2*a*. Action of strong bases.** In a *test tube* place 1 drop of the Co^{++} test solution. To it add 2 drops of $6N$ NaOH.

Note color of the precipitate as first formed and after warming. Is $Co(OH)_2$ amphoteric? Does it change color in contact with air? Does it resemble in this respect Fe^{++} and Mn^{++}? Centrifuge the precipitate, wash twice with warm water, remove washings as completely as possible, and warm the residue with a few drops of saturated NH_4Cl solution. Does it dissolve? Explain.

***Experiment 2*b.** Repeat experiment 2*a*, using 1 drop of Ni^{++} test solution instead of Co^{++} solution. In what respects does the behavior of Ni^{++} in this experiment resemble that of Co^{++} and in what respects does it differ from it?

Experiment 3*a*. Action of hydrosulfide ion. In a centrifuge tube place 2 drops of Co^{++} test solution. To it add a drop of NH_4Cl solution, then 1 or 2 drops of NH_4HS reagent. Stir, test for complete precipitation, and then centrifuge. Wash the precipitate twice, each time with 4 drops of water containing a little NH_4Cl solution. Remove washings as completely as possible, and place on the sulfide residue 2 or 3 drops of 1 *N* HCl. Stir but do not warm. Does CoS appear to pass into solution to any extent?

Experiment 3*b*. Repeat experiment 3*a*, using Ni^{++} test solution instead of Co^{++} solution. Does the solubility of NiS appear to resemble closely that of CoS or to differ decidedly from it?

Experiment 4*a*. Action of dimethylglyoxime. To one drop of the test solution of Co^{++} on the spot plate add 2 drops of dimethylglyoxime reagent. Does a precipitate form? Is a colored solution formed? Compare with Nickel Expt. 4*b*.

Experiment 4*b*. Repeat experiment 4*a*, using Ni^{++} test solution instead of Co^{++} solution.

***Experiment 5. Amphoteric properties of nickel glyoximine.** To 19 drops of water add 1 drop of Ni^{++} test solution and mix thoroughly. Place 1 drop of this very dilute solution (what fraction of a mg of Ni^{++}?) in each of 6 depressions of the spot plate. To the drops in depressions 2 to 6 add: to 2, 2 drops of 3 *N* HCl; to 3, 1 drop of 6 *N* AcOH; to 4, 1 drop of 6 *N* NaOH; to 5, 2 drops of 3 *N* NH_3; to 6, 1 drop of Co^{++} test solution. Stir thoroughly, being careful not to contaminate one mixture by another. Then add to each of the 6 solutions 1 drop of dimethylglyoxime. Compare the results in solutions 2 to 6 with that in 1. In which ones does the red salt fail to form? Does this salt appear to be stronger as a base or as an acid? What precautions must be taken if a trace of Ni^{++} is to be precipitated by this reagent?

Experiment 6*a*. Action of thiocyanate ion. In a test tube place 1 drop of Co^{++} test solution. To it add 6 drops of KNCS reagent, 4 drops of amyl alcohol, and 2 drops of ether. Shake vigorously to mutually saturate the two liquid layers. Cool the mixture under the tap as much as possible. Then add 2 or 3 drops of 12*N* HCl. Shake vigorously. Compare color in the alcohol-ether layer with that in the water layer. If the alcohol-ether layer is purplish or reddish (presence of $[Fe(NCS)_6]^{-3}$) add a tiny crystal of $Na_2S_2O_3$ and shake. The color should become pure blue. This test is extremely delicate and will detect Co in many nickel salts.

***Experiment 6*b*. Detection of cobalt or iron, or both, in nickel salt.** Repeat experiment 6*a*, using 6 drops of Ni^{++} test solution. Does the test indicate presence of either Co^{++} or Fe^{+3} in the nickel solution? If no indication of Co^{++} is found, add to the mixture the smallest possible capillary drop of Co^{++} test solution, shake vigorously, and observe the effect.

***Experiment 7*a*. Action of cyanide ion.** In a crucible place 4 drops of the Co^{++} test solution. To it add KCN reagent dropwise with stirring until the precipitate (color?) first formed dissolves. The solution contains brown $[Co(CN)_6]^{-4}$. Warm gently, stir the solution for 2 or 3 minutes, and note whether it changes color. After the oxidation is complete, the solution contains only yellow $[Co(CN)_6]^{-3}$. This ion is much more stable than cyanocobaltoate ion. Reserve for experiment 7*b*.

***Experiment 7*b*. Detection of nickel in cobalt salt.** Dilute the solution prepared in experiment 7*a* with water to about 1 ml. Dilute 4 drops of this solution to 1 ml. Add 1 drop of dimethylglyoxime reagent, stir thoroughly, then add $AgNO_3$ solution dropwise with stirring after each drop until a small permanent white or pink precipitate results. A pure white precipitate, $Ag[Ag(CN)_2]$ or $Ag_3[Co(CN)_6]$, will indicate absence of Ni^{++} in the Co^{++} solution. If the precipitate is tinged with pink, presence of nickel is proved. Write equations for all reactions involved after studying pages 257, 258.

***Experiment 8. Action of thiocyanatomercurate ion.** Place on the spot plate 1 drop of Co^{++} test solution and to it add 1 drop of $K_2[Hg(NCS)_4]$ solution. Stir vigorously. The deep blue precipitate is $Co[Hg(NCS)_4]$.

***Experiment 9. Action of cyanoferroate ion.** To 2 drops of the Co^{++} test solution on a spot plate add 1 drop of $K_4[Fe(CN)_6]$

reagent. Compare color with that given by the same reagent with Fe^{+3} ion. *Important!*

Ions of Zinc

($[Zn(H_2O)_4]^{++}$ (for brevity, Zn^{++}), $[Zn(NH_3)_4]^{++}$, $[HZn(OH)_4]^-$)

Study pages 259, 260.

Experiment 1. Action of NH_3. Place 2 drops of Zn^{++} test solution in each of two test tubes. To one add a drop of saturated NH_4Cl solution. Stir and then add to both solutions 1 drop 6*N* NH_3. Is there any difference between the two results? If a precipitate forms in either tube, see whether more NH_3 will dissolve it. Compare the behavior of $Zn(OH)_2$ toward excess of NH_3 in this reaction with that of AlOOH in experiment 1, aluminum, and account for any observed difference.

Experiment 2. Action of strong bases. To 2 drops of the Zn^{++} test solution add 1 drop of 1*N* NaOH. If a precipitate forms add 6*N* NaOH dropwise until it dissolves. Is $Zn(OH)_2$ amphoteric? Does it resemble AlOOH in this respect? Write equations for all reactions.

Experiment 3. Action of hydrogen sulfide. In each of two test tubes place 2 drops of Zn^{++} test solution. To one add 2 drops of 0.3*N* HCl and to the other 2 drops of 6 *N* AcOH. Saturate both solutions with H_2S. Explain, using the solubility product principle and the common ion effect (Chapter 8), why $Zn(HS)_2$ precipitates in a concentration of acetic acid much greater than that of the HCl.

Experiment 4. Action of hydrosulfide ion. To 2 drops of the Zn^{++} test solution in a test tube add a drop of NH_4Cl solution and dilute to 1 ml. Add 1 drop of NH_4HS solution. Test for complete precipitation. Centrifuge. Discard centrifugate and wash precipitate twice with water containing NH_4Cl. What is the purpose of the NH_4Cl? Remove washings as completely as possible. Dissolve the ZnS in the least number of drops of 1*N* HCl. Boil out H_2S and use the solution for the following experiment.

Experiment 5. Coprecipitation of cobalt thiocyanatomercurate with zinc thiocyanatomercurate. On a spot plate place two drops of the Zn^{++} solution prepared in the preceding experiment. In an adjacent depression place 2 drops of water. To each solution add 1 drop of 0.02% Co^{++} solution and 1 drop of $K_2[Hg(NCS)_4]$ solution and stir each with a glass rod for 15 seconds. Note how much more

quickly a pale blue precipitate appears in the solution containing Zn^{++} than in the blank. This is an extremely delicate test for Zn^{++}. It has detected Zn^{++} in salts where its presence was not suspected. What would be observed if a *considerable* concentration of Co^{++} were in the Zn^{++} salt?

Review Questions

1. Which ions of Group III are completely precipitated by NH_3 in presence of NH_4^+?

2. Which ions are precipitated incompletely or not at all by NH_3 in presence of considerable NH_4^+?

3. Which ions form ammonocomplex ions?

4. Why are the other ions listed in answer 2 not, or only incompletely, precipitated in the conditions there specified?

5. What are the formulas and colors of products formed by NH_4HS?

6. Which of the hydroxides show amphoteric properties?

7. Formulas and colors of solid compounds or ions formed by Na_2O_2 with each of the ions?

8. Why do Co^{++} and Ni^{++}, the sulfides of which are very slowly soluble in $1N$ H^+, escape precipitation by H_2S in Group II where $C_{H^+} = 0.3N$?

Practice Analysis of an Unknown Solution Containing only Ions of Group III

Examine, pages 197–199, desirable form of notebook record.

Procure 1 ml of an unknown solution which may contain any of the ions of Groups III and IV and in addition $H_2AsO_4^-$ and $H_2PO_4^-$.

Follow Table 18, page 319, and directions on pages 319–325.

As soon as each ion of Group III is *proved* absent or present, check result with laboratory instructor to learn whether you have correctly followed and interpreted the systematic procedure. Group IV ions need not be tested for.

Analysis of an Unknown Mixture of Ions of Group III

Procure and analyze an unknown for ions of Group III only. Note carefully and record whether the NH_4HS precipitate (group

ppt.) is large, medium, or small. The individual amounts reported should total approximately the amount noted for the group precipitate.

IONS OF CATION GROUP II, THE HYDROGEN SULFIDE GROUP

Subgroup II-B: Arsenious, Mercuric, Antimony, Stannic
Subgroup II-A: Lead, Bismuth, Copper, Cadmium

This analytical group is characterized by the insolubility of the sulfides in $0.3\,N$ H^+. For reasons discussed elsewhere, the sulfides of the elements in Subgroup B are soluble in NaHS and NaOH, while those of the Subgroup A are insoluble in this reagent. Bi_2S_3, however, occasionally dissolves to a slight extent.

Making the Solution Approximately $0.3\,N$ in H^+

For the precipitation of Group II it is necessary that the C_{H^+} be very close to $0.3\,N$. Experiments have proved that at this C_{H^+} PbS and CdS (most soluble of the Group II sulfides) will be practically quantitatively precipitated, while large amounts of Zn^{++} (most insoluble of the Group III sulfides) will not give a precipitate. To make the C_{H^+} in a solution sufficiently close to $0.3\,N$ the following procedure is recommended.

Modified Methyl Orange Indicator (M.M.O.) is red-violet in acid solution and blue-green in basic solution. The color changes sharply at *p*H 3.8 ($C_{H^+} = 1.6 \times 10^{-4}\,M$). When the addition of 1 *capillary* drop of $3\,N$ HCl changes the solution from blue-green to some shade of red, the solution is so slightly acid that upon adding 2 drops (20 drops/ml) of $3\,N$ HCl for each ml. of solution, the resulting solution is nearly enough $0.3\,N$ in H^+ to be suitable for precipitation of Group II sulfides.

Two characteristics of the indicator must be remembered. It is quickly destroyed in hot solution by strong oxidants ($Cr_2O_7^=$, NO_3^-, ClO_3^-); more slowly destroyed in cold. Hence, if such ions are present they must be removed by adding 3 drops of $12\,N$ HCl and evaporating the solution just to dryness. The residue is then stirred up in 1 ml of water.

As a basic dye M.M.O. is adsorbed on the acid sulfides, As_2S_3, Sb_2S_3, and SnS_2, and modifies their colors when first precipitated. This, however, constitutes no interference in analysis since the dye is destroyed when the II-B precipitate is heated with $12\,N$ HCl,

The student should familiarize himself with the properties of this indicator by performing the following experiments.

Experiment 1. In a test tube place 1 ml of distilled water. To it add 1 drop of M.M.O. indicator. Is the *p*H of the distilled water greater or less than 3.8? Prepare very dilute solutions of acid and base as follows: In each of two test tubes place 1 ml of distilled water. To one add 2 drops of $3N$ HCl, to the other 1 drop of $6N$ NH_3 and stir both thoroughly. Now add to the indicator solution in the first tube *capillary* drops of the very dilute HCl, stirring after each drop, until the color just changes to violet-red. Now add 1 *capillary* drop of the very dilute NH_3. The color should become green. Again add a capillary drop of HCl and observe the change. Again add NH_3. Repeat the alternate additions of HCl and NH_3 until the color on either side of the change point is firmly fixed in mind.

Experiment 2. In one centrifuge tube place 1 ml of Zn^{++} test solution, in another 3 drops of Cd^{++} test solution and 17 drops of water, in a third 3 drops of Sb^{+3} test solution and 17 drops of water. Add $3N$ HCl dropwise with stirring until the precipitate redissolves. To each of the three solutions add 1 drop of M.M.O. Is the *p*H of each solution greater or less than 3.8? Counting the number of drops added, use the very dilute HCl or NH_3 to bring each solution to the change point of the indicator. If a precipitate forms on neutralization, centrifuge and, without removing the precipitate, add very dilute NH_3 or HCl to the liquid until the indicator changes color. Now add to each solution 2 drops (20 drops = 1 ml) of $3N$ HCl for each ml of solution. Stir thoroughly and saturate the three solutions with H_2S. Does any ZnS precipitate? Is it evident that H_2S can react with solid compounds of Sb^{+3}? (Compounds of BiO^+ react similarly.) Centrifuge the Cd tube. Pipet off the liquid into a test tube, add 4 drops of water, and saturate again with H_2S to make sure of complete reaction. When H_2S gives no more precipitate, add a drop of NH_3 to the solution. Was the Cd^{++} practically completely precipitated by H_2S in $0.3N$ H^+?

Experiment 3. Prepare 3 test tubes, one containing 1 ml of $CrCl_3$ test solution, one containing 1 ml of cobalt test solution, and one containing 1 ml of chromate test solution to which 1 drop of $3N$ HCl has been added. Note and record colors. To each solution add 1 drop of M.M.O. Note and record colors. Now add to each tube 1 *capillary* drop of $6N$ NH_3 solution. Note and record colors. If any solution has not become blue-green, add more

capillary drops of $6N$ NH_3 until it is blue-green. Now add to each tube capillary drops of $3N$ HCl stirring after each addition until each solution shows some shade of red on looking down through it. For comparison, one ml of the original solution *without indicator* should be placed beside the solution containing the indicator. Each of the solutions will now become nearly enough $0.3N$ in H^+ when 2 drops of $3N$ HCl for each ml are added. Make sure that you learn to recognize the color changes of the indicator in the presence of these interfering colored ions.

Alternate procedure for making the solution $0.3N$ in H^+. When the presence of strongly colored ions or strong oxidants makes M.M.O. unusable, the following alternate procedure is recommended. Evaporate 1 ml of the known or unknown solution, or the filtrate from Group I, on a water bath to about 1 drop. Add 3 drops of $3N$ HCl and stir for one minute. Add 9 drops of water and stir thoroughly. Transfer with a pipet as completely as possible to a centrifuge tube. Rinse out the crucible twice with 4 drops of water at a time and transfer the washings to the centrifuge tube. If the solution is not perfectly clear, centrifuge and transfer the clear liquid to another centrifuge tube. Treat the residue[4] with 3 drops of $3N$ HCl, warm, and stir thoroughly until the residue has dissolved. Add 17 drops of water. Combine the two solutions and precipitate Group II ions by H_2S.

Ions of Arsenic

($[AsCl_4]^-$, $[As(OH)_4]^-$, $HAsO_4^=$, and the like)

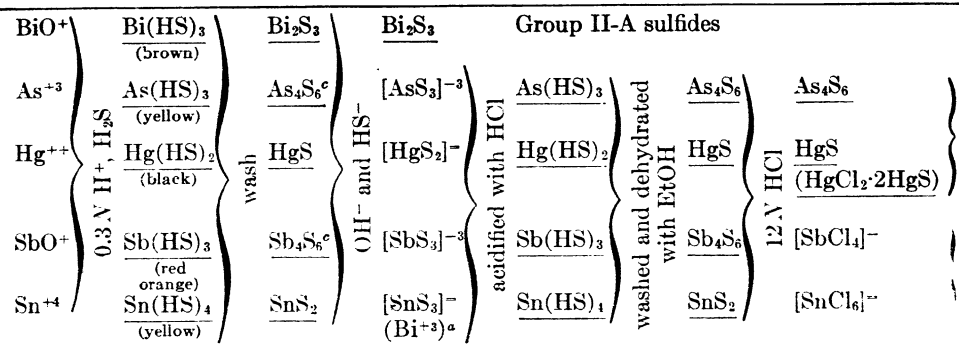
Study pages 222–226.

As an element standing three places before an inert gas, arsenic should tend strongly to complete its octet by covalence. As the next higher analog of phosphorus in Periodic Group V, tervalent arsenic shows a slight tendency to form a cation AsO^+ but almost none to form cations containing As^{+5}. H_3AsO_4 is very close to H_3PO_4 and HSO_4^- in strength. The ion $H_2AsO_4^-$ is extremely stable, and oxide ions are removed from it only by very high C_{H^+}.

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[4] The evaporation to a volume of 1 drop may have caused formation of hydroxides or basic salts of Group III which become difficultly and slowly soluble after being heated. Dilution of $3N$ HCl to $0.3N$ is likely to cause BiOCl and SbOCl to precipitate. The precipitation of these basic salts of Group II is not objectionable since H_2S will change them to sulfides.

TABLE 13
PRECIPITATION AND ANALYSIS OF GROUP II-B



$\left\{\begin{matrix}\underline{As_4S_6}\\ \underline{HgS}\\ \underline{(HgCl_2\cdot 2HgS)}\ \text{(wh. or yl)}\end{matrix}\right\}$ $\xrightarrow{NH_3}$ Soln. $AsS_3^{-3} + HCl$ and $H_2S \rightarrow \underline{As(HS)_3}$ (yellow, proof of As^{+3})
$\underline{HgS}$ (black, proof of Hg)

$\left\{\begin{matrix}[SbCl_4]^-\\ [SnCl_6]^-\end{matrix}\right\}$ $\xrightarrow{H_2C_2O_4}$ $\left|\begin{matrix}Sb^{+3}\\ [Sn(C_2O_4)_3]^-\end{matrix}\right.$ $\xrightarrow{H_2S}$ $\underline{Sb(HS)_3}$ (red-orange, proof of Sb)

$[Sn(C_2O_4)_3]^-$ $\xrightarrow{HNO_3,\ H_2SO_4,\ \text{boil}}$ Sn^{+4} $\xrightarrow{H_2S}$ $\left\{\begin{matrix}\underline{Sn(HS)_4}^b\ \text{(yellow)}\\ \underline{(Bi(HS)_3)}\ \text{(brown)}\end{matrix}\right.$ $\xrightarrow{NH_4HS}$ $[SnS_3]^- + H^+ \rightarrow \underline{Sn(HS)_4}$ (yellow, proof of Sn^{+4})
$\underline{(Bi_2S_3)}$

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[a] A little Bi_2S_3 sometimes dissolves here. It will follow Sn^{+4} through the subsequent step.
[b] If precipitate here is dark colored, it should always be extracted with NH_4HS.
[c] X-ray methods indicate these molecules in completely aged sulfides. As_2S_3 and Sb_2S_3 may well be intermediate compounds.

Experiment 1. Action of H_2S on H_3AsO_4 in small C_{H^+}. In a test tube prepare 1 ml of 0.3*N* HCl. To it add 2 drops of H_3AsO_4 test solution. Saturate the solution with H_2S. Does any sign of reaction appear? Heat the solution nearly to boiling and again saturate with H_2S. Does a white turbidity (sulfur) appear? Is much *yellow* precipitate (As_2S_3 or As_2S_5) formed?

Experiment 2. Action of H_2S on arsenious acid in small C_{H^+} and large C_{H^+}. Using centrifuge tubes instead of test tubes, repeat experiment 1, using 2 drops of the $[AsCl_4]^- \rightleftharpoons AsO^+$ test solution instead of the H_3AsO_4 test solution. Is As_4S_6 readily precipitated in small C_{H^+}? In another centrifuge tube place 1 ml of 12*N* HCl. To it add 2 drops of As^{+3} test solution, heat to boiling, and saturate with H_2S. Centrifuge the two precipitates and discard the centrifugates. Is any difference in shade of color or in grain size perceptible? Wash the precipitates twice with water containing a little HCl. Remove washings as completely as possible. Use the precipitates for experiment 3.

Experiment 3. Action of OH^- and HS^- on the sulfides of arsenic. To the precipitates (experiment 2) add 2 drops of 6*N* NaOH and stir. Unite the two solutions. Use in experiment 4.

Experiment 4. Action of hydrogen ion on thio-anions. To the combined solutions (experiment 3) add 2 drops of NaHS and stir. Then add 3*N* HCl dropwise with stirring until the solution is slightly acid. Why was the NaHS added, although the sulfides were already in solution? Centrifuge. Discard centrifugate. Wash as above with water containing a little HCl. Use for experiment 6.

Experiment 5. Action of 12*N* HCl on the sulfides of arsenic. Judging from the ready precipitation of As_2S_3 in 12*N* HCl (experiment 2), would you expect the precipitate obtained in the preceding experiment 4 to dissolve in 12*N* HCl? An experiment need not be tried at this time.

Experiment 6. Action of NH_3 on sulfides of arsenic. To the precipitate obtained in experiment 4 add 4 drops of 15*N* NH_3. Stir and warm slightly if necessary. Does the precipitate readily dissolve? (Separation from HgS.)

Experiment 7. Reduction of arsenites or arsenates to arsenic—the Bettendorf test. Half fill a small test tube with crystals of stannous chloride ($SnCl_2 \cdot 2H_2O$). Nearly fill the tube with 12*N* HCl and stir for some time. Divide this reagent ($H_2[SnCl_4]$) among 3 test tubes. To one tube add a drop of a solution prepared by

diluting 2 drops of H_3AsO_4 test solution with 8 drops of water. What fraction of a mg of arsenic will be in 1 drop of this solution? To another tube add 1 drop of a solution of $[AsCl_4]^-$ of the same concentration (1.0 mg per ml) as the H_3AsO_4 solution. Stir both mixtures thoroughly. The third tube is for comparison (the "blank"). Note the time required for a yellow color more intense than that of the blank to appear in each tube. The color is due to colloidal As^0. Higher concentrations may give brown suspensions. Very small amounts of As as H_3AsO_4 may require one hour for color to become clearly deeper than that of the blank.

This test is said to detect 0.03 mg of As in arsenite and 0.06 mg in arsenate. What fraction of a mg was present in your tests? The compounds of Hg, Ag, and Bi are also reduced to the metals and must be absent. Sb does not interfere.

Ions of Mercury

(Hg_2^{++}; Hg^{++}, $[HgS_2]^=$, $[HgCl_4]^=$, $[HgI_4]^=$, $[Hg(NCS)_4]^=$, and the like)

Study pages 219–222.

Experiment 1. Action of H_2S on $HgCl_2$. In one test tube place 1 ml of 0.3 *N* HCl. In each of two other test tubes place 1 ml of 12 *N* HCl. To each tube add 2 drops of $HgCl_2$ test solution. Saturate one of the 12 *N* HCl solutions with H_2S without heating. Heat the other two tubes nearly to boiling and saturate with H_2S. Is HgS precipitated in cold 12 *N* HCl? Is it precipitated from hot 12 *N* HCl? Would you judge that $HgCl_2 \cdot 2HgS$ was more soluble or less soluble than As_4S_6? Compare results with values of $K_{s.p.}$ in Table 5, page 110. Collect all precipitates obtained in this experiment, wash the combined precipitates thoroughly, and use for experiment 2.

Experiment 2. Action of HS^- and OH^- on mercuric sulfide. To the washed precipitates (experiment 1) add 2 drops of 6 *N* NaOH and stir thoroughly. Does the precipitate dissolve? Is HgS amphoteric like As_2S_3? Add 2 drops of NaHS solution and stir, warming if necessary. Does the precipitate now dissolve completely? Reserve the solution for experiment 3.

Experiment 3. Action of hydrogen ion on thiomercurate anion. To the solution (experiment 2) add 3 *N* HCl dropwise with stirring until the solution is slightly acid. What gas is formed? Centrifuge Wash twice with 0.3 *N* HCl, removing washings as completely as possible. Place on the precipitate 1 ml of ethyl alcohol, stir

thoroughly, and let stand five minutes. Remove the alcohol as completely as possible. Use the residue for experiment 4.

Experiment 4. Action of hot 12 *N* HCl on HgS. To the residue add 5 drops of 12 *N* HCl. Place in a nearly boiling water bath and stir for two minutes. Saturate again with H_2S. Does any HgS appear to dissolve? Does the black precipitate turn white? What compound is formed? (Separation of Hg and As from Sb and Sn.) Remove the liquid as completely as possible and wash the residue once with water. Discard washings. Use the residue for experiment 5.

Experiment 5. Action of NH_3 on HgS and on $HgCl_2 \cdot 2HgS$. To the residue add 3 drops of 6 *N* NH_3. Does the residue become black? Does it dissolve? (Separation of Hg from As.) Remove the ammonia as completely as possible. Transfer part of the residue to a crucible and use for experiment 6.

Experiment 6. Confirmatory test for Hg. To part of the black residue from experiment 5 add 5 drops of 12 *N* HCl and a small crystal of $KClO_3$. Heat and stir until nearly all the black sulfide has dissolved and only a little sulfur remains. Make sure that all Cl_2 has been removed from the solution, since this will interfere with the test. Do not evaporate to dryness. $HgCl_2$ is somewhat volatile. Take up the residue with 2 or 3 drops of 3 *N* HCl. Pour into 1 ml of $H_2[SnCl_4]$ reagent and stir vigorously. A white precipitate, frequently having a silky appearance, is Hg_2Cl_2. If the precipitate is gray, Hg^0 (black) also has been formed.

Experiment 7. Action of 3 *N* HNO_3 on HgS. In a crucible treat the rest of the black residue from experiment 5 with 5 drops of 3 *N* HNO_3 and boil. Does HgS dissolve? (Separation of HgS from Group II-A sulfides.) (Does it become white?)

Ions of Antimony

(SbO^+, $[SbCl_4]^-$, $[Sb(OH)_6]^-$, and the like)

Study pages 226–229.

Experiment 1. Action of H_2S. In a centrifuge tube place 1 ml of 0.3 *N* HCl. To it add two drops of Sb^{+3} test solution and saturate with H_2S. Centrifuge, wash precipitate with 0.3 *N* HCl, and use for experiment 2.

Experiment 2. Action of OH^- and HS^-. To the precipitate obtained in experiment 1 add two drops of 6 *N* NaOH and stir. Does the precipitate dissolve completely? Is Sb_2S_3 amphoteric like

As_2S_3? Add two drops of NaHS solution and stir. Use the resulting solution for experiment 3.

Experiment 3. Action of hydrogen ion on thioantimonite ion. To the solution from experiment 2 add $3N$ HCl dropwise with stirring until the solution is slightly acid. What gas is evolved? Centrifuge. Wash twice with $0.3N$ HCl removing washings as completely as possible. Place on the precipitate 1 ml of ethyl alcohol, stir thoroughly, and let stand 5 minutes. Remove the alcohol as completely as possible. Use the residue for experiment 4.

Experiment 4. Action of hot $12N$ HCl on Sb_2S_3. To the dehydrated residue from experiment 3 add 5 drops of $12N$ HCl. Place in a nearly boiling water bath and stir for two minutes. Saturate again with H_2S. Does the precipitate dissolve readily and completely? (Difference from As_2S_3 and HgS.)

Experiment 5. Action of Sb^{+3} on phosphomolybdic acid. Boil the solution of $[SbCl_4]^-$ (experiment 4) to remove H_2S. Add 5 drops of water. Spot a strip of filter paper in two places with a drop of phosphomolybdic acid solution. Warm till the spots are nearly dried. On one spot place a drop of $3N$ HCl (the blank) on the other a drop of the test solution. Hold the paper in steam for a few moments. If antimony is present, a blue color, more or less intense according to the amount of Sb^{+3} present, will result in a short time. Tin does not interfere with the test because it is present in quadrivalent form.

Experiment 6. Action of oxalic acid. To the rest of the solution from experiment 4 add oxalic acid, a crystal at a time, until the solution is saturated. Saturate with H_2S. Orange-red precipitate is Sb_2S_3 (separation from Sn). If a complex such as $[Sb(C_2O_4)_2]^-$ is formed, can it be very stable?

Ions of Tin

(Sn^{++}, $[SnCl_4]^=$, $[HSn(OH)_4]$; $[SnCl_6]^=$, $[Sn(OH)_6]^=$, and the like)

Study pages 229–231.

Experiment 1. Action of H_2S. In a centrifuge tube place 1 ml of $0.3N$ HCl. To it add two drops of Sn^{+4} test solution and saturate with H_2S. Centrifuge, wash precipitate with $0.3N$ HCl, and use for experiment 2.

Experiment 2. Action of OH^- and HS^-. To the precipitate obtained in experiment 1 add two drops of $6N$ NaOH and stir. Does the precipitate dissolve completely? Is SnS_2 amphoteric like

As_2S_3? Add two drops of NaHS solution and stir. Use the resulting solution for experiment 3.

Experiment 3. Action of hydrogen ion on thiostannate ion. To the solution from experiment 2 add 3 *N* HCl dropwise with stirring until the solution is slightly acid. What gas is evolved? Centrifuge. Wash twice with 0.3 *N* HCl, removing washings as completely as possible. Place on the precipitate 1 ml of ethyl alcohol, stir thoroughly, and let stand 5 minutes. Remove the alcohol as completely as possible. Use the residue for experiment 4.

Experiment 4. Action of hot 12 *N* HCl on SnS_2. To the dehydrated residue from experiment 3 add 5 drops of 12 *N* HCl. Place in a nearly boiling water bath and stir for two minutes. Saturate again with H_2S. Does the precipitate dissolve readily and completely? (Difference from As_2S_3 and HgS and similarity to Sb_2S_3.) Reserve the solution for experiment 6.

Experiment 5. Action of ammonium phosphomolybdate on Sb^{+3}, Sn^{+4}, and Sn^{++}.

(*a*) *Preparation of test paper.* Spot a strip of filter paper in two places with a drop of phosphomolybdic acid. Expose the spots to fumes from 15 *N* NH_3 until they become colorless because of formation of $(NH_4)_2HPO_4$ and $(NH_4)_2MoO_4$. When later the spots are acidified, yellow $(NH_4)_3[P(Mo_3O_{10})_4]$ is reformed.

(*b*) In a test tube place 1 drop each of Sb^{+3} and Sn^{+4} test solution and 3 drops of 3 *N* HCl. Place a drop of this mixture on *one* of the spots prepared in (*a*). Notice that alternate green and yellow rings form *around* the spot leaving the interior colorless. The green color is probably due to a trace of molybdenum blue absorbed on the yellow molybdophosphate.

(*c*) To the remainder of the Sb^{+3}–Sn^{+4} solution add a few grains of magnesium powder which has been *proved* free from tin. Stir and allow to act for at least a minute. Sn^{++} is formed and most of the Sb^{+3} reduced to metal. Place a drop of this solution on the other spot. Molybdenum blue (approximately Mo_3O_8) appears almost instantly and does not diffuse outward from the spot.

Note: The metal used to reduce Sn^{+4} to Sn^{++} must be *proved* free from tin. In the Purdue laboratories tin was found in all samples of aluminum but none in magnesium. Tin was found in all the compounds of antimony available except potassium antimonate and tartar emetic. In all cases both the above test and the cacothelin test showed tin present.

Experiment 6. Action of oxalic acid. Boil the solution from experiment 4 to remove H_2S. Add 5 drops of water and saturate

with oxalic acid. Then saturate with H_2S. The complex, such as $[Sn(C_2O_4)_3]^=$, is so stable that with H_2S it gives no precipitate of SnS_2. Destroy the oxalate in a crucible by adding 5 drops of 36 *N* H_2SO_4 and 5 drops of 15 *N* HNO_3 and evaporating until dense fumes of SO_3 are evolved. *Do not evaporate to dryness.* Take up and add to 10 drops of water in a centrifuge tube, rinse crucible twice with 3 drops of water at a time, and add to the solution. Make neutral to litmus with NaOH, then make slightly acid with HCl. Saturate with H_2S. Yellow SnS_2 proves Sn. If $C_2O_4^=$ is not completely destroyed, a little brown-black SnS may be precipitated after the SnS_2. Use precipitate for experiment 7.

Experiment 7. Action of NH_4HS on SnS_2. Centrifuge and wash the SnS_2 (experiment 6). Extract twice with colorless NH_4HS using 5 drops each time. Centrifuge if a *dark* residue remains. Remove centrifugate and make it slightly acid with HCl. Pure yellow SnS_2 should now precipitate. (Separation from a possible trace of Bi_2S_3 and SnS.)

Practice Analysis of an Unknown Solution Containing only the Ions of Subgroup II-B and BiO^+

Procure 1 ml of an unknown mixture containing any of the ions of Subgroup II-B and in addition BiO^+. Follow Table 17, page 311 and directions on pages 312–318. Check each ion as usual with the instructor. The residue insoluble in NaHS and NaOH need not be analyzed.

Analysis of an Unknown Mixture

Procure and analyze an unknown. This unknown may contain any of the ions of Subgroup II-B and an ion of Subgroup II-A. The II-A residue need not be analyzed. Merely report whether or not Group II-A is present.

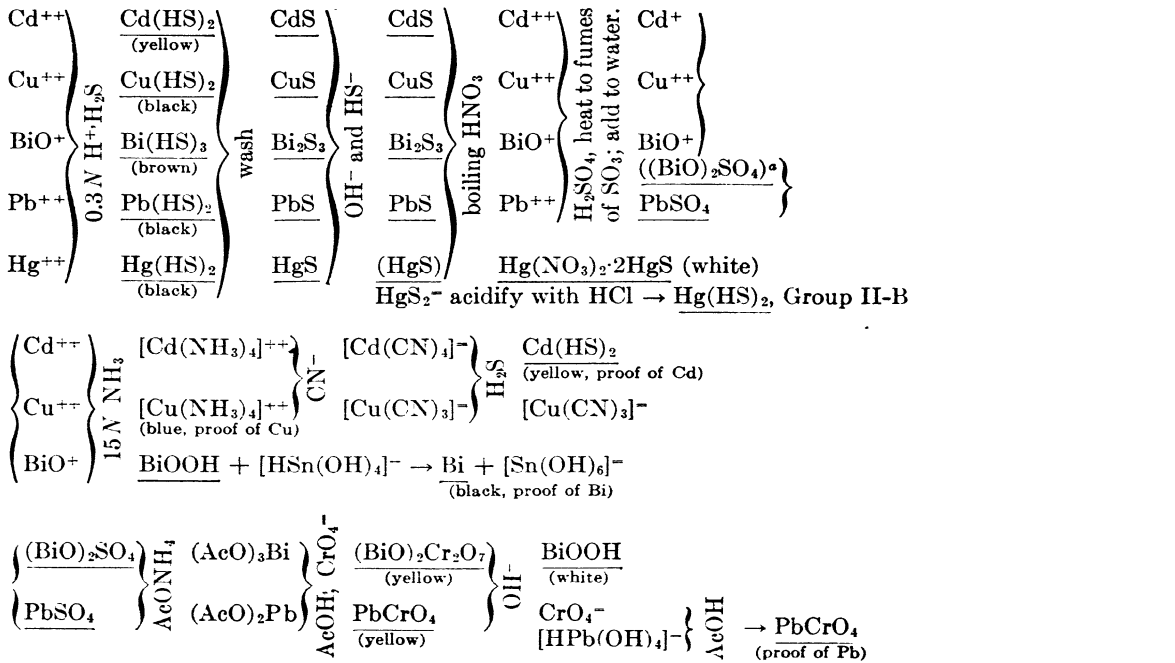
Ions of Lead

(Pb^{++}, $[HPb(OH)_4]^-$; $[PbCl_6]^=$ (unstable), $[Pb(OH)_6]^=$, and the like)

Study pages 210–213.

Experiment 1. Action of chloride ion. To 8 drops of Pb^{++} test solution add dropwise 3 *N* HCl, stirring after each drop, as long as precipitate forms. Centrifuge and transfer the liquid to a centrifuge tube and reserve for experiment 3.

TABLE 14
PRECIPITATION AND ANALYSIS OF GROUP II-A



a If too little H_2SO_4 is present, some Bi may precipitate here.

Experiment 2. Solubility of lead chloride. To the precipitate of $PbCl_2$ (experiment 1) add 10 drops of water, stir, and heat. Let the solution cool and note that $PbCl_2$ crystallizes out in needles.

Experiment 3. Action of H_2S. Neutralize the centrifugate from experiment 1. Make it slightly acid with HCl. Mix thoroughly and saturate with H_2S. Test for complete precipitation. Pipet off the centrifugate into a test tube and make it just alkaline with NH_3. A black color indicates incomplete precipitation of Pb^{++} as $Pb(HS)_2$ because of too large C_{H^+}. Wash the precipitate three times with water containing a little HCl, discarding washings. Use the residue for experiment 4.

Experiment 4. Action of HS^- and OH^- on PbS. To the washed precipitate (experiment 3) add 2 drops of NaHS and 2 drops of NaOH. Stir and warm. Centrifuge. Pipet off the liquid to a test tube and acidify it with $3N$ HCl to see if any PbS dissolved. Wash the PbS with $0.3N$ HNO_3 until the washings are no longer basic. Use the residue for experiment 5.

Experiment 5. Action of hot HNO_3 on PbS. To the PbS (experiment 4) add 4 drops of $3N$ HNO_3 and boil with constant stirring until only light-colored sulfur remains. Remove this. Transfer the liquid to a crucible and use it for experiment 6.

Experiment 6. Precipitation of $PbSO_4$. To the solution of $Pb(NO_3)_2$ (experiment 5) add 4 drops of conc. ($36N$) H_2SO_4; heat slowly and cautiously *in the hood* until dense, choking, white fumes of SO_3 are coming off rapidly. At this point all HNO_3 should have been destroyed. Not much more than a drop or two of liquid should remain. When the crucible is cold transfer the liquid to a small centrifuge tube in which 5 drops of water have been placed. Rinse out the crucible twice with 3 drops of water each time, making sure that any precipitates are completely transferred. Cool the centrifuge tube in the tap stream and stir vigorously 2 minutes. $PbSO_4$ tends to supersaturate and needs time and vigorous stirring to complete its precipitation. Let the tube stand five minutes. Centrifuge. Estimate the amount of Pb^{++} indicated by the volume of $PbSO_4$. Reserve the $PbSO_4$ for experiment 7. Remove the centrifugate to a test tube, make it just basic with ammonia, and add a capillary drop of NH_4HS. Does a dark color indicate incomplete precipitation of Pb^{++} as $PbSO_4$?

Experiment 7. Action of ammonium acetate on $PbSO_4$. To the $PbSO_4$ in the centrifuge tube add 3 drops of $AcONH_4$ solution. Warm and stir until precipitate dissolves. Use the solution for experiment 8.

Experiment 8. Action of chromate ion. To the solution of $(AcO)_2Pb$ add 2 drops of AcOH and a drop of K_2CrO_4 solution. Use the precipitate in experiment 9. The yellow precipitate at this point in systematic analysis is not absolute proof of Pb^{++} because $(BiO)_2Cr_2O_7$ having the same color may precipitate here.

Experiment 9. Action of NaOH on $PbCrO_4$ and on $(BiO)_2Cr_2O_7$. In a centrifuge tube place 4 drops of Bi^{+3} test solution. Add K_2CrO_4 solution until precipitation is complete. Centrifuge and discard liquid. To the $PbCrO_4$ (experiment 6) and to this $(BiO)_2Cr_2O_7$ add NaOH. Note that $PbCrO_4$ dissolves completely but $(BiO)_2Cr_2O_7$ slowly forms BiOOH and $CrO_4^{=}$. Centrifuge the Bi tube and transfer most of the liquid to a test tube. Now acidify both solutions with AcOH. Does any $(BiO)_2Cr_2O_7$ now precipitate?

Ions of Bismuth

$(Bi^{+3}, BiO^{+}, [BiCl_4]^{-})$

Study pages 213–215.

Experiment 1. Action of H_2S. To 10 drops of water add two drops of Bi^{+3} test solution. Stir thoroughly and saturate with H_2S. Note carefully the color of the precipitate. Centrifuge. Pipet off the centrifugate into a test tube and make it just alkaline with NH_3 to test for complete precipitation. Wash the precipitate 3 times with water containing a little HCl, discarding washings. Use the residue for experiment 2.

Experiment 2. Action of HS^{-} and OH^{-}. To the washed precipitate (experiment 1) add 2 drops of NaHS and 2 drops of NaOH. Stir and warm. Centrifuge and transfer the liquid to another centrifuge tube. Make it slightly acid with HCl and centrifuge. Notice very carefully whether any Bi_2S_3 dissolved in the NaHS and NaOH. Use the Bi_2S_3 which did not dissolve for experiment 3.

Experiment 3. Action of hot HNO_3 on Bi_2S_3. To the Bi_2S_3 residue (experiment 2) add 4 drops of $3N$ HNO_3 and boil with constant stirring until only light-colored sulfur remains. Remove this. Transfer the liquid to crucible and use for experiment 4.

***Experiment 4. Possible precipitation of $(BiO)_2SO_4$.** To the solution of $Bi(NO_3)_3$ (experiment 3) add 4 drops of $36N$ H_2SO_4 and heat slowly in the *hood* until dense white fumes of SO_3 are evolved. When the crucible is cold, transfer the liquid to a centrifuge tube which contains 5 drops of water. Rinse out the crucible twice with 3 drops of water, making sure that any precipitate is completely

transferred. Stir the solution vigorously and cool in a stream of tap water. If no precipitate forms use the liquid for experiment 5.

Experiment 5. Action of NH_3 on BiO^+. To the solution of $Bi_2(SO_4)_3$ add ammonia until, after vigorous shaking, the solution smells strongly of it. (Separation from Cu^{++} and Cd^{++}.) Centrifuge the precipitate of BiOOH. Remove the solution as completely as possible and to the precipitate add a drop of *colorless* $Na[HSn(OH)_4]$ solution. (This reagent is made by adding NaOH dropwise to 1 drop of reagent $H_2[SnCl_4]$ until the precipitate just redissolves, then 2 drops in excess.) *Instant* black color proves Bi. Consult footnote 2, p. 315.

Ions of Copper

(Cu^+, $[Cu(NH_3)_3]^+$, $[CuCl_3]^=$, $[Cu(CN)_3]^=$; $[Cu(H_2O)_4]^{++}$ (for brevity, Cu^{++}), $[Cu(NH_3)_4]^{++}$, $[Cu(CO_3)_2]^=$, and the like)

Study pages 215–218.

Experiment 1. Action of H_2S. To 10 drops of 0.3 *N* HCl add two drops of Cu^{++} test solution. Stir thoroughly and saturate with H_2S. Note carefully the color of the precipitate. Centrifuge. Pipet off the centrifugate into a test tube and make it just alkaline with NH_3 to test for complete precipitation. Wash the precipitate 3 times with water containing a little HCl, discarding washings. Use the residue for experiment 2.

Experiment 2. Action of SH^- and OH^-. To the washed precipitate (experiment 1) add 2 drops of NaSH and 2 drops of NaOH. Stir and warm. Centrifuge and transfer the liquid to another centrifuge tube. Make it slightly acid with HCl and centrifuge. Notice very carefully whether any CuS dissolved in the NaSH and NaOH. Use the CuS which did not dissolve for experiment 3.

Experiment 3. Action of hot HNO_3 on CuS. To the CuS residue (experiment 2) add 4 drops of 3 *N* HNO_3 and boil with constant stirring until only light-colored sulfur remains. Remove this. Transfer the liquid to crucible and use for experiment 4.

Experiment 4. Action of NH_3 on Cu^{++}. To the solution of Cu^{++} (experiment 3) add 6 *N* NH_3 till the solution smells strongly of it. Use the deep blue solution for experiment 5.

Experiment 5. Reduction of $[Cu(NH_3)_4]^{++}$ by CN^- and stability of $[Cu(CN)_3]^=$. To the blue solution (experiment 5) add KCN reagent dropwise with constant stirring until the color just disap-

pears. Then add 1 drop more. To the solution add 1 drop of NH_4HS reagent. Does black Cu_2S form?

Experiment 6. Detection of a trace of cupric ion. In a test tube place 1 drop of Cu^{++} test solution. To it add NH_3 until the precipitate dissolves. Place 1 drop of this solution in another test tube and dilute with water until no blue color can be seen on looking down through the solution. Place 1 drop of this solution on a spot plate. Add 1 drop of $6N$ AcOH. Stir and add 1 drop of 1% $(AcO)_2Zn$ and 1 drop of $0.3M$ $K_2[Hg(NCS)_4]$ solution. Stir for 15 seconds. Red-violet precipitate indicates a trace of Cu^{++}.

Ions of Cadmium

$([Cd(H_2O)_4]^{++}$ (for brevity, Cd^{++}), $[Cd(NH_3)_4]^{++}$, $[Cd(CN)_4]^{=}$, $[CdCl_4]^{=}$, $[CdI_4]^{=}$, and the like)

Study pages 218, 219.

Repeat experiments 1 to 5, copper, using 2 drops of Cd^{++} test solution in 10 drops of $0.3N$ HCl. In experiment 5 note that addition of CN^- to a solution containing $[Cd(NH_3)_4]^{++}$ forms $[Cd(CN)_4]^{=}$, sufficiently unstable so that HS^- precipitates $Cd(HS)_2$ from the solution. Centrifuge and examine the precipitate carefully. Is it the same shade of yellow as that obtained in experiment 1? $Cd(HS)_2$ precipitated here tends to be colloidal and to have an orange tint.

Practice Analysis of an Unknown Solution Containing Any of the Ions of Subgroup II-A and Hg^{++}

Procure 1 ml of an unknown mixture containing these ions. Follow Table 17, page 311, and directions on pages 312-316. Note carefully whether any HgS remains undissolved by HS^- and OH^- Check each ion with instructor as usual.

Analysis of an Unknown Containing Any of the Ions of Group II

Procure and analyze an unknown solution.

Review Questions

1. For the precipitation of Group II sulfides, why may not the solution be $0.6N$ in H^+? Why may it not be neutral (2 reasons)?

2. Calculate C_{HS^-} and $C_{S^=}$ in a solution 0.3 *M* in H^+ and saturated with H_2S. A saturated solution of H_2S in water is 0.1 *M*. Judging from the concentrations just calculated, would the ions of Group II be more likely to precipitate as sulfides or as hydrosulfides? Give the probable formula and the color of each of the products formed by H_2S in 0.3 *N* H^+.

3. Name the following ions or compounds: $[SbCl_4]^-$, $H[Sb(OH)_6]$, $HAsO_2$, $[AsCl_4]^-$, $H_2[SnCl_6]$, $(BiO)_2SO_4$, $[HgS_2]^=$, $[AsOS]^-$, $Cu(HS)_2$, $[Cu(CN)_3]^=$, $[Cd(CN)_4]^=$, $H_2[PbCl_6]$, $H_2[SnCl_4]$.

4. How would you proceed to find out whether a precipitate of $PbSO_4$ had any $(BiO)_2SO_4$ in it?

5. If all Pb^{++} is not completely removed as $PbSO_4$ in the systematic procedure, what compounds will it form in the tests for Bi^{+3}, Cu^{++}, and Cd^{++}?

6. If the final precipitate of CdS is brown instead of yellow, what should you do about it? What ion usually causes this discoloration?

7. If a *large* amount of Pb^{++} or Cd^{++} is present in a solution, why might some of it escape precipitation even though the solution is saturated with H_2S when precipitation ceases?

IONS OF CATION GROUP I, THE CHLORIDE GROUP

Ions of Lead

These ions are found in Group II, pages 210–213.

In semimicro analysis Pb^{++} precipitates in Group I only when it is present in unusually large amount and then only incompletely. Review experiments 1, 2, 8, and 9, pages 298–301.

Mercurous Ion, Hg_2^{++}

Study pages 208, 209.

Experiment 1. Action of chloride. To 2 drops of the test solution of $Hg_2(NO_3)_2$ add HCl until precipitation is complete. Centrifuge and discard the liquid. Use the precipitate for experiment 2.

Experiment 2. Solubility of mercurous chloride. To the precipitate of Hg_2Cl_2 add 10 drops of water. Stir thoroughly and heat. Centrifuge, remove the liquid, and saturate it with H_2S. Does any of the precipitate appear to have dissolved? Use residue for experiment 3.

Experiment 3. Action of NH_3 on Hg_2Cl_2. To the residue of Hg_2Cl_2 (experiment 2) add 1 or 2 drops of NH_3. A mixture of black Hg^0 and white $HgNH_2Cl$ is formed (test for Hg_2^{++}).

Ions of Silver

(Ag^+, $[AgCl_3]^-$, $[Ag(S_2O_3)_2]^{-3}$, $[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$, $[Ag(CN)_3]^-$, and the like)

Study pages 205–207.

Repeat experiments 1, 2, and 3, mercurous ion. In experiment 3 note the behavior of AgCl toward NH_3. Is it different from that of Hg_2Cl_2? To the solution of AgCl in NH_3 add HNO_3 until the solution is acid. What is the precipitate?

Review Questions

1. What would be formed if a mixture of Hg^0 and $HgNH_2Cl$ were treated with 6*N* HCl?

2. Read note 3, page 310. If 0.5 mg of AgCl were in 6 mg of Hg_2Cl_2, what reaction might take place when the mixture was treated with NH_3?

3. If a mixture of Hg^0, Ag^0, and $HgNH_2Cl$ were treated with 12*N* HCl and $KClO_3$, what compound would be formed by each of the three components of the mixture?

SUCCESSIVE REMOVAL FROM SOLUTION OF THE CATION GROUPS

In the preceding study of the reactions of the cations, Groups I to IV were considered in reverse order because in Groups IV, III, and II both analytical difficulties and the complexity of the chemistry involved increase in this order.

In systematic analysis the cations must be removed from the solution in the order Groups I, II, III, and IV, as shown in Table 15. The centrifugate from a Group I precipitate thus becomes the solution from which Group II is to be removed, the centrifugate from Group II the solution from which Group III is to be precipitated, and the centrifugate from the latter is to be tested for the Group IV ions, Ba, Sr, Ca, and Mg.

It is absolutely essential that each group in its turn be *completely* removed from the solution since no provision is made in succeeding groups for detecting ions of earlier groups and such ions may

seriously interfere with the analysis of groups to which they do not belong.

Practice Analysis of an Unknown Solution Containing Any of the Cations

Procure an unknown solution understood to contain no more than one ion of any group except Group II, of which two may be given.

Follow Table 15, page 307, and directions on pages 307–327 for analyzing each group precipitate.

Check with the instructor each ion as found.

Place 1 ml of the solution in a crucible on the water bath to obtain the residue to be tested for Na^+, K^+, and NH_4^+. While this solution is evaporating, take another ml of the solution and test for Group I, and so on.

Unknown Solution Containing Any of the Cations Studied

Procure and analyze an unknown solution.

CHAPTER 16

SYSTEMATIC ANALYSIS OF CATIONS

In this chapter are collected, for purposes of reference, outlines and specific directions for the successive removal of the cation groups from solution and the analysis of the group precipitates.

The preliminary examination, the preparation of materials for analysis, and the methods for bringing them into solution are discussed in Chapter 21, page 415, and Chapter 22, page 421.

TABLE 15
SEPARATION OF THE CATIONS INTO GROUPS

<table>
<tr><td colspan="3">Test for Na^+, K^+, and NH_4^+ on a small portion of original unknown.</td></tr>
<tr><td colspan="3">To 1 ml of unk. soln. add 3 N HCl until pptn. is complete or, if no ppt., until soln. is distinctly acid to litmus. Centrifuge and wash any ppt.</td></tr>
<tr><td rowspan="3">Ppt. 1. Gr. I chlorides; (possibly BiOCl, SbOCl). Follow Table 16 and procedures.</td><td colspan="2">Soln. 1. Gr. II, III, IV, Na^+, K^+, NH_4^+. Make 0.3 N in H^+, using M.M.O., p. 289, and saturate with H_2S until pptn. is complete. Centrifuge and wash any ppt.</td></tr>
<tr><td>Ppt. 2. Gr. II sulfides. Follow Table 17 and procedures.</td><td>Soln. 2. Gr. III, IV, Na^+, K^+, NH_4^+. Boil to remove H_2S. Add NH_3 and NH_4HS. Centrifuge and wash any ppt.</td></tr>
<tr><td>Ppt. 3. Hydroxides and sulfides of Gr. III. Follow Table 18, and procedures.</td><td>Soln. 3. Gr. IV, Na^+, K^+, NH_4^+. Acidify with HCl. Evaporate to dryness and ignite off all ammonium salts. Take up in 1 ml of water. Follow Table 19 and procedures.</td></tr>
</table>

DETECTION OF SODIUM, POTASSIUM, AND AMMONIUM IONS

These ions are invariably to be tested for at the beginning of each analysis of a general unknown. Unknown solid mixtures can be tested directly. Portions of liquid unknowns should be evaporated to dryness and the solid residues used for the tests.

Sodium. Bring a little of the solid material on a *clean* platinum wire into the flame. *Bright* yellow flame indicates presence of Na.

Note: Many, if not most, commercial salts contain a trace, or more, of Na^+. When brought into the flame, such salts give at least a flash of yellow. Whether or not Na should be reported is a matter of judgment based on the brilliance and persistence of the yellow flame. However, this depends on the amount of sample on the wire, the temperature of that part of the Bunsen flame where the wire is placed, and the anion of the Na salt. The procedure should uniformly be that recommended on page 189. If this procedure is followed, the flame should persist at least 10 seconds to justify reporting "small" Na.

Potassium. Bring a little of the solid material into the flame and observe it through *two* thicknesses of blue glass *at the instant* the wire enters the flame.

Note: Potassium salts are considerably more volatile than sodium salts. For this reason the flame must be observed when the wire is introduced into it. Even a little Na covers the flame of K. Two blue glass plates will completely absorb the Na yellow even when a large amount is present. Colors due to Ba, Sr, or Ca are also absorbed so that even a trace of K is detectable in presence of any of them. When the lavender flame of K is visible to the unaided eye, no more than a trace of Na can be present.

Ammonium. Place 10 drops of NaOH reagent in the Erlenmeyer flask, Fig. 5, page 189. Do not let the solution or dropper touch the wall of the flask. Insert a "wedge-point" pin into the bottom of a No. 6 cork, which should fit the flask. In the loop of the pin place a piece of red litmus paper about one-fourth of an inch long. Moisten the paper and insert the cork. Carefully warm the flask (preferably on a steam plate). The solution must not boil. Paper turning blue proves NH_4^+ *in the reagent.* Even a trace of NH_3 will affect the test paper within 5 minutes. If NH_4^+ is present, remove the cork and heat the NaOH until a test with a fresh piece of paper proves it free from NH_4^+.

To the NaOH proved *free from* NH_4^+ add 2 to 3 mg of the material to be tested and proceed as directed above. Paper becoming blue now proves presence of NH_4^+ *in the unknown.* The time required for the paper to become blue is a very good measure of the amount of NH_4^+ present. If a large amount is present the paper will change color almost instantly when the cork is inserted in the flask. A trace may require 3 to 4 minutes to produce the color change.

Note: The test conducted as directed is extremely sensitive. NaOH reagent can absorb NH_3 from the air of the laboratory. For this reason the reagent must always be *proved* free from NH_3 before the unknown is added to it.

PRECIPITATION AND ANALYSIS OF CATION GROUP I

TABLE 16
ANALYSIS OF GROUP I

<table>
<tr><td colspan="3">Add dropwise 3 N HCl as long as a ppt. forms then 2 drops in excess. Stir vigorously for 2 min. Centrifuge.</td></tr>
<tr><td colspan="2">Ppt. 1. AgCl, Hg_2Cl_2, ($PbCl_2$), (SbOCl, BiOCl). Stir thoroughly with 2–4 drops of 3 N HCl. Centrifuge. Add washings to soln. 1. Extract with hot water.</td><td>Soln. 1. Groups II, III, IV, Na^+, K^+, NH_4^+.</td></tr>
<tr><td>Residue 2. Hg_2Cl_2, AgCl. Add NH_3 and stir vigorously.</td><td colspan="2">Soln. 2. $PbCl_2$. Add $AcONH_4$ and $CrO_4^=$. Yellow $PbCrO_4$ proves Pb^{++}.</td></tr>
<tr><td>Residue 3. Hg^0 (black) and $HgNH_2Cl$ (white). Immediate black proves Hg_2^{++}.</td><td colspan="2">Soln. 3. $Ag(NH_3)_2^+, Cl^-$. Make acid with 3 N HNO_3. White AgCl proves Ag^+</td></tr>
</table>

Procedures

A solution to be tested for Group I is ordinarily an aqueous solution of the nitrates of the group or an HNO_3 solution of a solid unknown. A solution which contains Cl^- cannot contain Ag^+ or Hg_2^{++}, since their chlorides are insoluble in dilute acid.

Precipitation of Group I chlorides. To 1 ml of a known or unknown solution add 1 drop of 3 *N* HCl and stir. Test solution with litmus. If alkaline, make acid with HCl. No precipitate shows absence of Ag^+ and Hg_2^{++}. If a precipitate appears, add HCl a drop at a time with stirring until no more forms. Then add 2 drops more and stir thoroughly. If the precipitate dissolves completely, Hg_2^{++} and Ag^+ are absent. A little BiOCl or SbOCl may have precipitated. Centrifuge and test liquid for complete precipitation. Wash the precipitate twice with 4 drops of 3 *N* HCl, adding the washings to the residual liquid.

Note: It is always possible that some BiOCl or SbOCl may precipitate in Group I, since the basic nitrates are much more soluble than the basic chlorides. This is likely to take place only when these ions are present in rather large amounts. The excess of reagent HCl will tend to redissolve these basic chlorides.

$$\underline{Bi(OH)_2Cl} + 2H^+ + 3Cl^- \rightleftarrows 2H_2O + [BiCl_4]^-$$

For the same reason the group precipitate is washed with 3 *N* HCl instead **of with** water.

Separation of lead. Extract the washed precipitate with 4 drops of *hot* water. Centrifuge, remove the liquid, and add to it a drop of $AcONH_4$ and a drop of K_2CrO_4. Yellow $PbCrO_4$ proves Pb^{++} present. No precipitate shows no Pb^{++} in Group I, but it may be found in Group II. If Pb^{++} is present, continue the extraction with hot water until the extracts show no Pb^{++}. To find the amount of Pb^{++}, combine the $PbCrO_4$ precipitates.

Note: Since Pb^{++} is found in Group I only when present in large amount, time is saved by testing at once the first extract.

When practice unknowns containing only ions of Group I are being analyzed, the liquid from the group precipitate should always be tested for Pb^{++} with CrO_4^-. All or most of the Pb^{++} may be found in this solution.

Separation of silver from mercury; confirmation of mercurous ion. To the residue from the extraction of $PbCl_2$ add 2 drops of 6 *N* NH_3 and stir very thoroughly. Black residue proves Hg_2^{++}. Centrifuge and remove the liquid.

Confirmation of silver. Acidify the NH_3 extract with 3 *N* HNO_3. White AgCl proves Ag^+.

Note: When an unusually large amount of Hg_2^{++} is present, a small amount of Ag^0 may remain entirely in the residual Hg^0 and $HgNH_2Cl$ The cause of this is that finely divided Hg^0 in intimate contact with moist AgCl is able to reduce it.

$$2Hg^0 + \underline{2AgCl} \rightleftarrows \underline{Hg_2Cl_2} + \underline{2Ag^0}$$

Ag^0 does not react with NH_3. The reaction will be forced nearly to completion toward the right only when Hg^0 is unusually large and AgCl unusually small. The reaction is less likely to occur in semimicro analysis than in macro analysis, but its possibility must be considered whenever a very large amount of Hg_2^{++} has been found. In case treatment

of Hg_2Cl_2 and AgCl with NH_3 leaves an unusually large black residue and no Ag^+ is found, proceed as follows:

Dissolve the black residue in 12 *N* HCl, adding a small crystal of $KClO_3$.

$$HgNH_2Cl + 2H^+ + 2Cl^- = [HgCl_3]^- + NH_4^+$$
$$Hg^0 + Cl_2 + Cl^- = [HgCl_3]^-$$
$$2Ag^0 + Cl_2 + 4Cl^- = 2[AgCl_3]^-$$

[*Continued on page 312*]

PRECIPITATION AND ANALYSIS OF CATION GROUP II

TABLE 17
ANALYSIS OF GROUP II

Soln. **Known or unknown or filtrate from Group I made 0.3 *N* in H^+.** Saturate hot with H_2S.

Ppt. 1. **$Pb(HS)_2$, $Bi(HS)_3$, $Cu(HS)_2$, $Cd(HS)_2$, $As(HS)_3$, $Hg(HS)_2$, $Sb(HS)_3$, $Sn(HS)_4$.** Wash with 0.3 *N* HCl. Extract with colorless NaHS and NaOH.

Soln. 1. **Groups III, IV, Na^+, K^+, NH_4^+.**

Residue 2. **PbS, Bi_2S_3, CuS, CdS.** Repeat extraction with NaHS and NaOH. Add extract to soln. 2. To *thoroughly washed* residue add HNO_3 and boil. Residue S. (Possibly HgS or $Hg(NO_3)_2 \cdot 2HgS$.)

Soln. 2. **AsS_2^-, HgS_2^-, SbS_2^-, SnS_3^-, trace Bi.** Make just acid with 3 *N* HCl.

Ppt. 3. **As_2S_3, HgS, Sb_2S_3, SnS_2, S, trace of Bi_2S_3.** Wash once with 0.3 *N* HCl. Then add 1 ml of ethyl alcohol, stir thoroughly, and let stand 5 min. Discard washings. Treat residue with 10 drops of 12 *N* HCl. Follow directions *very* exactly.

Soln. 3. **Pb^{++}, BiO^+, Cu^{++}, Cd^{++}, (HNO_3).** Transfer to large crucible, add H_2SO_4, heat to dense fumes of SO_3. Add to H_2O.

Residue 6. **As_2S_3, HgS black or $HgCl_2 \cdot 2HgS$ white.** Wash with 6 *N* HCl. Discard washings. To residue add 15 *N* NH_3. Stir thoroughly 1 min.

Soln. 6. **$[SbCl_4]^-$, $[SnCl_6]^-$, trace $[BiCl_4]^-$.** Boil to remove H_2S, make up to 0.5 ml with 12 *N* HCl, add 8 drops water. Make spot tests with phosphomolybdic acid, first for Sb^{+3} then for Sn^{++}.

Saturate with $H_2C_2O_4$, then with H_2S. Orange-red ppt. Sb_2S_3.

Ppt. 4. **$PbSO_4$.** Extract with $AcONH_4$.
Soln. 4A. **$(AcO)_2Pb$.** Add AcOH and CrO_4^-.
Ppt. **$PbCrO_4$** soluble in excess of NaOH.

Soln. 4. **BiO^+, Cu^{++}, Cd^{++}, (H_2SO_4).** Add NH_3 in excess.

Ppt. 5. **BiOOH.** Add $NaHSn(OH)_4$. Bi^0 (black) instantly.

Soln. 5. **$Cu(NH_3)_4^{++}$, $Cd(NH_3)_4^{++}$.**
(*a*) Blue soln. proves Cu. If *blue*, add CN^-. Add H_2S. *Ppt.* CdS.
(*b*) Colorless soln. Test for trace Cu^{++} with Zn^{++} and $Hg(NCS)_4^-$. Saturate the rest of the soln. with H_2S. *Ppt.* CdS.

Res. 7. **HgS** black, proves Hg^{++}.

Soln. 7. **AsS_2^-, $AsOS^-$.** Acidify strongly with 12 *N* HCl and again saturate with H_2S. Canary yellow ppt. proves As.

Soln. 8. **$[Sn(C_2O_4)_3]^-$, (Bi).** Transfer to large crucible. Add 6 drops each of conc. HNO_3 and H_2SO_4. Evap. *just* to dryness. Take up with 1 ml. 1.5 *N* HCl. Saturate with H_2S. Yellow ppt. SnS_2. If ppt. is dark showing possible Bi_2S_3 or SnS, extract with NH_4HS. Centrifuge. *Soln.* **$[SnS_3]^-$.** Acidify with HCl. Yellow ppt. SnS_2.

Procedures

Making the solution 0.3 *N* in H^+. Use modified methyl orange (see page 289).

Note: Dilution of the HCl solution from 3 *N* to 0.3 *N* is likely to cause BiOCl and SbOCl to precipitate. The precipitation of these basic salts of Group II is not objectionable, since H_2S will change them to sulfides.

Precipitation of sulfides. Heat the contents of the centrifuge tube nearly to boiling and saturate with H_2S. Centrifuge. To the clear liquid add 1 drop of water, stir without disturbing the precipitate, and again pass in H_2S to insure complete precipitation. Remove the clear liquid to a crucible if this solution may contain ions of Groups III or IV. Otherwise discard it. In the former case boil to remove H_2S; centrifuge out any precipitate; make the volume 1 ml, and reserve for Group III.

Note: The presence or absence of arsenic (in arsenite, arsenate, or as As_2S_3 or As_2S_5) will have been determined in the anion analysis. Arsenate is little affected by H_2S in 0.3 *N* H^+. Upon boiling the centrifugate from Group II to remove H_2S, a little yellow sulfide of arsenic may precipitate if the solution contained an arsenate.

Separation of II-A from II-B. Wash the H_2S precipitate three times with 3–6 drops at a time of 0.3 *N* HCl (see note 1). Add the first washing to the group filtrate which was transferred to the crucible. Treat the washed sulfides with 4–6 drops of *colorless* NaHS. Immerse in a bath of hot water and stir for two minutes. Then add two drops of 6 *N* NaOH and again warm and stir vigorously for three minutes. Centrifuge. Pipet off the clear liquid to another centrifuge tube and acidify with 3 *N* HCl to see whether II-B sulfides are present. No precipitate, or only a white turbidity due to sulfur (see note 2) shows absence of Hg^{++}, As^{+3}, Sb^{+3}, and Sn^{+4}. If a residue remains, indicating II-A sulfides, repeat the extraction (see note 3) with 3 drops of NaHS and 1 drop of NaOH until the acidified extract shows that no more II-B sulfides are being extracted. Add any precipitates to the II-B precipitate. Centrifuge and discard centrifugate. Wash any *colored* II-B precipitate with 0.3 *N* HCl. Remove liquid as completely as possible. Stir up

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Evaporate to small bulk to remove Cl_2 and add 1 ml of water. $HgCl_2$ is soluble and AgCl precipitates. Centrifuge, wash the AgCl thoroughly with water containing a little HNO_3. Dissolve in NH_3 and reprecipitate with HNO_3.

residue with 1 ml of ethyl alcohol (see note 4) and let stand while Group II-A sulfides are being analyzed.

Notes: 1. Since the washing solution is used several times during the analysis of this group, it is well to prepare at one time a sufficient amount for all the operations.

2. When colorless NaHS solution is acidified, only H_2S should be formed.

$$HS^- + H^+ \rightarrow \overline{H_2S}$$

NaHS when exposed to air rapidly absorbs oxygen and becomes yellow because of formation of persulfide ions, S_2^-, S_3^-, and so on.

$$4HS^- + O_2 \rightleftarrows 2S_2^- + 2H_2O$$

On acidification these yellow persulfides give H_2S and S.

$$S_2^- + 2H^+ = \underline{S} + \overline{H_2S}$$

During the treatment of the sulfides the solution will have become more or less yellow and when acidified will give more or less sulfur as a pure white precipitate or turbidity. This sulfur will rarely be formed in sufficient amount to interfere with seeing even small particles of the strongly colored sulfides of II-B.

3. The NaHS–NaOH solution used as directed should remove in one extraction all the As, Sb, and Sn and all the Hg^{++} except when a rather large amount of Cd^{++} is present. HgS seems to coprecipitate with CdS in a form which is only slowly decomposed by NaHS and NaOH. Except in unusual cases the second extraction with NaHS–NaOH should complete the dissolution of the Group II-B sulfides. However, this is never to be assumed and each extraction should be acidified separately and the extraction continued until colored flocculent sulfides are no longer formed.

4. The precipitate is allowed to stand in alcohol for several minutes in order to extract from it as completely as possible the water which otherwise would considerably dilute the 12 *N* HCl and greatly diminish the sharpness of the separation of Sb and Sn from Hg and As.

Separation and Detection of II-A Sulfides

Wash the residue (II-A sulfides) from the NaHS–NaOH treatment three times with 0.3 *N* HCl. Transfer the precipitate to a crucible. Treat the washed sulfides with 5 drops of 3 *N* HNO_3 and boil until only a light-colored residue remains (S, possibly $Hg(NO_3)_2 \cdot 2HgS$) (see note 1). At this point a residue of sulfur will usually appear as a yellow waxy globule floating on the liquid. $Hg(NO_3)_2 \cdot 2HgS$ (see note 2) will be a heavy white or yellowish white powder, readily settling to the bottom of the liquid. Transfer the contents

of the crucible to a centrifuge tube. Centrifuge. If black HgS or white $Hg(NO_3)_2 \cdot 2HgS$ remains undissolved, wash it thoroughly with 0.3 *N* HCl. Dissolve precipitate in 3 drops of 12 *N* HCl with addition of a tiny crystal $KClO_3$ and test for mercury (see note 3) as directed in experiment 6, mercury, page 295.

To the HNO_3 solution of the II-A sulfides add 5 drops of 36 *N* H_2SO_4 and heat until dense fumes of SO_3 are evolved copiously (see note 4). Draw up the mixture (see note 5) from the crucible with a pipet and allow it to drop slowly into a centrifuge tube containing 10 drops of water. Rinse out the crucible twice with 3 drops of water, transferring *all* of any precipitate to the centrifuge tube. Centrifuge. A white precipitate is probably $PbSO_4$ but may be $(BiO)_2SO_4$ (see note 6). Remove the liquid to another centrifuge tube. This liquid may contain BiO^+, Cu^{++}, and Cd^{++}.

Notes: 1. It was stated above that a large amount of cadmium may carry Hg^{++} into II-A. This possibility must be kept in mind and any black residue as well as a heavy white one examined for Hg^{++}.

2. When the II-A sulfides are treated with hot 3 *N* HNO_3, sulfur is formed which collects in a waxy layer about particles of undissolved sulfides and protects them from action of the acid. For this reason students are likely to infer incorrectly that Hg^{++} is in the II-A precipitate. If the heating is continued as prescribed until nearly all the black color has disappeared, this error will not be made. Probably this amount of heating will cause black HgS, if present, to change into white $Hg(NO_3)_2 \cdot 2HgS$ which should be readily recognized by its rapid settling.

3. Mercury should never be reported in II-A unless its presence has been definitely confirmed by H_2SnCl_4.

4. $PbSO_4$ is distinctly soluble in HNO_3 and cannot be completely precipitated so long as any HNO_3 is present. Since H_2SO_4 decomposes into SO_3 and water rapidly only above 200° while nitric acid is volatilized below 150°, if the heating is continued until dense, choking fumes of SO_3 are being evolved copiously, all the nitric acid will have been removed. Beginners are likely to mistake grayish fumes of steam laden with HNO_3 for SO_3 and thus to stop the heating before all HNO_3 has been removed. The volume of the solution must be reduced to 3 drops (the volume of H_2SO_4 originally added) before much SO_3 can be evolved. Unless Pb^{++} is completely removed, PbS will darken the yellow CdS.

5. When an unusually large quantity of BiO^+ is present, $Bi_2(SO_4)_3$ may appear in the crucible as distinctly crystalline particles. In high-copper alloys white anhydrous $CuSO_4$ may appear.

6. Some $(BiO)_2SO_4$ may precipitate here if the H_2SO_4 is too dilute. This is most likely to occur when an unusually large amount of BiO^+ is present.

Confirmation of lead. Wash the lead sulfate twice with 2 drops of water and 1 drop of 3 *N* H_2SO_4. Centrifuge and add the washings

to the above (BiO^+, Cu^{++}, Cd^{++}) solution. To the lead sulfate add 2 drops of $AcONH_4$, warm gently and stir until the residue dissolves. Add 3 drops of AcOH and 1 drop of $1N$ K_2CrO_4. A yellow precipitate, completely soluble in NaOH and reprecipitated when the solution is acidified with AcOH, is $PbCrO_4$.

Note: In the confirmation of lead any $(BiO)_2SO_4$ will dissolve in $AcONH_4$ and possibly may precipitate as $(BiO)_2Cr_2O_7$, although the amount of AcOH prescribed should prevent this. Lead chromate and $(BiO)_2Cr_2O_7$ differ in their reactions to NaOH. Lead chromate dissolves completely, because of formation of $[HPbO_2]^-$ and $CrO_4^=$, while $(BiO)_2Cr_2O_7$ gives a precipitate of BiOOH and $CrO_4^=$. The confirmation of lead therefore is not absolute until it has been shown that it dissolves without residue in NaOH. In case a mixture of $PbCrO_4$ and $(BiO)_2Cr_2O_7$ were present, BiOOH can be centrifuged out after treatment of the mixed chromates with NaOH. If the clear yellow solution is then acidified with AcOH, $PbCrO_4$ will again precipitate uncontaminated by $(BiO)_2Cr_2O_7$.

Separation and detection of bismuth. To the H_2SO_4 solution from the $PbSO_4$ add $15N$ NH_3 with constant stirring until the solution smells strongly of it. Centrifuge whether or not a precipitate is visible. A blue solution proves copper. A precipitate is probably BiOOH but can be $Pb(OH)_2$ if all HNO_3 was not fumed off in removing lead as $PbSO_4$. Pipet off the liquid to a test tube. Wash any residue with water containing a drop of $6N$ ammonia. Centrifuge and add washings to the original liquid from the precipitate.

Confirmation of bismuth (see note 1). Remove the BiOOH precipitate with a capillary pipet to a spot plate. Prepare a solution of $Na[HSn(OH)_4]$ by adding to a drop of cold $H_2[SnCl_4]$ solution NaOH dropwise with stirring and cooling under the tap after each addition until the precipitate which first forms dissolves. Then add 1 drop NaOH in excess. Centrifuge. Cool the clear solution well and add a capillary drop of this $Na[HSn(OH)_4]$ to the BiOOH precipitate. Immediate (see note 2) black due to formation of Bi^0 proves bismuth. ($Pb(OH)_2$ will not react.)

Notes: 1. Since a small white precipitate formed by NH_3 may possibly be $Pb(OH)_2$, a confirmatory test should always be applied to this precipitate.

2. BiOOH becomes black instantly on contact with $[HSn(OH)_4]^-$. A dark color which appears slowly is not to be considered, since H_2S in the air of the laboratory may precipitate a little SnS (dark brown). Bistannite on standing spontaneously decomposes into Sn^0 and $[Sn(OH)_6]^=$. Colloidal Sn^0 may darken the solution. The forward reaction

$$2[HSn(OH)_4]^- \rightleftarrows \underline{Sn} + [Sn(OH_6)]^= + 2H_2O$$

is favored by high temperature, the reverse reaction by large C_{OH^-} (probably because colloidal Sn can dissolve in it). Since neutralization of the rather large C_{HCl} in the H_2SnCl_4 reagent produces much heat, the mixture must be cooled.

Detection of copper. A blue solution due to $Cu(NH_3)_4^{++}$ is sufficient proof of Cu^{++}, and the depth of color is proportional to the amount of Cu^{++} present. If no blue color can be observed, minute traces of Cu^{++} may still be present. In such a case proceed as follows: In the depression of a spot plate place 1 drop of AcOH and 1 drop of the test solution. To the mixture add 1 drop of 1% solution of $(AcO)_2Zn$ and 1 drop of 0.3 *M* $K_2[Hg(NCS)_4]$ solution. Stir with a glass rod for 15 seconds. Red violet precipitate indicates a trace of copper.

Note: As little as 0.5 mg of Cu as $Cu(NH_3)_4^{++}$ will impart a distinct blue color to 1 ml of solution if one looks *down the tube.*

Detection of cadmium in presence of copper. If a blue solution containing $[Cu(NH_3)_4]^{++}$ was obtained, add to it CN^-, a drop at a time with stirring, until the blue color *just* disappears, then 1 drop more. Pass in H_2S. Yellow CdS proves Cd^{++}.

Note: When very much Cu^{++} is present so that a large amount of CN^- has been required to reduce it, hydrogen sulfide sometimes forms a red to orange precipitate of hydrorubianic acid $(CSNH_2)_2$. To be certain of Cd^{++} in this case, centrifuge and dissolve the precipitate in 3 *N* HNO_3, neutralize with NH_3, and again pass in H_2S. A yellow precipitate now will be CdS.

Detection of cadmium in absence of copper. If no blue solution was observed, pass in H_2S. Yellow CdS proves Cd^{++}.

Separation and Detection of II-B Ions

Centrifuge the II-B precipitate and discard the alcohol. Treat the residue with 10 drops of 12 *N* HCl (see note 1); place in a nearly boiling water bath and stir for two minutes. Saturate again with H_2S. Centrifuge and remove centrifugate to a crucible. Wash the residue twice with 3 drops of 6 *N* HCl. Add the first washing to the liquid in the crucible. Test this solution for Sb and Sn as directed below. Extract the residue with 4 drops of 6 *N* NH_3. Repeat extraction until all As is removed. Stir thoroughly for one minute. Black residue proves Hg (see note 2). Centrifuge. Remove centrifugate to another centrifuge tube.

Notes: 1. The 12 *N* HCl usually turns black HgS to white $HgCl_2 \cdot 2HgS$, but the black color of HgS reappears as soon as the white compound is treated with NH_3.

2. Since only HgS and As_2S_3 or As_2S_5 are insoluble in 12 *N* HCl, the distinctive colors of these sulfides make further confirmation unnecessary.

Detection of arsenic. Acidify the NH_3 centrifugate with 12 *N* HCl and saturate with H_2S. Yellow As_2S_3 proves arsenic. If the As_2S_3 has not its characteristic color, dissolve it in HCl and $KClO_3$ and confirm by Bettendorf test (page 293).

Separation and detection of antimony and tin (see note 1). Boil the 12 *N* HCl solution in the crucible to remove H_2S. *Restore to original volume of* 10 *drops* by adding 12 *N* HCl. Add 8 drops of water and stir thoroughly. Test drops of the solution for Sb and Sn as directed in experiment 5, antimony (page 296) and in experiment 5, tin (page 297). Saturate the remainder of the solution with $H_2C_2O_4$. Saturate with H_2S. Orange-red precipitate is Sb_2S_3. Centrifuge, add to the liquid 3 drops of water to insure complete removal of Sb. Centrifuge if more Sb_2S_3 forms. Remove centrifugate to a crucible. Add 6 drops of 36 *N* H_2SO_4 and 6 drops of 16 *N* HNO_3. Evaporate till dense fumes of SO_3 are evolved. *Do not evaporate to dryness.* Take up and add to 10 drops of water in a centrifuge tube. Rinse crucible twice with 3 drops of water each time, adding this liquid to that in the tube. Make neutral to litmus with NaOH, then slightly acid with HCl. Saturate with H_2S. Buff yellow SnS_2 proves Sn. If the SnS_2 is darkened by SnS (incomplete oxidation of $H_2C_2O_4$) (see note 2) or by Bi_2S_3 (see note 3), centrifuge and extract the precipitate with colorless NH_4HS (see note 4). Centrifuge, remove liquid, and make it acid with 3 *N* HCl. Buff yellow SnS_2 proves Sn.

Notes: 1. If the spot tests for Sb^{+3} and Sn^{++} are both negative, both these elements are probably absent. In this case considerable time can be saved by nearly neutralizing 4 drops of the solution with NH_3 and saturating with H_2S. No *colored* precipitate would prove both antimony and tin absent.

2. In case the $H_2C_2O_4$ has not been completely removed by oxidation, some of the Sn^{IV} may be reduced to Sn^{++} which will be precipitated by H_2S as brown-black SnS. This sulfide is somewhat more soluble than SnS_2 and will be precipitated *after* the latter.

3. For a reason which has not yet been determined, a little Bi_2S_3 nearly always dissolves in the NaHS–NaOH solution. The amount of this is rarely more than 1 mg. This bismuth is always precipitated with the tin and makes the buff SnS_2 appear greenish brown.

4. Both Bi_2S_3 and SnS are insoluble in *colorless* NH_4HS in which SnS_2 dissolves readily. Yellow NH_4HS would oxidize and dissolve SnS.

$$\underline{SnS} + S_2^{=} \rightarrow SnS_3^{=}$$

PRECIPITATION AND ANALYSIS OF CATION GROUP III

Interference of anions. Cation Groups I and II were precipitated from acid solution. For the precipitation of Cation Group III the solution is made basic. But many of the salts of the Group IV cations are insoluble in basic or neutral solution and will be precipitated in Group III. Of these salts all except the salts of F^-, $C_2O_4^{=}$, and BO_2^- are decomposed in the following procedures for analyzing the Group III precipitate, and the Group IV cations are recovered. Oxalate and fluoride ions form very stable complex ions with Fe^{+3}, Al^{+3}, and Cr^{+3} and prevent precipitation of these cations. To ensure that these cations are completely precipitated and that Group IV cations are not lost, any of these three anions must be removed before precipitating Cation Group III. Their presence will have been detected in the analysis for anions. Accordingly at this point two cases have to be considered:

1. *In the analysis for anions, F^-, $C_2O_4^{=}$, or BO_2^- were proved absent.* The centrifugate from Group II is ready for analysis.

2. *In the anion analysis, F^-, $C_2O_4^{=}$, or BO_2^- were proved present.* These anions are to be removed by the following procedure.

Removal of fluoride, oxalate, and borate. In a crucible evaporate to dryness on a water bath the filtrate from Group II. To the residue add 10 drops of 70% $HClO_4$ (see note 1), and, with a flame kept in motion below the crucible, heat *just* to dryness (see note 2). Add 5 drops of $HClO_4$ and repeat the evaporation *just* to dryness. $HClO_4$ gives off dense white fumes somewhat like those of SO_3. Moisten the residue with 2 drops of 12*N* HCl (see note 3). Warm and stir thoroughly. Remove the residue to a centrifuge tube using a total of 1 ml of water. Centrifuge. Pipet off the clear liquid if a residue remains. To the residue add 12*N* HCl 1 drop at a time with thorough stirring and heating until all is dissolved (except, possibly, white crystalline $KClO_4$). Not more than 3 drops of HCl should be necessary. Add this solution to the first and proceed with the precipitation of Group III.

Notes: 1. Larger quantities of $HClO_4$, especially in presence of a small amount of organic material, can cause dangerous explosions. The proce-

dure outlined above assumes absence of organic matter in the materials analyzed. Since filtration is never used, fibers of paper are never present. The small quantity (0.5 ml) of the acid used appears to be perfectly safe. The evaporation has been carried out by students more than 300 times. In no case has any indication of violent reaction been observed.

2. Whether or not the residue from fuming with $HClO_4$ is soluble in water appears to depend upon whether or not the fuming is carried *just* to dryness or beyond that point. For this reason the flame should be removed when no more than 1 drop of liquid remains. The heat of the crucible and wire gauze will sufficiently complete the evaporation.

3. $HClO_4$ oxidizes Cr^{+3} to CrO_3 or $H_2Cr_2O_7$, but this is reduced when warmed with 12 *N* HCl.

TABLE 18
ANALYSIS OF GROUP III

<table>
<tr><td colspan="5">Centrifugate from Group II from which H_2S has been removed or solution after evaporation with $HClO_4$. Add NH_3 until a ppt. begins to form or until soln. is just basic to litmus. Heat to boiling. Add NH_4HS until pptn. is complete. Centrifuge. Test for complete pptn.</td></tr>
<tr><td colspan="4">Ppt. 1. AlOOH ($AlPO_4$, $AlAsO_4$), CrOOH, $Fe(HS)_{2\text{-}3}$, $Mn(OH)(HS)$, $Co(HS)_2$, $Ni(HS)_2$, $Zn(HS)_2$, Group IV phosphates and/or arsenates. Wash thoroughly. Add cold 1 N HCl.</td><td>Soln. 1. To which soln. 5 will be added. Alk. earth ions, phosphate, arsenate, thioarsenate ions, etc. Acidify with HCl. Boil to remove H_2S. Test for Group IV ions.</td></tr>
<tr><td rowspan="2">Res. 2. CoS, NiS, (FeS). Dissolve in HCl and $KClO_3$. Divide into 2 portions. Test one for Co, the other for Ni.</td><td colspan="3">Soln. 2. Al^{+3}, Cr^{+3}, Mn^{++}, Zn^{++}, Fe^{++}, Group IV ions ($H_2PO_4^-$, $H_2AsO_4^-$ if present). Add NaOH, Na_2CO_3, and Na_2O_2.</td><td rowspan="2">Soln. 3. $[Al(OH)_4]^-$, CrO_4^-, $[HZn(OH)_4]^-$. Add solid NH_4Cl and boil off NH_3.</td></tr>
<tr><td colspan="3">Ppt. 3. FeOOH, ($FePO_4$, $FeAsO_4$), MnO_2H_2O (Zn), Group IV phosphates, arsenates, carbonates. Wash till all CrO_4^- is removed. Extract with AcOH.</td></tr>
<tr><td>Res. 4. MnO_2, ($BaCrO_4$). Dissolve in HNO_3 and H_2O_2. If soln. 3 contains CrO_4^-, add K_2SO_4 to ppt any Ba^{++}. Test soln. for Mn with $NaBiO_3$.</td><td colspan="2">Soln. 4. Fe^{+3}, Zn^{++}, Group IV ions, ($H_2PO_4^-$, $H_2AsO_4^-$). Test 1 drop for Fe^{+3}. Saturate rest of soln. with H_2S.</td><td>Ppt. 6. AlOOH. Dissolve and confirm by aluminon.</td><td>Soln. 6. $[Zn(NH_3)_4]^{++}$, CrO_4^-. Add NH_4HS.</td></tr>
<tr><td></td><td>Ppt. 5. ZnS, S. Extract with 1 N HCl and confirm Zn^{++}.</td><td>Soln. 5. Fe^{++} (Mn^{++}), Group IV ions, ($H_2PO_4^-$, $H_2AsO_4^-$). Add 3 N HCl. Boil out H_2S and cool.
(a) Fe^{+3} is absent. Add this soln. to soln. 1.
(b) Fe^{+3} is present. Add Br_2 water and shake thoroughly. Extract Fe^{+3} as $Fe[Fe(NCS)_6]$ with amyl alc.-ether. Add aqueous layer to soln. 1.</td><td>Ppt. 7. ZnS. Dissolve in 1 N HCl and confirm.</td><td>Soln. 7. CrO_4^-. Confirm if doubtful.</td></tr>
</table>

Procedures

Precipitation of Group III. To a Group III known or unknown, to the centrifugate from Group II (case 1, page 318), or to the solution after evaporation with $HClO_4$ (case 2), add 6 *N* NH_3 dropwise with vigorous stirring until a precipitate begins to form

or until the solution becomes alkaline to litmus. Warm and stir the mixture vigorously for 1 minute. Without removing any precipitate that may have formed add NH_4HS dropwise with vigorous stirring until precipitation of the hydrosulfides and hydroxides is complete (see note 1). Centrifuge and test for complete precipitation. If the solution is dark colored indicating colloidal hydrosulfides (most frequently $Ni(HS)_2$), remove the liquid (see note 2) to a crucible, add a small crystal of NH_4NO_3, and boil until the hydrosulfide flocculates. Centrifuge. Add the precipitate to the original precipitate. Remove the liquid to a crucible. Acidify with HCl (see note 3). Boil to remove H_2S and reserve until solution 5 is obtained. Use the combined solutions 1 and 5 for analysis of alkaline earth ions (see note 4).

Notes: 1. When Group III is precipitated in presence of HPO_4^- and $HAsO_4^-$, the compounds formed will depend on the relative solubilities of the sulfides, hydroxides, and phosphates or arsenates. The compounds formed will depend on the relative proportions of HPO_4^- and/or $HAsO_4^-$, tervalent cations and bivalent cations. Thus, a small amount of HPO_4^- might be precipitated entirely as $AlPO_4$ and thus bring no alkaline earths into the Group III precipitate. On the other hand since the hydrosulfides of Fe^{+3} and the 2-valent ions of Group III are more insoluble than the phosphates or arsenates, it might be possible, in absence of AlO^+ or CrO^+, for a sufficient amount of phosphate or arsenate to be present so that the alkaline earths are completely precipitated in Group III. It is evident that the nature of the Group III precipitate will vary widely from case to case and cannot be predicted.

2. If the centrifugate from the sulfide precipitate (solution 1) is at all brown, some $Ni(HS)_2$ has passed into a colloidal state. This dispersion of $Ni(HS)_2$ is favored by high C_{NH_3} and by presence of yellow persulfide ions (S_2^-, S_3^-, etc.) in the NH_4HS reagent, which should be colorless. To prevent formation of colloidal $Ni(HS)_2$, the least excess possible of NH_4HS should be used.

3. If arsenate is present in Group III, some thioarsenate may be present in the centrifugate from the group because of reactions such as

$$2H_2O + HAsO_4^- + S^- \rightarrow HAsO_3S^- + 2OH^-$$

When solution 1 is acidified and boiled, a little yellow arsenous sulfide may precipitate.

$$3H_2S + H_2AsO_3S^- + H^+ \rightleftarrows \underline{As(HS)_3} + \underline{S} + 3H_2O$$

However, when the residue is ignited, the $As(HS)_3$ will be oxidized again to arsenate.

4. Theoretically, sufficient NH_4^+ should completely prevent precipitation of $Mg(OH)_2$. We have found that either $Al(OH)_3$ or $Cr(OH)_3$ may bring as much as 75% of the Mg^{++} into Group III. When HPO_4^- and/or

$HAsO_4^-$ is present, part or all of the alkaline earths will usually be precipitated in this group. Provision is made for the alkaline earth ions which precipitate in Group III to be added to the centrifugate from this group.

Separation of CoS and NiS from the remainder of Group III. Wash the NH_4HS precipitate (precipitate 1) at least three times (see note 1) with 6 to 20 drops (at a time) of water containing 3 drops of NH_4NO_3 solution and 1 drop of $6N$ NH_3 per ml. Add the first washing to solution 1. To the precipitate add 1 ml of cold $1N$ HCl (14 drops of water and 7 drops of $3N$ HCl). Stir thoroughly for two minutes. Remove solution and repeat the extraction (see page 186) with 0.5 ml $1N$ HCl (see note 2). Add this extract to the first (solution 2). Wash the residue (CoS, NiS) (see note 3) with water containing 3 drops of ammonium nitrate and 1 drop of HCl per ml. Discard the washings.

Notes: 1. Several of the Group III hydrosulfides are readily dispersed to the colloidal state in alkaline solution. For this reason all wash liquids should contain an electrolyte which tends to flocculate the colloids. NH_4NO_3 is preferable to NH_4Cl because Cl^- tends to form complex anions such as $[ZnCl_4]^=$. Warming to remove H_2S may help to flocculate sulfides which have become colloidal.

2. When present in large amount FeS is not completely dissolved by 2 extractions with $1N$ HCl. If the CoS–NiS residue is large, a third extraction with $1N$ HCl should be made.

3. The solubility of NiS and CoS in $1N$ HCl appears to depend chiefly on the thoroughness of the washing. Presumably during the washing $Co(HS)_2$ and $Ni(HS)_2$, which are soluble in dilute HCl, are converted into the much less soluble CoS and NiS. Evidently a more thorough and longer washing will be required for this conversion when much $Co(HS)_2$ and $Ni(HS)_2$ are present. A *large* black precipitate may need to be washed six times, a small one no more than twice. Traces of CoS and NiS always dissolve in cold $1N$ HCl.

Confirmation of cobalt and nickel. To the residue (residue 2) add 10 drops of $12N$ HCl, warm, and add a small crystal of $KClO_3$. Continue heating until the residue of S is nearly free from black sulfides. Remove the S. Evaporate the clear solution just to dryness. $[CoCl_4]^=$ is *blue*. Take up with 1 ml of water. *Divide into two portions.*

Portion 1. Test for cobalt by both of the following methods: On a spot plate place 1 drop of alpha-nitroso beta-naphthol (which must have been prepared the same day) and a drop of the test solution. Bright brick-red precipitate proves cobalt. To the remainder of the solution add 10 drops of $4N$ KNCS and 6 drops of amyl

alcohol-ether (2:1). Shake vigorously then add 4 drops 12*N* HCl and shake vigorously again. Blue ether layer proves cobalt. A purple color is due to a mixture of $H_3Fe(NCS)_6$ and $H_2Co(NCS)_4$. If the layer is red or purple, instead of blue, add a very small fragment of $Na_2S_2O_3$ and shake vigorously to reduce Fe^{+3}. (A white turbidity is sulfur.)

Portion 2. Add 2 drops of 3*N* $AcONH_4$ and 2 drops of dimethylglyoxime. Stir vigorously. If cobalt is present, more dimethylglyoxime will be required (see note). Scarlet precipitate proves nickel. For amphoterism of $NiDn_2$, see page 257.

Note: If Co^{++} is present, brown soluble $CoDn_2$ forms before the red $NiDn_2$. In this case more reagent must be added than is required to react with the Co^{++} before $NiDn_2$ will precipitate.

Separation of Al^{+3}, Cr^{+3}, and Zn^{++} from Fe^{+3}, Mn^{++} and Group IV phosphates or arsenates. Evaporate solution 2 to 1 ml (see note 1). Add 6*N* NaOH dropwise with constant stirring until solution is strongly basic. Add 1 drop of 3*N* Na_2CO_3 (see note 2). Then add a little Na_2O_2, stir, and warm. Centrifuge. If the liquid has become at all yellow (see note 3), $CrO_4^{=}$ may be forming; if a brown color appears, Mn^{++} or Fe^{++} is being oxidized. In either case addition of Na_2O_2 a few grains at a time (see note 4), warming, and vigorous stirring must be continued until oxidation of Cr^{+3}, Fe^{++}, Mn^{++} is complete. Add 10 drops of water, stir thoroughly, centrifuge, and wash the precipitate three times with hot water. The precipitate (*precipitate 3*) may contain ($FePO_4$), FeOOH, $MnO_2 \cdot H_2O$, (Zn?) (see note 5), Group IV phosphates, carbonates or arsenates, traces of CoOOH, and $Ni(OH)_2$. The solution (*solution 3*) may contain $[Al(OH)_4]^-$, $CrO_4^{=}$, $[HZn(OH)_4]^-$.

Notes: 1. H_2S must be removed before making the solution basic, since sulfides would be precipitated.

2. Although $FePO_4$ is the most insoluble of the phosphates that could be formed by ions of Groups III and IV, $Fe(HS)_2$ and $Fe(HS)_3$ are still more insoluble. In consequence any phosphate (or arsenate) enters the Group III precipitate combined with AlO^+, CrO^+, or alkaline earth ions. After FeS and Fe_2S_3 have been dissolved in 1 *N* HCl and H_2S removed, Fe^{++}, after oxidation to Fe^{+3} by Na_2O_2, is free to combine with phosphate or arsenate. As a result Ba^{++}, Sr^{++}, and Ca^{++} may become free at this point. Na_2CO_3 is added to insure their precipitation and prevent them from passing into solution 3.

3. A distinct yellow color is sufficient test for $CrO_4^{=}$ but in case of doubt the very sensitive formation of blue $OCr(O_2)_2$ may be resorted to as directed on page 281.

4. Na_2O_2 forms an equivalent amount of NaOH which, as has been stated, increases peptization. For this reason a large and useless excess of Na_2O_2 should be avoided.

5. We have found no method of preventing zinc from being precipitated with iron and manganese. Cases have been observed where practically *all* of the zinc went into the precipitate. Whether or not this is due to compound-formation is uncertain.

Separation of MnO_2 from Fe^{+3} and alkaline earth phosphates and arsenates. To precipitate 3 add 6 to 20 drops of 3 *N* AcOH, according to the amount of precipitate. Warm and stir. All of the precipitate except $MnO_2 \cdot H_2O$, $FePO_4$ (and $BaCrO_4$) should dissolve. Estimate amount of Mn from volume of the residue. Centrifuge and remove centrifugate to another centrifuge tube. A residue (*residue 4*) may contain $MnO_2 \cdot xH_2O$, $FePO_4$, ($BaCrO_4$). The solution (*solution 4*) may contain Fe^{+3}, $[Fe(AcO)_6]^{-3}$ (red), Group IV ions, Zn^{++}, $H_2PO_4^-$, $H_2AsO_4^-$. Repeat the extraction with fresh portions of AcOH until no more precipitate dissolves. A reddish residue ($FePO_4$) does not interfere with the following test.

Confirmation of manganese (detection of barium in the MnO_2). Dissolve residue 4 ($MnO_2 \cdot H_2O$, $FePO_4$, FeOOH, ($BaCrO_4$)) (see note 1) by adding 8 drops of 3 *N* HNO_3 and 1 to 2 drops of H_2O_2, stirring vigorously, and warming if necessary. If no $CrO_4^=$ is in solution 3, add to the solution 5 drops of 15 *N* HNO_3, then $NaBiO_3$ a little at a time until an excess has been added. Stir thoroughly and centrifuge. Purple color due to MnO_4^- proves Mn^{++} (see note 2).

If $CrO_4^=$ is present in solution 3, heat the solution nearly to boiling and add 2 drops of K_2SO_4 reagent. Stir vigorously. White $BaSO_4$ proves that $BaCrO_4$ was in the MnO_2. Centrifuge any precipitate, wash thoroughly, and confirm by flame test.

Confirm Mn^{++} in the solution if K_2SO_4 formed no precipitate, or in the centrifugate from any $BaSO_4$ precipitate, by adding $NaBiO_3$ as directed.

Notes: 1. If any Ba^{++} enters a Group III precipitate which contains CrOOH, it may precipitate as $BaCrO_4$ as soon as the chromium is oxidized by Na_2O_2 to $CrO_4^=$. Any $BaCrO_4$ precipitated with Fe^{+3}, Mn^{++} etc. will remain practically insoluble in AcOH and thus be found in the MnO_2 residue.

2. $NaBiO_3$ must be in excess to prevent $MnO_4^- + Mn^{++} \rightleftarrows \underline{MnO_2 \cdot H_2O}$.

Confirmation of iron. Place a drop of solution 4 on a spot plate. Add 1 drop of 3 *N* HCl and 1 drop of $[Fe(CN)_6]^{-4}$. Dark blue color proves iron.

Precipitation and confirmation of zinc. Saturate remainder of solution 4 with H_2S. The precipitate (*precipitate 5*) may be sulfur (and possibly some $Zn(HS)_2$). Large Fe^{+3} may give a precipitate of FeS. The solution (*solution 5*) may contain Fe^{++}, Group IV ions, phosphate, and arsenate ions. If the precipitate is black or gray, extract three times with hot 6*N* AcOH 5 drops at a time. Extract the white or light gray residue with 1*N* HCl and test for Zn^{++} as directed for precipitate 7 below.

Separation of iron from Group IV phosphates and arsenates. Add three drops of 3*N* HCl to the solution (centrifugate 5). Boil to remove H_2S. If Fe was absent, add this solution to solution 1. *If Fe was present,* add 2 drops of Br_2 water to oxidize Fe^{++} and boil again. Place the boiled and cooled solution in a centrifuge tube and add 3 drops of KNCS and 0.5 ml of amyl alcohol-ether mixture (2:1). Shake thoroughly. Allow the two liquids to separate and remove the top layer (alcohol-ether layer) with a capillary pipet. Repeat the extraction, using fresh portions of amyl alcohol-ether mixture until the water layer is colored only faintly pink. Then add the water solution to solution 1 (the centrifugate from the Group III precipitate).

Separation of aluminum from chromium and zinc. To solution 3 in a small beaker or flask add solid NH_4Cl until the solution is saturated. Boil until the solution smells only faintly of NH_3. Add more NH_4Cl to make sure that all NaOH has reacted and precipitation of AlOOH is complete. Centrifuge and wash the precipitate with hot water containing NH_4Cl until *all* yellow color is removed.

Confirmation of aluminum. Dissolve the precipitate in the least amount of hot 1*N* HCl. To the solution add 4 drops of 3*N* ammonium acetate solution and 2 drops of aluminon solution. Stir vigorously. Add NH_3 solution until, after stirring, the solution smells of it. Then add 3 drops of $(NH_4)_2CO_3$ solution. (Solution *must* be basic.) The aluminum hydroxide should precipitate dyed brilliant red. A precipitate of uncertain color should be washed with $(NH_4)_2CO_3$ solution.

Separation and confirmation of zinc. Add to solution 6 no more than 2 drops at most of NH_4HS to precipitate ZnS (precipitate 7). Centrifuge. Wash precipitate with water containing NH_4NO_3 and NH_3 until washings no longer are yellow. Dissolve ZnS in 1*N* HCl, boil out H_2S, and test solution for zinc by placing a drop of it on a spot plate and, in an adjacent depression, place a drop of water.

Add to each 1 drop of 0.02% Co^{++} solution and 1 drop of $K_2[Hg(NCS)_4]$ solution. Stir with a glass rod for 15 seconds. If Zn^{++} is present, a pale blue precipitate (see note) will appear in the test solution much more quickly than in the blank. If Zn^{++} is present its amount should be estimated from the combined volumes of ZnS precipitates 5 and 7.

Note: $Co[Hg(NCS)_4]$ is *deep* blue. The precipitate of white $Zn[Hg(NCS)_4]$ containing no more than a trace of this blue salt is *pale* blue. Particular attention should be paid to the *shade* of any blue precipitate obtained in the test for zinc. The light blue $Zn(Co)[Hg(NCS)_4]$ will appear within 15 seconds to two minutes while the deep blue $Co[Hg(NCS)_4]$ will appear only within 2–3 minutes. When only a trace of Zn^{++} is to be detected it is advisable to run a "blank" using 1 drop of water instead of the solution to be tested. [Feigl, *Tüpfelreactionen* (2nd ed.), p. 236.]

If for any reason as much as 1 mg per ml of Co^{++} were in the Zn^{++} solution, a *deep* blue precipitate might appear within 15–30 seconds. In our system this is unlikely to occur.

PRECIPITATION AND ANALYSIS OF CATION GROUP IV

TABLE 19
ANALYSIS OF GROUP IV (ALKALINE EARTH IONS)

<table>
<tr><td colspan="2">Known or unknown or centrifugate from Group III. Add 5 drops 16 N HNO_3 and evaporate to dryness. Ignite to remove NH_4 salts. Moisten the cooled residue with 1 drop 3 N HCl. Take up with 1 ml H_2O. Test 1 drop with sodium rhodizonate for Ba^{++} or Sr^{++}. Heat the remainder of the soln. nearly to boiling. Add K_2SO_4 until pptn. is complete.</td></tr>
<tr><td>Ppt. 1. $BaSO_4$, $SrSO_4$, ($CaSO_4$). Wash with hot 0.15 N H_2SO_4, add first washing to soln. 1. Test second washing for Ca^{++} with NH_3 and $(NH_4)_2C_2O_4$. Continue washing until no test for Ca^{++} is obtained.
Residue. $BaSO_4$, $SrSO_4$. Moisten with 12 N HCl and make flame tests.</td><td>Soln. 1. Ca^{++}, Mg^{++}, ($H_2PO_4^-$, $H_2AsO_4^-$). Make just alkaline with NH_3, then acid with AcOH, heat nearly to boiling, add $(NH_4)_2C_2O_4$ until pptn. is complete.
Ppt. 2. CaC_2O_4. Wash with H_2O. Add first washings to soln. 2. Confirm by flame test.
Soln. 2. Mg^{++}, $H_2PO_4^-$, $H_2AsO_4^-$. Add 2 drops 3 N HCl. Add S. and O. reagent. Then add NaOH until color becomes red-violet or blue. Centrifuge and estimate amt. of $Mg(OH)_2$,($MgHPO_4$, $MgHAsO_4$).</td></tr>
</table>

Procedures

Preparation of the solution. To the acidified centrifugate from Group III add 5 drops of 16*N* HNO_3 (see note 1) and evaporate carefully just to dryness over a free flame (see page 188) and ignite

until ammonium salts are *completely* removed (see note 2). *Care!* Moisten the cooled residue with no more than 1–2 drops of 3 *N* HCl. Take up the residue with 10 drops of water and with a pipet transfer the liquid and any solid to a centrifuge tube. Rinse out the crucible thoroughly twice with 5 drops of water each time. Add washings to the solution and mix thoroughly. Do not centrifuge out any residue (see note 3).

Notes: 1. The centrifugate from Group III contains AcOH. If the AcOH were not destroyed by boiling with HNO_3, a dark residue (carbon) might result upon ignition of the residue.

2. Experiments have shown that NH_4^+ tends to prevent complete precipitation of $SrSO_4$. For this reason it is important that ammonium salts be removed as completely as possible.

3. Whenever a sulfide solution is evaporated to dryness, there is always a possibility of sulfate ion being formed. The sulfate would then react with Ba^{++} or Sr^{++} to precipitate $BaSO_4$ and/or $SrSO_4$. Therefore a small residue should not be discarded.

Preliminary test for barium. Place two drops of this mixture in a test tube. Make just alkaline with NH_3, then just acid with AcOH. Spot a strip of filter paper with 1 drop of this solution and test with *recently prepared* sodium rhodizonate solution (see note) exactly as directed, experiment 4, barium (page 276). (Test for Ba^{++} in presence of Sr^{++}, or for Sr^{++} in absence of Ba^{++}.)

Note: In aqueous solution this reagent is not stable. Before using, the reagent solution should always be tested with a drop of Ba^{++} test solution as directed on page 276. If a bright red spot is obtained, the reagent is suitable for use. For detection of traces of Ba and Sr, it is desirable to allow the test spot to dry for 5 to 10 minutes. The red color will form slowly on standing. A blank should always be run.

Separation and confirmation of barium and strontium. Heat the remainder of the mixture nearly to boiling and add K_2SO_4 (see note 1) dropwise with stirring after each addition. Test for complete precipitation. Continue stirring at least two minutes to ensure complete precipitation of strontium. Centrifuge and remove the centrifugate as completely as possible to another centrifuge tube. Wash the precipitated sulfates twice with 4 drops at a time of hot 0.15 *N* H_2SO_4 (1 drop 3 *N* H_2SO_4 and 19 drops H_2O). Add the first washings to the centrifugate. Pipet off the second washing into a test tube and add 1 drop 6 *N* NH_3 and a drop of $(NH_4)_2C_2O_4$. If a turbidity appears Ca^{++} is still in the sulfate precipitate. The washing must be continued until *no turbidity* results when 1 drop of

$(NH_4)_2C_2O_4$ is added. Remove the wash liquid as completely as possible from the sulfates. Stir them up with 1 drop of 12*N* HCl and confirm Ba and/or Sr by flame test (see note 2).

Notes: 1. For the reason stated in note 2, "Preparation of the Solution" (p. 326), this reagent is to be preferred to the more commonly used $(NH_4)_2SO_4$. It is preferable to Na_2SO_4 because of less interference with the flame tests.

2. Detection of a small amount of Sr in presence of a large amount of Ba^{++} is not difficult since the Ba migrates up the wire leaving the Sr at the tip.

Detection of a small amount of Ba in much Sr is more difficult. One mg of Ba^{++} is readily detectable in presence of 4 mg of Sr^{++}. Amounts less than 1 mg cannot be very certainly identified by flame test. But even a trace should have been detected by the sodium rhodizonate test.

Separation and confirmation of calcium. To the centrifugate (Ca^{++} and Mg^{++}) add ammonia solution until solution becomes just basic to litmus (see note). Acidify with AcOH. Heat nearly to boiling and add $(NH_4)_2C_2O_4$ dropwise with vigorous stirring as long as a precipitate continues to form. Centrifuge and test for complete precipitation. Remove centrifugate to another centrifuge tube. Wash the CaC_2O_4 precipitate twice with 4 drops of water. Each time remove liquid as completely as possible. Mix the precipitate with 1 drop of 12*N* HCl and confirm Ca by flame test.

Note: When phosphate or arsenate are present, Ca or Mg phosphate or arsenate may precipitate when the solution is made basic. However, the precipitate will redissolve when solution is made acid with AcOH.

Precipitation and confirmation of magnesium. To the centrifugate from the CaC_2O_4 precipitate add 2 drops 3*N* HCl and apply S. and O. test as directed under magnesium, page 277. Centrifuge the precipitate and note the volume it occupies.

CHAPTER 17

INTRODUCTION TO THE ANALYSIS OF ANIONS

Qualitative analysis of the anions has never been made so "systematic" as that of the cations. This is to say that no entirely satisfactory method has yet been devised for subdividing the anions into groups by successive precipitations.

Bunsen in 1878 devised a grouping of the anions based on solubilities of Ba (or Ca) salts in neutral solution, in dilute AcOH, and in dilute HCl, and of silver salts in neutral solution and in dilute HNO_3. Many later modifications have been, and still are being, devised.

Experience in the Purdue laboratory has demonstrated the usefulness of the grouping devised by Duschak and Sneed,[1] which, however, did not include arsenate, arsenite, oxalate, and acetate.

It is obvious that if the anions can be divided into groups, the analytical procedure frequently may be considerably shortened, since an entire group may be proved absent by a single reagent. In the end it will be necessary to test for only those anions belonging to groups indicated as present by their group reagents.

The procedure outlined hereafter is based on a grouping which combines the Duschak-Sneed system in modified form, the Noyes and Bray grouping of oxidant and reductant anions and the solubilities of the silver salts. We believe this procedure to be an innovation in that the group tests are used to prove the *absence* of anions rather than their presence. When these preliminary group tests have been completed and recorded on the Anion Elimination Sheet (hereafter designated by A.E.S.), a brief study of the sheet makes evident that only a *relatively few* anions can be present. All others having been thus proved absent, a few quick tests will usually suffice to determine which of the remaining possible anions are actually present. It has been found in the Purdue laboratories that much time is saved by this method. Two examples of the use of the A.E.S. are given at the end of this chapter.

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[1] J. Chem. Ed., **8**, 1177–1186; 1386–1395 (1931).

THE ANALYTICAL GROUPING OF THE ANIONS

The grouping below is most valuable when a group test is negative, since the absence of *all* anions in that group is at once assured. The ions listed under each of the various groups will always appear in that group if present.

Precipitates in Groups IV to VIII are not *proofs* that any ion of those groups is present, since, as stated under each group, certain *other* ions *may* appear in that group (1) when present in unusually large amount; (2) as a result of too high C_{OH^-}, for example, $Ca(AsO_2)_2$ in Group IV; (3) as a result of incomplete precipitation in preceding groups, for example, if all $HPO_4^=$ is not precipitated in Group IV, it will be precipitated by Ba^{++} in Group V. Therefore, before making a group test by precipitation the solution should be tested for complete precipitation of the preceding group.

Group I. Anions that will oxidize colorless $[MnCl_6]^{-4}$ (12*N* HCl saturated with $MnCl_2$) to brown $[MnCl_6]^{-3}$: ClO_3^-, $CrO_4^=$, $[Fe(CN)_6]^{-3}$, MnO_4^-, (possibly NO_3^-, NO_2^-).

Group II. Anions that will reduce $KMnO_4$ in dilute H_2SO_4: $[Fe(CN)_6]^{-4}$, $SO_3^=$, $S_2O_3^=$, AsO_2^-, $C_2O_4^=$, I^-, Br^-, NCS^-, $S^=$, NO_2^-.

Group II-A. Anions that will reduce one or the other ion of $FeFe(CN)_6$ reagent, producing a blue or green solution or precipitate: $S^=$, $SO_3^=$, $S_2O_3^=$, I^-, NO_2^-. Also included in this group are NCS^- and $[Fe(CN)_6]^{-4}$, which react with Fe^{+3} of the reagent to form $[Fe(NCS)_6]^{-3}$ (red) and Prussian blue. Large $C_2O_4^=$ may form $[Fe(C_2O_4)_3]^{-3}$, a green solution.

Group III. Anions which form silver salts insoluble in dilute nitric acid: I^-, Br^-, NCS^-, Cl^-, $S^=$, $[Fe(CN)_6]^{-3}$, $[Fe(CN)_6]^{-4}$, $S_2O_3^=$, CN^-.

Group III-A. Anions whose silver salts are colored and soluble in dilute nitric acid but insoluble in neutral solution: $CrO_4^=$, $HAsO_4^=$, $HPO_4^=$, and AsO_2^-.

Group IV. Anions whose calcium salts are insoluble in cold neutral or slightly basic solution: $CO_3^=$, 0.1 (see note 1); $HPO_4^=$, 0.04; $C_2O_4^=$, 0.03; F^-, 0.1. Also possibly $SO_4^=$, 0.75; $SO_3^=$, 0.8 (see note 2); BO_2^-, 13.5; $[Fe(CN)_6]^{-4}$, 17.5. ($HAsO_4^=$, AsO_2^-, see the note to Group VI.)

Notes: 1. In Groups IV to VII are given the number of milligrams of the anion stated by Duschak and Sneed to be required to give a precipitate (turbidity) in 1 milliliter of solution, *when the anion is present alone.* Copre-

cipitation and salt effect probably modify these figures considerably and to varying degrees for different anions. Anions in parentheses may partially precipitate if present in sufficiently large concentration. The data for arsenate and arsenite given in the note to Group VI were obtained in the Purdue laboratory.

2. We find that 0.3 mg of SO_3^- in 1 ml gives a precipitate with 2 drops of 1 *M* $(AcO)_2Ca$, but only after stirring about three minutes.

Group V. Anions whose Ba salts are insoluble in cold neutral or slightly basic solution, but whose Ca salts are soluble in neutral or slightly basic solution: $SO_4^=$, 0.025; $SO_3^=$, 0.2; $CrO_4^=$, 0.05. Also possibly $S_2O_3^=$, 4.5; $[Fe(CN)_6]^{-4}$, 3.0. ($HAsO_4^=$, AsO_2^-, see the note to Group VI.)

Group VI. Anions whose Cd salts are insoluble in hot neutral or slightly basic solution but whose Ca and Ba salts are soluble in cold neutral or slightly basic solution: $S^=$, 0.025; $[Fe(CN)_6]^{-3}$, 0.05; $[Fe(CN)_6]^{-4}$, 0.05; $HAsO_4^=$, 0.07; AsO_2^-, 0.03 (see note). Also possibly CN^-, 5.0.

Note: The peculiar behavior of arsenite and arsenate toward Ca^{++}, Ba^{++}, and Cd^{++} seems to belie the solubility data. The explanation appears to be (1) that all these salts have negative coefficients of solubility with temperature and (2) that their solubilities are extraordinarily dependent upon C_{H^+}.

The data below illustrate the latter relation. The figures state the least amount of the anions AsO_2^- and $HAsO_4^=$ which in a volume of 1 ml gives a turbidity with 2 drops of the 2 *N* precipitants after the solution is stirred for 1 minute. The solutions used, $NaAsO_2$ and Na_2HAsO_4, were *basic* to *phenolphthalein*, the former strongly, the latter faintly.

Cold	$Ca(AsO_2)_2$	1 mg	$CaHAsO_4$	5 mg
Cold	$Ba(AsO_2)_2$	2.5 mg	$BaHAsO_4$	0.6 mg
Cold	$Cd(AsO_2)_2$	0.4 mg	$CdHAsO_4$	0.13 mg
Hot	$Cd(AsO_2)_2$	0.03 mg	$CdHAsO_4$	0.07 mg

The same test solutions made faintly basic to *litmus* by addition of AcOH:

Cold	$Ca(AsO_2)_2$	30 mg no turbidity[a]	$CaHAsO_4$[c]	28 mg turbidity
Cold	$Ba(AsO_2)_2$	30 mg no turbidity[b]	$BaHAsO_4$	3 mg turbidity

[a] Medium precipitate on heating. [b] Slight precipitate on heating. [c] Heavy precipitate on heating.

Group VII. Anion whose Co salt is insoluble in neutral or slightly basic solution containing a rather large excess of Co^{++} but whose Ca, Ba, and Cd salts are soluble in neutral or slightly basic solution: CN^-, 0.2 mg per ml.

Group VIII. Anions whose Ag salts are insoluble in dilute HNO_3, but whose Ca, Ba, Cd, and Co salts are soluble in neutral or slightly basic solutions: Cl^-, Br^-, I^-, NCS^-, $S_2O_3^=$.

Group IX. Anions not precipitated in Groups IV to VIII: AcO^-, BO_2^-, NO_2^-, NO_3^-, ClO_3^-.

Table 20 shows the behavior of each anion toward such of the group reagents as it encounters. The use of ? indicates that the anion may react if present in *unusually large* amount. Blank spaces mean either that there is no reaction or that in this system the ion does not encounter the reagent.

Two sample A.E.S. and the notebook entries accompanying them show that many anions can be eliminated by group tests.

ANION ELIMINATION SHEET

ENTRIES FOR UNKNOWN 1

	Certainly Present	Certainly Absent	Possibly Present	Doubtful, Try Other Tests
1. $CO_3^=$		HCl_I	IV	
2. $HPO_4^=$			III-A, IV	✓
3. $C_2O_4^=$			II, IV	✓
4. F^-			IV	✓
5. $SO_4^=$	HCl_{III}		V	
6. $SO_3^=$		II-A	II	
7. $CrO_4^=$		A		
8. $S^=$		II-A	II	
9. $Fe(CN)_6^{-4}$		II-A	II	
10. $Fe(CN)_6^{-3}$		A		
11. CN^-		VII	III	
12. $S_2O_3^=$		II-A	II	
13. NCS^-		II-A	II	
14. Cl^-			III, VIII	✓
15. Br^-	II			
16. I^-		II-A	II	
17. ClO_3^-		III	I	
18. BO_2^-		HCl_{II}		
19. AsO_2^-		HCl_V	II, III-A, VI	
20. $HAsO_4^=$	III-A			
21. NO_2^-		II-A, IX-A	I, II	
22. AcO^-		IX-C		
23. NO_3^-	IX-B		I	

TO BE DONE: Test Group IV ppt. for: $HPO_4^=$, $C_2O_4^=$, and F^-.
Test Group VIII ppt. for: Cl^-.

[NOTE: Notebook entries on page 334.]

TABLE 20
PRELIMINARY TESTS FOR ANION GROUPS

Group Reagent / Ion	I $[MnCl_4]^-$ + H^+ Unkn. Soln.	II MnO_4^- + H^+ Unkn. Soln.	II-A Fe^{+3} $[Fe(CN)_6]^{-3}$ Unkn. Soln.	III Ag^+ + HNO_3 Unkn. Soln.	III-A Ag^+ + NH_3 Soln. from III
AcO^-					
$HAsO_4^=$					Ag_3AsO_4 (red-brown)
AsO_2^-		$HAsO_4^=$			Ag_3AsO_3 (yellow)
BO_2^-					
Br^-		Br_2		AgBr (cream)	
$CO_3^=$					White?
ClO_3^-	Cl^-				
Cl^-				AgCl	
$CrO_4^=$	Cr^{+3} (green)				Ag_2CrO_4 (brown-red)
CN^-		?		AgCN	
$[Fe(CN)_6]^{-4}$		$[Fe(CN)_6]^{-3}$	Prussian blue	$Ag_4[Fe(CN)_6]$	
$[Fe(CN)_6]^{-3}$	$[Fe(CN)_6]^{-4}$			$Ag_3[Fe(CN)_6]$ (orange-brown)	
F^-					
I^-		$I_2(IO_3^-)$	I_2 and Prussian blue	AgI (yellow)	
NO_3^-	NO (slowly!)				
NO_2^-	NO	NO_3^-	NO_3^- and Prussian blue		
$C_2O_4^=$		CO_2	Green soln.?		White?
$HPO_4^=$					Ag_3PO_4 (yellow)
$SO_4^=$					
$S^=$		$SO_4^=$	S and Turnbull's blue	Ag_2S (black)	
$SO_3^=$		$SO_4^=$, $S_2O_6^=$	$SO_4^=$ and Turnbull's blue		
NCS^-		$SO_4^=$, NCO^-	$[Fe(NCS)_6]^{-3}$ (red!)	AgNCS	
$S_2O_3^=$		$SO_4^=$, $S_2O_6^=$	$S_4O_6^=$ and Turnbull's blue	$Ag_2S_2O_3$ → Ag_2S	

TABLE 20.—(*Continued*)
PRECIPITATION TESTS FOR ANION GROUPS

IV $(AcO)_2Ca$ Unkn. Soln.	V $(AcO)_2Ba$ Soln. from IV	VI $(AcO)_2Cd$ Soln. from V	VII Co^{++} Soln. from VI	VIII $Ag^+ + H^+$ Soln. from VII	Ions not eliminated by the group tests (Group IX)
.....	.....	.....	.....	.....	Acetone by nitroprusside
?	?	$CdHAsO_4$	.....	.....	.....
?	?	$Cd(AsO_2)_2$	.....	.....	.....
.....	.....	.....	.....	.....	Turmeric test or BF_3
.....	.....	.....	.....	$AgBr$	.....
$CaCO_3$	.....	.....	.....	.....	.....
.....	.....	.....	.....	.....	In filtrate from Group VIII. $AgCl$
.....	.....	.....	.....	$AgCl$	.....
.....	$BaCrO_4$	.....	.....	.....	.....
.....	.....	.....	$Co(CN)_2$ (tan)	.....	.....
.....	.....	$Cd_2[Fe(CN)_6]$	.....	.....	.....
.....	.....	$Cd_3[Fe(CN)_6]_2$ (yellow)	.....	.....	.....
CaF_2	.....	.....	.....	.....	.....
.....	.....	.....	.....	AgI	.....
.....	.....	.....	.....	.....	Special tests
.....	.....	.....	.....	.....	Special tests
CaC_2O_4	.....	.....	.....	.....	.....
$CaHPO_4$	.....	.....	.....	.....	.....
?	$BaSO_4$	.....	.....	.....	.....
.....	.....	CdS (orange-yellow)	.....	.....	.....
$CaSO_3$?	$BaSO_3$	.....	.....	.....	.....
.....	.....	.....	.....	$AgNCS$	.....
.....	?	.....	.....	Ag_2S	.....

Students will do well to study these examples thoroughly until they clearly see in the notebook record the justification of each entry on the A.E.S.

Unknown 1

Recorded Observations and Deductions

Test A. The unknown water solution was colorless and neutral to litmus. A drop of it with 3 *N* Na_2CO_3 gave no precipitate. No "prepared solution" need be made.

Deduction. A colorless solution *proves* absence of $CrO_4^{=}$ and $[Fe(CN)_6]^{-3}$ and indicates absence of $[Fe(CN)_6]^{-4}$.

Enter on the A.E.S. in the "certainly absent" column an "A" opposite these two ions.

Deduction. That the solution was neutral and contained no heavy metal ions (no ppt. by Na_2CO_3) suggested, but did not *prove*, absence of anions of weak acids. (Heavy metal salts of strong acids hydrolyze to form acid solutions. It is conceivable that the hydrolysis of such a salt might offset that of the salt of a weak acid and strong base so that a *neutral* solution resulted.)

Group I. Brown color appeared 2 minutes after heating.

Deduction. An oxidant is indicated. Since $CrO_4^{=}$ and $[Fe(CN)_6]^{-3}$ were already eliminated, only ClO_3^-, NO_2^-, or NO_3^- need be considered.

Enter in the "possibly present" column a "I" for these three ions.

Group II. Three drops of 0.01 *N* $KMnO_4$ and then 2 drops 0.1 *N* $KMnO_4$ were bleached *in the cold.* On shaking with CCl_4 the latter was colored brown-yellow.

Deduction. A reductant anion is present. No information is given about $C_2O_4^{=}$ since, in presence of another reductant, $C_2O_4^{=}$ is reduced in the cold.

Brown CCl_4 layer *proved* Br^- present.

In the "certainly present" column enter "II" opposite Br^-. In the "possibly present" column enter "II" opposite $C_2O_4^{=}$, $SO_3^{=}$, $S^{=}$, $[Fe(CN)_6]^{-4}$, $S_2O_3^{=}$, NCS^-, I^-, AsO_2^-, NO_2^-.

Group II-A. No change of color as compared with the blank.

Deduction. Since neither ion of ferric ferricyanide was affected, $SO_3^{=}$, $S^{=}$, $[Fe(CN)_6]^{-4}$, $S_2O_3^{=}$, NCS^-, and NO_2^- are *proved* absent. An extremely informing test!

In the "certainly absent" column enter "II-A" opposite $SO_3^=$, $S^=$, $[Fe(CN)_6]^{-4}$, $S_2O_3^=$, NCS^-, I^-, NO_2^-.

Group III. Cream-white precipitate. In the filtrate NO_2^- formed no AgCl.

Deduction. All ions forming silver salts insoluble in HNO_3 have been already eliminated, except CN^-, Br^-, and Cl^-. Br^- has already been *proved* present and the precipitate has the cream tint of AgBr.

In the filtrate from the Ag^+ ppt. NO_2^- forms no AgCl and ClO_3^- is thus *proved* absent. Since NO_2^- has been eliminated, it must be NO_3^- that gave the Group I test.

In the "possibly present" column enter "III" opposite CN^- and Cl^-. In the "certainly absent" column enter a "III" opposite ClO_3^-.

Group III-A. Red-brown precipitate.

Deduction. A red-brown ppt. at once *proves* $HAsO_4^=$ present, inasmuch as $CrO_4^=$ has been already eliminated. Since the color of Ag_3AsO_4 might cover the yellow of Ag_3AsO_3 and Ag_2HPO_4, these two ions may be present.

In the "certainly present" column enter "III-A" opposite $HAsO_4^=$. In the "possibly present" column enter "III-A" opposite $HPO_4^=$ and AsO_2^-.

Note that the above simple tests and observations, requiring no more than ten minutes, have detected with certainty three ions, Br^-, $HAsO_4^=$, and NO_3^-, and with equal certainty have proved the absence of 10 others. Already the analyst has positive information about 13 of the 23 anions to be considered.

Group IV. White Ca precipitate.

Deduction. The Ca ppt. may contain $CO_3^=$, $HPO_4^=$, F^-, $C_2O_4^=$. $SO_3^=$ was eliminated by test II-A.

In the "possibly present" column enter "IV" opposite $CO_3^=$, $HPO_4^=$, $C_2O_4^=$, F^-.

Group V. White Ba precipitate.

Deduction. This ppt. suggests $BaSO_4$, since both $CrO_4^=$ and $SO_3^=$ have been eliminated. This precipitate must not be taken as proof of $SO_4^=$, since other anions *can* precipitate here.

In the "possibly present" column enter "V" opposite $SO_4^=$.

Group VI. White Cd precipitate.

Deduction. This ppt. can be $Cd(AsO_2)_2$ or $CdHAsO_4$, since $S^=$ and $[Fe(CN)_6]^{-3}$, which would give yellow ppts., and $[Fe(CN)_6]^{-4}$ have been proved absent.

In the "possibly present" column enter "VI" opposite AsO_2^-.

Group VII. No Co^{++} precipitate.

Deduction. Since Co^{++} forms no ppt., CN^- is *proved* absent.

In the "certainly absent" column enter "VII" opposite CN^-.

Group VIII. Cream-white precipitate, same tint as in Group III.

Deduction. The AgBr ppt. may contain some white AgCl.

In the "possibly present" column enter "VIII" opposite Cl^-.

Test HCl_I. Calcium acetate film did not become cloudy.

Deduction. $CO_3^=$ is absent.

In the "certainly absent" column enter "HCl_I" opposite $CO_3^=$.

Test HCl_{II}. Both turmeric and BF_3 tests negative.

Deduction. Borate is *proved* absent.

In the "certainly absent" column enter "HCl_{II}" opposite BO_2^-.

Test HCl_{III}. Ba^{++} gave a white precipitate.

Deduction. Since $BaSO_4$ is the only Ba salt insoluble in HCl, $SO_4^=$ is *proved* present.

In the "certainly present" column enter "HCl_{III}" opposite $SO_4^=$.

Test HCl_{IV}. Unnecessary.

Deduction. Unnecessary because NCS^- and $[Fe(CN)_6]^{-4}$ were proved absent by II-A and $[Fe(CN)_6]^{-3}$ by A.

Test HCl_V. H_2S gave no ppt. in 0.3 *N* H^+.

Deduction. Arsenite is *proved* absent.

In the "certainly absent" column enter "HCl_V" opposite AsO_2^-.

Group IX-A. The original soln. gave *no red color* with sulfanilic acid and α-naphthylamine.

Deduction. Not even a trace of NO_2^- is present.

In the "certainly absent" column enter "IX-A" opposite NO_2^-.

Group IX-B. Devarda's alloy added to the above. Strong red color slowly developed.

Deduction. NO_3^- is *proved* present.

In the "certainly present" column enter "IX-B" opposite NO_3^-.

Group IX-C. No effect on Na nitroprusside.

Deduction. Acetate is *proved* absent.

In the "certainly absent" column enter "IX-C" opposite AcO^-.

Place checks in the "doubtful column" opposite $HPO_4^=$, $C_2O_4^=$, F^-, Cl^-.

Summary

Proved present: Br^-, $SO_4^=$, $HAsO_4^=$, NO_3^-.

To be done: Test Group IV ppt. for $HPO_4^=$, F^-, $C_2O_4^=$. Test Group VIII ppt. for Cl^-.

ANION ELIMINATION SHEET

ENTRIES FOR UNKNOWN 2

	Certainly Present	Certainly Absent	Possibly Present	Doubtful, Try Other Tests
1. $CO_3^=$	HCl_I		IV	
2. $HPO_4^=$	III-A by elimination		III-A, IV	
3. $C_2O_4^=$			II, IV	✓
4. F^-			IV	✓
5. $SO_4^=$	HCl_{III}		V	
6. $SO_3^=$	II-A by elimination		II, II-A, IV, V	
7. $CrO_4^=$		A		
8. $S^=$		III	II, II-A	
9. $Fe(CN)_6^{-4}$		III	II, II-A	
10. $Fe(CN)_6^{-3}$		A		
11. CN^-		III		
12. $S_2O_3^=$		III	II, II-A	
13. NCS^-		III	II, II-A	
14. Cl^-		III		
15. Br^-		II		
16. I^-		III	II, II-A	
17. ClO_3^-		I		
18. BO_2^-	HCl_{II}			
19. AsO_2^-		VI	II, III-A	
20. $HAsO_4^=$		III-A		
21. NO_2^-		IX-A	II, II-A	I
22. AcO^-		IX-C		
23. NO_3^-		IX-B		I

TO BE DONE: Test Group IV ppt. for $C_2O_4^=$, F^-.

Unknown 2

Recorded Observations and Deductions

Test A. Solid unknown, colorless, partly soluble in water. Water extract decidedly basic. "Prepared solution" 50 mg of

unknown + 2.5 ml 3*N* Na_2CO_3. Large white residue. No odor of NH_3. Solution made just basic to litmus. No H_2S detected when HCO_3^- was being decomposed.

Deductions. (1) $CrO_4^=$ and $[Fe(CN)_6]^{-3}$ are absent. (2) Highly colored sulfides are absent. (3) Alkali salts of weak acids are probably present. (4) NH_4^+ salts are absent. (5) No transposable sulfides are present.

Group I. No brown color after 10 minutes.

Deduction. Proves absence of ClO_3^-. No more than small amounts of NO_2^- or NO_3^- can be present.

Note entries made on A.E.S.

Group II. $KMnO_4$ was reduced in the cold. CCl_4 not colored.

Deduction. A reductant anion is present. Br^- is *proved* absent.

Note entries on A.E.S.

Group II-A. Blue color appears instantly.

Deduction. A *strong* reductant anion or else $[Fe(CN)_6]^{-4}$ is present.

Note entries on A.E.S.

Group III. Ag^+ in HNO_3 soln. gives no ppt.

Deduction. All anions of Group III are *proved* absent. ClO_3^- (proved absent by Group Test I) need not be tested for.

Note entries on A.E.S.

Group III-A. Yellow Ag^+ ppt. in neutral soln.

Deduction. Proves absence of $HAsO_4^=$ and presence of AsO_2^- and/or $HPO_4^=$.

Note entries on A.E.S.

Group IV. White Ca ppt.

Deduction. All ions of this group are possibly present.

Note entries on A.E.S.

Group V. White Ba ppt.

Deduction. $SO_4^=$ and/or $SO_3^=$ possible. Color of ppt. and test A prove $CrO_4^=$ absent.

Note entries on A.E.S.

Group VI. No Cd ppt.

Deduction. All ions of Group VI absent from the "prepared solution." The yellow ppt. in III-A could be only Ag_2HPO_4. This *proves* $HPO_4^=$ present.

Note entries on A.E.S.

Group VII. No test necessary. Why?

Group VIII. No test necessary. Why?

Test HCl_I. After addition of Br_2 water (to oxidize any $SO_3^=$ to $SO_4^=$), film of $(AcO)_2Ca$ became cloudy. Visible evolution of gas indicated *large* $CO_3^=$.

Deduction. $CO_3^=$ is present.

Note entry on A.E.S.

Test HCl_{II}. Immediate red spot on turmeric paper which with 1% NaOH became dark green.

Deduction. BO_2^- is present.

Note entry on A.E.S.

Test HCl_{III}. Immediate white ppt.

Deduction. $SO_4^=$ is present.

Note entry on A.E.S.

Test HCl_{IV}. Unnecessary. Why?

Test HCl_V. Unnecessary. Why?

Group IX-A. No red color.

Deduction. NO_2^- is absent.

Note entry on A.E.S.

Group IX-B. Devarda's alloy in soln. IX-A gives no color.

Deduction. NO_3^- is absent.

Note entry on A.E.S.

Group IX-C. Nitroprusside is not colored.

Deduction. Acetate is not present.

Note entry on A.E.S.

STUDY OF A.E.S.

1. Positive test for Group II-A could have been given only by $SO_3^=$, since all other ions of this group have been eliminated.

2. Yellow ppt. in Group III-A must have been due to $HPO_4^=$, since AsO_2^- was proved absent.

3. Group IV ppt. must be tested for $C_2O_4^=$ and F^-. This is all that remains to be done.

Note 1. The quickly performed preliminary group tests, followed by a thoughtful study of the A.E.S., have detected or eliminated all except two of the 23 ions to be considered.

Note 2. It was noticed that in HCl_{I-V} tests the solid unknown dissolved completely. Therefore, halides of Ag^+ or Hg_2^{++} could not be in the unknown, and the solid residue from making the "prepared solution" need not be tested for halide ions. If Zn^{++} should be found in the cation analysis, this residue must be tested for $S^=$. If F^- is not found in the Group IV ppt., it must be tested for in the insoluble residue.

CHAPTER 18

PROPERTIES AND REACTIONS OF THE ANIONS

ANIONS OF GROUP IV

Carbonic Acid and Its Ions

Occurrence. Carbon dioxide is the product of complete oxidation of carbon. In the average it constitutes about 0.3 % by volume of the earth's atmosphere, although this varies considerably with the seasons and also with the location.

Solubility. Carbon dioxide is soluble in water to the extent of 0.034 mol per liter at 25° and under a pressure of 1 atmosphere. Rain water dissolves atmospheric CO_2 to the extent of about 1.22×10^{-5} mol per liter. The gas combines to a slight extent with water to form the unstable acid H_2CO_3.

All bicarbonates are soluble in water. For this reason when rain water percolates through limestone rock a little of the rock is dissolved.

$$\underline{CaCO_3} + H_2CO_3 \rightleftarrows 2HCO_3^- + Ca^{++}$$

The temporary hardness of ground water is due to this reaction. When such hard water is boiled, $CaCO_3$ precipitates.

$$2HCO_3^- + Ca^{++} = \underline{CaCO_3} + H_2O + \overline{CO_2}$$

When CO_2 is passed into a solution of NH_3, NH_4^+ and HCO_3^- are formed in proportion to the partial pressures of the CO_2 and NH_3 over the solution. This reaction is important in the Solvay process for making Na_2CO_3.

Reactions of Carbonate Ion

Solubility. All normal carbonates except those of the alkali metals and NH_4^+ are insoluble in water.

Dilute mineral acids and acetic acid decompose carbonates with evolution of CO_2 (test for carbonates).

$$\underline{MCO_3} + H^+ \rightarrow M^{++} + HCO_3^-$$
$$HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow \overline{CO_2} + H_2O$$

Calcium ion precipitates, from neutral or slightly basic solutions, $CaCO_3$, soluble in AcOH. This is a sensitive test for CO_2.

Barium ion reacts like calcium ion.

Phenolphthalein is pink in solutions containing chiefly $CO_3^=$ but colorless in solutions containing chiefly HCO_3^-. It indicates the end point in the reaction,

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

because the pink color just disappears at 8.2, the *p*H of $NaHCO_3$ solution.

Silver nitrate precipitates, from solutions containing $CO_3^=$ or HCO_3^-, white Ag_2CO_3, usually yellowish due to colloidal Ag_2O.

PRACTICE EXERCISE

Write balanced equations for the following reactions:

1. $\underline{CaCO_3} + AcOH \rightleftarrows$
2. $CO_3^= + Ca^{++} \rightleftarrows$
3. $CO_3^= + H^+$ (sufficient to change phenolphthalein) $\rightleftharpoons$

Phosphoric Acid and Its Ions

Occurrence. Large quantities of phosphate are found in the earth's lithosphere. Among commercially important phosphate minerals are the calcium phosphates (apatite and rock phosphate) and monazite, a phosphate of thorium and rare earth ions which furnishes material for gas mantels.

Hydrates. Three different hydrates of P_2O_5 form stable salts:

$$P_2O_5 + H_2O = 2HPO_3 \text{ (metaphosphoric acid)}$$
$$P_2O_5 + 2H_2O = H_4P_2O_7 \text{ (pyrophosphoric acid)}$$
$$P_2O_5 + 3H_2O = 2H_3PO_4 \text{ (orthophosphoric acid)}$$

The last is the most important. The other two acids are changed to the ortho acid by boiling with water.

Commercial orthophosphoric acid is a colorless syrupy liquid with specific gravity 1.70 to 1.75 which contains about 85% of the anhydrous acid.

Acidic strength. The value of its K_{ion} shows that $HPO_4^{=}$ is nearly as weak an acid as water so that tertiary phosphates can be precipitated only in strongly basic solutions. Primary phosphates, for example, $Ca(H_2PO_4)_2$, are soluble in water. Advantage is taken of this fact to turn water-insoluble phosphates, such as rock phosphate, which are very slowly available for plant food, into the the quickly available primary phosphates, for example,

$$\underline{Ca_3(PO_4)_2} + 4H_3PO_4 = 3\underline{Ca(H_2PO_4)_2}$$

$$\underline{Ca_3(PO_4)_2} + 2H_2SO_4 + 2H_2O = \underline{Ca(H_2PO_4)_2} + \underline{CaSO_4 \cdot 2H_2O}.$$

The following table shows the C_{H^+} in 1 M solutions of H_3PO_4 and its sodium salts.

1 M	C_{H^+}
H_3PO_4	8.7×10^{-2}
NaH_2PO_4	2.2×10^{-5}
Na_2HPO_4	1×10^{-8}
Na_3PO_4	1×10^{-13}

The table shows that 1 M H_3PO_4 has about the same acidity as 0.1 M HCl, that a solution of NaH_2PO_4 is distinctly acid, that a solution of Na_2HPO_4 is faintly basic and that a 1 M solution of Na_3PO_4 is about as strongly basic as 0.1 M NaOH. If to a solution of H_3PO_4 containing methyl orange as indicator NaOH is added, the indicator changes color very nearly at the point when the first hydrogen has been neutralized. If phenolphthalein is now added, the pink color appears when very nearly the same amount of base has been added that was required for the neutralization of the first hydrogen. If trinitrobenzene is then added as indicator, about the same amount of alkali will be required to neutralize the third hydrogen. In other words, methyl orange is an indicator for the first H^+, phenolphthalein for the second H^+, and trinitrobenzene for the third H^+.

Solubility. The phosphates of 4-valent cations, such as Sn^{+4} and Zr^{+4}, are insoluble in dilute mineral acids. Those of 3-valent ions, such as Fe^{+3}, Al^{+3}, and Cr^{+3} are insoluble in strongly buffered acetic acid, while those of 2-valent ions are soluble in this medium. Those of 1-valent ions (alkalies) are soluble in water.

Reactions of Orthophosphate Ion

Calcium ion precipitates from neutral or slightly basic solutions $CaHPO_4$, soluble in AcOH.

Silver nitrate precipitates from neutral solutions yellow Ag_3PO_4, soluble in dilute HNO_3 and in NH_3 solution.

Magnesia mixture, Mg^{++}, NH_4^+, and NH_3, forms, in solutions containing a high concentration of NH_3, white *crystalline* $MgNH_4PO_4 \cdot 6H_2O$. Zn^{++} and Mn^{++} form crystalline ammonium phosphates, isomorphous with the Mg^{++} compound. Ca^{++}, Ba^{++}, and Sr^{++} under the same conditions form *amorphous* secondary phosphates.

Arsenates with magnesia mixture yield similar crystalline precipitates, for example, $MgNH_4AsO_4 \cdot 6H_2O$. When the latter are treated with $AgNO_3$ containing a little AcOH, red brown Ag_3AsO_4 is formed. This reaction serves to distinguish an arsenate from a phosphate.

Ammonium molybdate. When a HNO_3 solution of an orthophosphate is added to an excess of $(NH_4)_2MoO_4$ in HNO_3 and the mixture heated to 60°, a yellow crystalline precipitate of ammonium phosphomolybdate forms. According to recent X-ray measurements by J. B. Keggin the structure of the phosphomolybdate anion corresponds to $[P(Mo_3O_{10})_4]^{-3}$ and it should be named molybdatophosphate ion.

This is an extremely valuable test for phosphate, since in the HNO_3 solution no cations interfere. Strong reductants, such as H_2S and H_2SO_3, which reduce the reagent to molybdenum blue, and large quantities of HCl interfere. These can be removed by evaporating the test solution with excess of $16\,N$ HNO_3. H_3AsO_4 forms a similar yellow precipitate but, in absence of H_3PO_4, only at 100°. In presence of H_3PO_4 the arsenomolybdate appears to coprecipitate with it at 60°.

Benzidine acetate reduces phosphomolybdic acid, $H_3[P(Mo_3O_{10})_4]$, with formation of benzidine blue and molybdenum blue. This test is extremely sensitive and will detect H_3PO_4 in solutions so dilute that they give no precipitate with $(NH_4)_2MoO_4$. It is claimed that 2.5×10^{-5} mg of H_3PO_4 can be detected. For method of carrying out the test see page 410.

Zirconyl chloride precipitates, from solutions not much over $0.3\,N$ in H^+, gelatinous white $ZrO(H_2PO_4)_2$. This reaction has been

recommended for removing H_3PO_4 before proceeding with the analysis of Cation Groups III and IV.

Ferric chloride precipitates in buffered acetic acid solution white $FePO_4$ which appears yellow brown from adsorbed FeO^+. This reaction is frequently used for the removal of H_3PO_4 before proceeding with analysis of Cation Group III.

Sodium carbonate in hot $3N$ solution transposes *very little* of water insoluble phosphates.

$$\underline{CaHPO_4} + CO_3^{=} \rightleftharpoons \underline{CaCO_3} + HPO_4^{=}$$

PRACTICE EXERCISE

Write balanced equations for the following reactions:

1. $Ca^{++} + H_2PO_4^- \rightleftarrows$
2. $Ag^+ + HPO_4^{=} \rightleftarrows$
3. $Mg^{++} + NH_3 + HPO_4^{=} \rightleftarrows$
4. $HMoO_4^- + H_2PO_4^- + H^+ + NH_4^+ \rightarrow \underline{(NH_4)_3[P(Mo_3O_{10})_4]}$
5. $Fe^{+3} + HPO_4^{=} + AcO^- \rightleftarrows$

Oxalic Acid and Its Ions

Oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, is a colorless crystalline solid. Its solubility in water is about 95 mg per ml at 20°. The hydrated acid melts in its water of crystallization at 98°.

Acidic strength. Oxalic acid is a medium weak dibasic acid. Its ionization constants are: $K_1 = 5.9 \times 10^{-2}$; $K_2 = 6.4 \times 10^{-5}$. The first H^+ of $H_2C_2O_4$ is thus about as strong an acid as the first H^+ of H_3PO_4 and a little stronger than the second H^+ of H_2SO_4.

Properties of oxalates. All oxalates are decomposed by strong ignition and by fuming with H_2SO_4 or $HClO_4$. All are transposed by boiling with Na_2CO_3 solution.

Metal oxalates are insoluble or slightly soluble in water, except those of the alkali metals, Mg and Cr. Those insoluble in water readily dissolve in highly ionized acids.

Oxalate ion is a strong complex former, particularly with 3-valent cations such as Fe^{+3}, Cr^{+3}, and Al^{+3}. For example,

$$Fe^{+3} + 3C_2O_4^{=} \rightleftarrows [Fe(C_2O_4)_3]^{-3}.$$

On account of this reaction oxalic acid is commonly used to remove rust and ink stains from fabrics. The acid does not yield sufficiently

high C_{H^+} to injure the fabrics, and the iron can be washed out since it is now in a complex anion.

Oxalate ion forms with some of the ions of cation Group III stable complex anions from which the metal ions are not precipitated by NH_3. Oxalate ion would also precipitate alkaline earth metals in cation Group III. For these reasons oxalate must be destroyed in analysis before precipitation of cation Group III.

Reactions of Oxalate Ion

Calcium ion precipitates oxalate ion almost completely from neutral or slightly basic solutions. CaC_2O_4 is insoluble in dilute AcOH.

Barium and cadmium ions react similarly to calcium ion.

Dilute mineral acids. As a weak acid, $HC_2O_4^-$ is set free from salts (for example, CaC_2O_4) by dilute mineral acids.

Potassium permanganate in hot H_2SO_4 solution is reduced by $H_2C_2O_4$, slowly at first, more rapidly after formation of some Mn^{++} which catalyzes the reaction. In presence of other acids which reduce MnO_4^- to Mn^{++}, $H_2C_2O_4$ is reduced at room temperature.

Ferric ferricyanide reagent (reagent for anion Group II-A). Medium to large amounts of oxalate ion react with the light brown ferric ferricyanide reagent to give green solutions. Probably this is because of formation of green $[Fe(C_2O_4)_3]^{-3}$.

Destruction of oxalate. Fuming $HClO_4$ oxidizes oxalic acid. $HClO_4$ is reduced to Cl^-.

Sodium carbonate in hot $3N$ solution partially transposes all water insoluble oxalates.

$$\underline{CaC_2O_4} + CO_3^{=} \rightleftarrows \underline{CaCO_3} + C_2O_4^{=}$$

PRACTICE EXERCISE

Write balanced equations for the following reactions:

1. $Ca^{++} + C_2O_4^{=} =$
2. $\underline{CaC_2O_4} + H^+ \rightleftarrows$
3. $H_2C_2O_4 + MnO_4^- + H^+ \rightleftarrows \overline{CO_2} + Mn^{++}$
4. $Fe^{+3} + C_2O_4^{=} \rightleftarrows$
5. $H_2C_2O_4 + HClO_4 \rightleftarrows \overline{CO_2} + Cl^-$

Hydrofluoric Acid and Its Ions

Occurrence. Fluorine is rather widely distributed in the earth's lithosphere. Its chief minerals are fluorspar, CaF_2, and cryolite, Na_3AlF_6. It also occurs in small amounts in apatite and in many silicates where F^- seems to replace OH^-.

Properties. Liquid hydrogen fluoride and its vapor appear to consist of $(HF)_6 \rightleftarrows HF$. $(HF)_6$ is said to constitute about 80% of the gas phase.

Reagent HF is about 27 N and contains about 48% HF by weight.

The constant boiling mixture contains 35.4% HF and boils at 120°. It is extremely corrosive and even the vapors can cause painful sores. The best treatment for HF "burns" is borax because of the readiness with which the complex ion $[BF_4]^-$ is formed.

In concentrated aqueous solution of HF the ions are chiefly H_3O^+ and HF_2^-. This is due to the strong tendency of F^- to solvate itself. This is analogous to the solvation of the proton in NH_3 and in water.

$$F^- + HF \rightleftarrows HF_2^-$$
$$H^+ + NH_3 \rightleftarrows NH_4^+$$
$$H^+ + H_2O \rightleftarrows H_3O^+$$

Acidic strength. In 0.1 N solution conductivity measurements indicate HF to be only 10% ionized while HCl, HBr, and HI are indicated to be from 93 to 95% ionized. In a solution of HF the following equilibria are maintained:

$$\frac{C_{H^+} \times C_{F^-}}{C_{HF}} = 7.2 \times 10^{-4}; \quad \frac{C_{HF_2^-}}{C_{F^-} \times C_{HF}} = 5$$

In 1.0 N solution about 5% of the HF is in the form of HF_2^- and about 1% in the form of F^-. In very dilute solutions HF_2^- has nearly disappeared, F^- being now solvated by water instead of by HF. Recent work[1] indicates that the ratio $(C_{H^+} \times C_{F^-})/C_{HF}$ is not constant but varies from 2.2×10^{-3} in more concentrated solutions to 5.5×10^{-4} in 0.04 M solution, at which point it becomes constant. There is no evidence of a polymer H_2F_2 which is given in most books as the molecule in aqueous solution.

[1] Roth, *et al.*, Z. Elektrochemie, **43**, 350 (1937).

Reactions of Fluoride Ion

Calcium ion precipitates fluoride ion completely from neutral or slightly basic solutions. The gelatinous precipitate tends to be colloidal. Calcium fluoride is supposed to be insoluble in acetic acid but the freshly formed gelatinous precipitate dissolves or disperses in it to a considerable extent.

Fuming H_2SO_4 or $HClO_4$ decomposes all fluorides with liberation of HF.

The etching test. HF readily etches glass and all silicious material with formation of volatile SiF_4. This contributes a sensitive test for fluoride.

When making the so-called etching test for fluoride, great pains must be taken to insure complete absence of water, which would form silicic and fluorosilicic acid.

$$3\overline{SiF_4} + 3H_2O \rightleftarrows \underline{H_2SiO_3} + 2H_2SiF_6$$

When the test is properly carried out, the concentrated H_2SO_4 absorbs the water formed in the following reactions.

$$\underline{CaF_2} + H_2SO_4 \rightleftarrows \underline{CaSO_4} + 2HF$$
$$\underline{SiO_2} + 4HF \rightleftarrows \overline{SiF_4} + 2H_2O$$

Borates interfere to some extent with this test through formation of $[BF_4]^-$, but they should not be present if the material used is a Group IV precipitate. Phosphate, if present in large quantity, has been observed to etch glass when the test plate is too strongly heated.

Zirconium alizarin sulfonate test. This very sensitive test for fluoride depends upon the complex-forming properties of the fluoride ion. A zirconium alizarin sulfonate lake is formed by mixing an equal number of drops of a solution of 0.05 g zirconium nitrate in 60 ml 2*N* HCl and a solution of 0.05 g "Alizarin red S" in 50 ml of water. After being stirred, the mixture should stand for at least 2 minutes before being used. This lake has a characteristic pinkish or violet-red color. When fluoride is added to this reagent the color is almost completely discharged, leaving the solution a greenish yellow. The F^- forms stable $[ZrF_6]^=$ removing ZrO^{++} from the lake and setting free the alizarin, which is greenish yellow.

Large amounts of phosphate, oxalate, or sulfate may interfere with this test. However, they act much more slowly than even small amounts of fluoride.

Sodium carbonate in hot $3N$ solution transposes artificial fluorides. The mineral fluorspar is not transposed to any considerable extent.

PRACTICE EXERCISE

Write balanced equations for the following reactions:

1. $Ca^{++} + F^- =$
2. $\underline{CaF_2} + H_2SO_4 \rightleftarrows$
3. $\underline{SiO_2} + HF_2^- + H^+ \rightleftarrows \overline{SiF_4} + H_2O$
4. $Fe^{+3} + F^- \rightleftarrows$
5. $\overline{SiF_4} + H_2O \rightarrow [SiF_6]^= + \underline{[(H_2O)_2Si(OH)_4]}$

ANIONS OF GROUP V

Sulfuric Acid and Its Ions

Occurrence. Sulfate occurs in the earth's lithosphere as barite, $BaSO_4$; celestite, $SrSO_4$; anglesite, $PbSO_4$; and in two forms of $CaSO_4$, gypsum and anhydrite. The salt deposits from evaporated sea water contain large amounts of sulfates of Ca, Mg, Na, and K.

Solubility. The sulfates of Ba^{++}, Pb^{++}, and Sr^{++} are very slightly soluble, those of Ag^+, Ca^{++}, and Hg_2^{++} sparingly soluble, all others largely soluble. When metal sulfates are strongly heated, basic sulfates or anhydrous sulfates are formed, which are insoluble in water but dissolve slowly in hot mineral acids.

Bisulfates are always more soluble than sulfates. For this reason even $BaSO_4$ dissolves in concentrated H_2SO_4.

$$\underline{BaSO_4} + H_2SO_4 \rightleftarrows 2HSO_4^- + Ba^{++}$$

When the solution is poured into water, $BaSO_4$ precipitates.

Acidic strength. H_2SO_4 is a strong acid in its primary ionization but HSO_4^- is rather weak, its K_{ion} being 1×10^{-2}.

Hot concentrated H_2SO_4 is a strong dehydrating agent. It forms $H_2SO_4 \cdot H_2O$ with liberation of much energy in the form of heat. It extracts H and O from organic matter and leaves C. It extracts

H and O from $H_2C_2O_4$ and CO_2 and CO volatilize. It is reduced to SO_2 by many metals and by Br^- and I^-.

With solid chlorates it forms ClO_2, a greenish gas violently explosive above 100°.

$$3KClO_3 + 2H_2SO_4 = 2ClO_2 + 2KHSO_4 + KClO_4 + H_2O$$

Precipitation and Properties of Barium Sulfate

Barium acetate precipitates sulfate ion in Group V. On account of the sparing solubility of $CaSO_4$, SO_4^{--} may be partially precipitated in Group IV if present in large amounts, but it is removed by washing the precipitate with water.

$BaSO_4$ is the *only* sulfate insoluble in dilute HCl. Addition of Ba^{++} to the HCl extract of any solid unknown shows at once the presence or absence of SO_4^{--}, except when $BaSO_4$ itself is in the unknown.

$BaSO_4$ is partially transposed by boiling with 3 *N* Na_2CO_3. The solution contains about 1.3 mg per ml of SO_4^{--}. The other sulfates are almost completely transposed. If the Na_2CO_3 extract is acidified with HCl and CO_2 is removed by boiling, addition of Ba^{++} indicates whether SO_4^{--} is present.

Sulfurous Acid and Its Ions

Occurrence. Sulfites are readily oxidized to sulfates; consequently they occur rarely if ever as minerals in the earth's lithosphere. SO_2 is usually a constituent of volcanic gases. Sulfur is estimated to form 0.03% by weight of the lithosphere and, as sulfate ion, constitutes 0.09% by weight of sea water. Volcanic gases always contain much H_2S or SO_2. The enormous sulfur deposits of certain regions (Louisiana, Texas) probably were formed by the reaction

$$2SO_2 + 4H_2S \rightleftarrows 6S + 4H_2O.$$

About 7 million tons of sulfur are mined annually.

Solubility. At 25° and 1 atm. the solubility of SO_2 in water is stated to be about 94 g per liter. This saturated solution should be about 1.47 *M*. The solution consists chiefly of SO_2 molecules, a little $SO_2 \cdot 6H_2O$ and very little H_2SO_3.

Acidic strength. H_2SO_3 is a medium weak bibasic acid. In consequence, all bisulfites and sulfites readily give off SO_2 when treated with dilute mineral acids.

Solubility of salts. All bisulfites are soluble in water. Most normal sulfites are rather insoluble, except those of the alkali metals.

In consequence of oxidation by air, solutions of SO_2 and all sulfites contain more or less $SO_4^{=}$.

Reactions of Sulfite Ion

Dilute mineral acids, when added to a sulfite, decompose it with evolution of SO_2. $S_2O_3^{=}$ gives SO_2 and S.

Calcium ion precipitates *slowly* $CaSO_3 \cdot 2H_2O$. This salt appears to be soluble in water to the extent of about 0.04 mg per ml at 20° and 0.03 mg per ml at 90°. Since HSO_3^- ($K_a = 5 \times 10^{-7}$) is somewhat weaker than AcOH ($K_a = 1.8 \times 10^{-5}$), $CaSO_3 \cdot 2H_2O$ will be dissolved by moderately concentrated acetic acid.

Barium ion precipitates instantaneously from neutral solution $BaSO_3$ anhydrous. $BaSO_3$ appears to be about ten times more soluble at 20° than at 100°.

Potassium permanganate in cold dilute H_2SO_4 is reduced by sulfurous acid. If very dilute $KMnO_4$ is added dropwise to H_2SO_3 the latter may be oxidized only to dithionic acid, $H_2S_2O_6$. More concentrated $KMnO_4$ solution can oxidize this to H_2SO_4.

$$2H_2SO_3 \rightleftarrows S_2O_6^{=} + 4H^+ + 2e^-$$
$$S_2O_6^{=} + 2H_2O \rightleftarrows 2HSO_4^- + 2H^+ + 2e^-$$

Bromine and **iodine** are reduced by H_2SO_3.

Ferric ion is reduced to Fe^{++} by sulfurous acid more rapidly than is $[Fe(CN)_6]^{-3}$ to $[Fe(CN)_6]^{-4}$. Accordingly, in the test for Anion Group II-A sulfite solutions form colloidal "Turnbull's blue."

Hydrogen sulfide is oxidized to free S by sulfurous acid. A little pentathionic acid, $H_2S_5O_6$, is also formed.

$$H_2S \rightleftarrows \underline{S} + 2H^+ + 2e^-$$
$$5H_2SO_3 + 10H^+ + 10e^- \rightleftarrows H_2S_5O_6 + 9H_2O$$
$$H_2SO_3 + H_2O \rightleftarrows HSO_4^- + 3H^+ + 2e^-$$

Thus, when a mixture of sulfide and sulfite is acidified with HCl a white precipitate of sulfur forms which may confuse the student, as this is a characteristic reaction of thiosulfate.

Zinc nitroprusside paste is colored by SO_2, evolved from a sulfite by H^+, dark red to rose according to the amount of SO_2 present.

$$2Zn^{++} \text{ (excess)} + [Fe(CN)_5NO]^{=} + NH_3 \rightarrow \underset{\text{(salmon pink)}}{\underline{Zn[Fe(CN)_5NO]}} + [Zn(NH_3)_4]^{++}$$

$$[Zn(NH_3)_4]^{++} + \underline{Zn[Fe(CN)_5NO]} + SO_2 \rightarrow \underset{\text{(dark red)}}{\underline{Zn_2[Fe(CN)_5NOSO_2]}}\text{(probable)} + 4NH_3$$

Sulfide and thiosulfate interfere with this test because of the following reactions but can be removed by adding $HgCl_2$ to the test solution *before acidifying*. On acidifying the test solution,

$$2H_2S + \overline{SO}_2 \rightarrow 3\underline{S} + H_2O$$

$$S_2O_3^{=} + 2H^+ \rightarrow \overline{SO}_2 + \underline{S} + H_2O$$

Before acidifying,

$$S^{=} + Hg^{++} \rightarrow \underline{HgS}$$

$$S_2O_3^{=} + Hg^{++} + H_2O \rightarrow \underline{HgS} + SO_4^{=} + 2H^+$$

Chlorostannous acid reduces sulfite to H_2S when heated. This is one of the rare instances of H_2SO_3 acting as oxidant.

$$[SnCl_4]^{=} + 2Cl^- \rightleftarrows [SnCl_6]^{=} + 2e^-$$

$$H_2SO_3 + 6H^+ + 6e^- \rightleftarrows H_2S + 3H_2O$$

If C_{H^+} is not too high, SnS_2 will gradually precipitate.

PRACTICE EXERCISE

Write balanced equations for the following reactions:

1. $\underline{BaSO_3} + H^+ \rightleftarrows$
2. $MnO_4^- + H_2SO_3 \rightleftarrows$
3. $Fe^{+3} + H_2SO_3 \rightleftarrows$
4. $H_2S + H_2SO_3 \rightleftarrows$
5. $H_2AsO_4^- + H_2SO_3 \rightleftarrows$
6. $Br_2 + H_2SO_3 \rightleftarrows$

Chromic Acid and Its Ions

The equilibrium between $CrO_4^{=}$ and $Cr_2O_7^{=}$ is discussed in Chapter 6.

Color and solubility. Chromates are yellow, orange, red, or brown and are, in general, much less soluble than dichromates. $Ag_2Cr_2O_7$ and $(BiO)_2Cr_2O_7$ appear to be the only dichromates which can be precipitated from aqueous solution.

The solubilities of the chromates closely resemble those of the corresponding sulfates. The most insoluble are those of Pb^{++}, Ba^{++}, Sr^{++}, Ag^+, Hg_2^{++}, and Hg^{++}. Pb^{++} is the reagent most commonly used to remove $CrO_4^=$ or $Cr_2O_7^=$ from neutral or AcOH solution. $PbCrO_4$ is soluble in 3 *N* HNO_3 in consequence of formation of $Cr_2O_7^=$.

Formation. Chromates are formed when Cr^{+3} is oxidized by Na_2O_2, ClO^-, or BrO^-, or by PbO_2 in hot concentrated alkali, or when it is fused with Na_2CO_3 and an oxidant such as $NaNO_3$ or $KClO_3$. Cr^{+3} is oxidized to $Cr_2O_7^=$ or CrO_3 by fuming $HClO_4$.

Reactions of Chromate Ion

Chromates as oxidant. Dichromates are reduced in acid solution to Cr^{+3} by $H_2C_2O_4$, $[Fe(CN)_6]^{-4}$, NCS^-, H_2S, $S_2O_3^=$, H_2SO_3, I^-, H_2O_2, and ethyl alcohol.

Barium ion precipitates light yellow barium chromate ($BaCrO_4$) practically insoluble in water and in buffered acetic acid.

Silver nitrate precipitates red silver chromate (Ag_2CrO_4) from neutral solutions. Ag_2CrO_4 is soluble in dilute HNO_3 and in ammonia solutions.

Lead ion precipitates yellow lead chromate ($PbCrO_4$). The precipitate is insoluble in water, acetic acid, and ammonia solution but is soluble in sodium hydroxide solution (difference from $BaCrO_4$).

Hydrogen peroxide. A sensitive test for chromate is the formation of the so-called "blue perchromic acid," more probably diperoxochromic anhydride, $OCr(O_2)_2$, in which two of the oxygen atoms of CrO_3 are replaced by the O_2 groups of H_2O_2 (compare page 241).

This test can be used to detect H_2O_2 in exactly the same way, using a capillary drop of $CrO_4^=$ solution as reagent.

PRACTICE EXERCISE

Write balanced equations for the following reactions:

1. $Ba^{++} + CrO_4^= \rightleftarrows$
2. $CrO_4^= + H^+ \rightleftarrows$

3. $Pb^{++} + CrO_4^{=} \rightleftarrows$

4. $\underline{PbCrO_4} + OH^- \rightleftarrows$

5. $\underline{BaCrO_4} + H^+ \rightleftarrows$

6. $Ag^+ + CrO_4^{=} \rightleftarrows$

7. $Cr_2O_7^{=} + H_2S + H^+ =$

ANIONS OF GROUP VI

Hydrosulfic Acid and Its Ions

Occurrence. It is suspected that a layer of metallic sulfides lies between the lithosphere and the metallic core. Metallic sulfides, especially those of iron and copper, are abundant in the earth's lithosphere.

Acidic strength. Hydrogen sulfide, in solution *hydrosulfic* acid, is an extremely weak dibasic acid. The ionization constants are $K_1 = 9 \times 10^{-8}$; $K_2 = 1.2 \times 10^{-15}$. At room temperature and atmospheric pressure water saturated with H_2S is about $0.1\,M$ in hydrosulfic acid. All cations are precipitated by H_2S from neutral solutions except Al^{+3}, Cr^{+3}, Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, NH_4^+, Na^+, K^+.

Hydrolysis of sulfides. Because of the extreme weakness of HS^- all except the more insoluble sulfides are largely hydrolyzed. Of sulfides which can be prepared only in absence of water, those of Mg^{++}, Al^{+3}, and Cr^{+3} are completely hydrolyzed because of the insolubility of their hydroxides and the small solubility and slight ionization of H_2S. The sulfides of Ba^{++}, Sr^{++}, and Ca^{++} are sparingly soluble in water but are slowly hydrolyzed to the more soluble bisulfides.

$$\underline{CaS} + H_2O \rightleftarrows Ca^{++} + HS^- + OH^-$$

The very soluble sulfides of Na^+, K^+, and NH_4^+ are largely hydrolyzed (see Chapter 9, pages 133–136).

H_2S as a reductant. H_2S is a strong reductant and is oxidized by air to S so that a solution of the gas in water exposed to air soon becomes cloudy. Basic solutions of alkali sulfides are rapidly oxidized by air to yellow polysulfide ions, such as $S_2^=$, $S_3^=$, and so on up to $S_6^=$. All these form sulfur when acidified. For this reason reagent $(NH_4)HS$ or NaHS should be stored in completely filled

small containers since, as soon as air is admitted, the yellow persulfide ions begin to form.

$$4S^{=} + 8NH_4^{+} + O_2 + 4OH^{-} = 2S_2^{=} + 8NH_3 + 6H_2O$$

Persulfide ions, $S_2^{=}$, and so on, are oxidants and change brown SnS to $SnS_3^{=}$ from which H^{+} precipitates yellow SnS_2. They also oxidize $[AsS_3]^{-3}$ to $[AsS_4]^{-3}$ and $[SbS_3]^{-3}$ to $[SbS_4]^{-3}$.

Properties. Finely powdered sulfides, when heated in air to moderate temperature, lose their $S^{=}$ as SO_2, leaving a residue of oxides or sulfates of the cations. In mixtures consisting largely of sulfides it is frequently advantageous to burn off the sulfur before proceeding with the analysis for cations.

H_2S is extremely poisonous. Its first action is to paralyze the olfactory nerves. It has recently been shown that the lethal concentration is about the same as that of HCN. In view of these facts extreme care must be exercised in its use.

Reactions of Hydrosulfic Acid and Its Ions

Hydrochloric acid 6*N* decomposes many of the sulfides with evolution of H_2S, which is easily recognized by its characteristic odor and by its blackening of lead acetate paper (test for sulfide).

HgS, Bi_2S_3, CuS, CoS, NiS, As_4S_6, and stibnite, Sb_4S_6, are only slightly attacked by 6*N* HCl. However, zinc and HCl will liberate H_2S from these compounds. Sulfites and thiocyanates also yield H_2S under these conditions. If these are present, they should be removed before testing for sulfides by this method.

Potassium permanganate in dilute H_2SO_4 is bleached by hydrosulfic acid (test for anion Group II).

Ferric ion is reduced to ferrous (Fe^{++}) by hydrosulfic acid (test for anion Group II-A).

Dichromate ion is reduced to chromic ion by H_2S in acid solution.

Silver nitrate precipitates black Ag_2S, insoluble in cold dilute HNO_3, NH_3, NH_4HS, and dilute KCN solutions.

Sodium nitroprusside, $Na_2[Fe(CN)_5NO]$, gives with basic sulfide solution a red-violet color. An aqueous solution of H_2S does not give the test. The reaction is said to detect 0.001 mg of $S^{=}$. The test can be made on a spot plate using 1 drop of the saturated solution of the reagent.

$$[Fe(CN)_5NO]^{=} + S^{=} \rightarrow [Fe(CN)_5NOS]^{-4}$$

Na_2CO_3 in hot $3N$ solution transposes only the more soluble sulfides. Even ZnS is not much affected. When the Na_2CO_3 solution is neutralized, practically all of any $S^=$ in it may be carried out by the CO_2. Hence, absence of CdS in Group VI does not prove absence of sulfide in an unknown.

PRACTICE EXERCISE

Write balanced equations for the following reactions:

1. $\underline{ZnS} + H^+ \rightleftarrows$
2. $\underline{CuS} + H^+ + \underline{Zn} \rightleftarrows$
3. $H_2S + (AcO)_2Pb \rightleftarrows$
4. $MnO_4^- + H_2S =$
5. $Fe^{+3} + H_2S =$
6. $Ag^+ + H_2S =$

Cyanoferroic Acid and Its Ions

Salts containing cyanoferroate and cyanoferriate ions are prepared synthetically and do not occur in the earth's lithosphere.

$$Fe^{++} + 2CN^- \rightarrow Fe(CN)_2$$
$$\underline{Fe(CN)_2} + 4CN^- \rightarrow [Fe(CN)_6]^{-4}$$

$H_4Fe(CN)_6$ can be obtained in white crystals by treating $K_4Fe(CN)_6$ with $12N$ HCl. The free acid is not stable.

All ferrocyanides, except those of the alkali and alkaline earth ions, are insoluble in water.

Reactions of Cyanoferroate Ion

Dilute acids do not decompose cyanoferroate in the cold. However, boiling acid (even acetic) will partially decompose cyanoferroate with the liberation of Fe^{++} and HCN.

Potassium permanganate in dilute H_2SO_4 is reduced by ferrocyanide. (Test for anion Group II.)

Ferrous and ferric ions. For reactions with cyanoferroate, see reaction 7, page 244, and reaction 6, page 246.

Silver nitrate precipitates white silver cyanoferroate ($\underline{Ag_4Fe(CN)_6}$), insoluble in dilute HNO_3 and NH_3 solution but soluble in cyanide solutions.

Cadmium ion precipitates white cadmium cyanoferroate from neutral solutions.

PRACTICE EXERCISE

Write balanced equations for the following reactions:

1. $Cd^{++} + [Fe(CN)_6]^{-4} \rightleftarrows$
2. $[Fe(CN)_6]^{-4} + MnO_4^- + H^+ \rightarrow$
3. $Ag^+ + [Fe(CN)_6]^{-4} \rightleftarrows$
4. $Fe^{+3} + [Fe(CN)_6]^{-4} \rightarrow$
5. $Fe^{++} + [Fe(CN)_6]^{-4} \rightarrow$
6. $[Fe(CN)_6]^{-4} + H^+ \rightleftarrows$
7. $\underline{Fe[Fe(CN)_6Fe]_3} + OH^-$ (boiling) =

Cyanoferriic Acid and Its Ions

Alkali cyanoferriates are prepared from ferric salts and excess of alkali cyanide. The free acid $H_3Fe(CN)_6$ can be obtained in brown needles by the same method as $H_4Fe(CN)_6$. In aqueous solution cyanoferriate ion is slowly reduced by light to ferrocyanide ion. For this reason a reagent solution of $K_3[Fe(CN)_6]$ should always be freshly prepared. With ferric ion cyanoferriate forms a brown solution supposed to be caused by unionized ferric cyanoferriate. Cyanoferriate ion is an oxidant somewhat milder than Fe^{+3}. It can oxidize $MnCl_2$ in 12 *N* HCl to brown $[MnCl_6]^{-3}$. Cyanoferriate ion is reduced in faintly acid solution by several of the stronger reductants. For this reason a solution of $Fe[Fe(CN)_6]$ is an excellent detector of some of the strongly reductant anions. Some of these anions reduce the ferric ion to ferrous, with formation of Turnbull's blue, more rapidly than they reduce cyanoferriate to cyanoferroate, with formation of Prussian blue. In this latter class appear to be all the reductant anions containing sulfur, $S^=$, $SO_3^=$, $S_2O_3^=$. Ions which act more rapidly on the cyanoferriate ion are NO_2^- and I^-.

Reactions of Cyanoferriate Ion

Cadmium ion precipitates yellow cadmium cyanoferriate $Cd_3[Fe(CN)_6]_2$ from neutral solutions.

Chloromanganous acid, H_4MnCl_6, is oxidized to brown chloromanganic acid, H_3MnCl_6, by cyanoferriate.

Ferrous and ferric ions. For reactions with cyanoferriate see reaction 8, page 244, and reaction 7, page 246.

Silver nitrate precipitates orange-brown silver cyanoferriate $Ag_3[Fe(CN)_6]$, insoluble in dilute HNO_3 but soluble in NH_3 (difference from $Ag_4Fe(CN)_6$) and soluble in CN^- solutions.

Dilute acids at 100° decompose cyanoferriate ion to about the same slight extent as they do cyanoferroate ion.

Manganous ion in syrupy H_3PO_4 forms brown $Mn_3[Fe(CN)_6]_2$. This precipitate must be removed before the mixture is heated.

PRACTICE EXERCISE

Write balanced equations for the following reactions:

1. $Cd^{++} + [Fe(CN)_6]^{-3} \rightleftarrows$
2. $[MnCl_6]^{-4} + [Fe(CN)_6]^{-3} \rightleftarrows$
3. $Ag^+ + [Fe(CN)_6]^{-3} \rightleftarrows$
4. $Ag_3Fe(CN)_6 + NH_3 \rightleftarrows$
5. $[Fe(CN)_6]^{-3} + I^- \rightleftarrows$
6. $[Fe(CN)_6]^{-3} + NO_2^- \rightleftarrows$
7. $[Fe(CN)_6]^{-3} + Fe^{++} \rightleftarrows$

Arsenious Acid and Its Ions

The common commercial form of 3-valent arsenic is the oxide As_4O_6, commonly known as "white arsenic." As an amphoteric oxide it is soluble in bases, even in $NaHCO_3$ solution, to form AsO_2^- or $As(OH)_4^-$, and it is sparingly soluble also in HCl, probably because of formation of $[AsCl_4]^-$ and AsO^+.

Acidic strength. Arsenious acid is an extremely weak acid. Its K_{ion} has been found to have the value 6×10^{-10} at 25°. So weak an acid should be monobasic. Nearly all arsenites appear to be salts of the meta-acid, $HAsO_2$, except the yellow silver salt, of which the composition appears to correspond to Ag_3AsO_3. Alkali arsenites are soluble in water; other arsenites dissolve in dilute acids. For the peculiar solubilities of the arsenites of Ca^{++} and Ba^{++} see page 330.

Reactions of Arsenious Acid and Arsenite Ion

Hydrogen sulfide precipitates arsenious sulfide from acid solutions.

Silver nitrate precipitates yellow silver arsenite (Ag_3AsO_3), soluble in dilute HNO_3 and in NH_3 solution.

Potassium permanganate in dilute H_2SO_4 is reduced by arsenious acid.

Na_2CO_3 in hot $3N$ solution transposes all arsenites nearly completely.

PRACTICE EXERCISE

Write balanced equations for the following reactions:

1. $Cd^{++} + AsO_2^- \rightleftarrows$
2. $HAsO_2 + H_2S =$
3. $Ag^+ + AsO_2^- + H_2O \rightleftarrows$

Arsenic Acid and Its Ions

As is the case with P_2O_5, salts are formed by three hydrates of As_2O_5: namely, $HAsO_3$, $H_4As_2O_7$, and H_3AsO_4, meta-, pyro-, and orthoarsenic acids. Most arsenates are salts of the ortho- acid and their properties and reactions resemble very closely those of orthophosphates. In contrast to As_4O_6, As_2O_5 is largely soluble in water, and H_3AsO_4 is a rather strong "weak acid."

Like the phosphates, arsenates of the alkali metals and all *primary* arsenates are soluble in water. The water-insoluble arsenates dissolve readily in dilute mineral acids.

Reactions of Arsenate Ions

Cadmium ion precipitates white cadmium arsenate from neutral solution.

Hydrogen sulfide precipitates a mixture of As_2S_5 and As_4S_6 from hot $12N$ HCl.

When H_2S is passed into a cold $0.3N$ H^+ solution of an arsenate, almost no reaction takes place but much more H_2S is absorbed than is required to saturate an equal volume of water.

This has been explained[2] as arising from the following reactions which take place with extreme slowness in $0.3N$ H^+ at 25°. They are all greatly accelerated by heat and large C_{H^+}.

[2] McCay, Am. Chem. J., **10**, 459 (1888).

$$H_3AsO_4 + H_2S \rightleftarrows H_3AsO_3S + H_2O \quad (1)$$

$$H_3AsO_3S \rightleftarrows HAsO_2 + H_2O + \underline{S} \quad (2)$$

$$HAsO_2 + 3H_2S \rightleftarrows \underline{As(HS)_3} + 2H_2O \quad (3)$$

Silver nitrate precipitates brown-red silver arsenate (Ag_3AsO_4), soluble in dilute HNO_3 and NH_3 solution.

Iodide ion reduces arsenate to arsenious acid in acid solution.

Magnesia mixture precipitates crystalline $MgNH_4AsO_4 \cdot 6H_2O$ from solutions containing orthoarsenate ion and much NH_3.

Na_2CO_3 in hot $3N$ solution transposes all arsenates (difference from phosphates).

Zirconyl ion in hot neutral or slightly alkaline solution precipitates completely $ZrO(H_2AsO_4)_2$. The precipitate dissolves in $0.3N$ H^+ considerably more rapidly than does $ZrO(H_2PO_4)_2$.

Ferric ion in strongly buffered AcOH precipitates $HAsO_4^=$ completely as yellowish white $FeAsO_4$ or $Fe_2(HAsO_4)_3$.

PRACTICE EXERCISE

Write balanced equations for the following reactions:

1. $Cd^{++} + HAsO_4^= \rightleftarrows$
2. $\underline{CdHAsO_4} + H^+ \rightleftarrows$
3. $Ag^+ + HAsO_4^= \rightleftarrows$
4. $H_3AsO_4 + 12N\ HCl \rightleftarrows$
5. $[AsCl_6]^- + H_2S \rightleftarrows$

ANION OF GROUP VII

Hydrocyanic Acid and Its Ion

Pure anhydrous hydrogen cyanide is a colorless liquid, boiling point, 26.5°. It is extremely poisonous, 50 mg causing death to a human in a few seconds. Even in small concentrations it has a pronounced odor of bitter almonds. It is largely soluble in water and there behaves as an extremely weak acid, $K_{ion} = 4 \times 10^{-10}$ at 25°. Cyanogen, $(CN)_2$, and thiocyanogen, $(NCS)_2$, are frequently called "pseudohalogens" because of the many resemblances of these gases and the salts of their hydrogen compounds to the halogens and halides.

Because of its structure, $[:C \overset{\times}{\times}\overset{\times}{\times} N:]$, cyanide ion forms extremely stable complex ions. $[Fe(CN)_6]^{-4}$ and $[Co(CN)_6]^{-3}$ give none of the

reactions of Fe^{++}, Co^{+3}, or CN^- until broken down by powerful reagents. Davidson, in proposing "berlinic acid," $H^+[Fe(CN)_6Fe]^-$, to explain the "iron blues," assumes Fe^{+3} coordinated to N: and Fe^{++} coordinated to :C of the CN^-.

Cyanides soluble in water are those of the alkali and alkaline earth elements and $Hg(CN)_2$. The heavy metal ions all form insoluble cyanides, which, however, dissolve in excess CN^- because of formation of complex anions. A typical case is silver cyanide:

$$Ag^+ + CN^- \rightleftarrows \underline{AgCN}$$
$$\underline{AgCN} + CN^- \rightleftarrows [Ag(CN)_2]^-$$
$$[Ag(CN)_2]^- + Ag^+ \rightleftarrows \underline{Ag[Ag(CN)_2]}$$
$$\underline{Ag[Ag(CN)_2]} + 4CN^- \rightleftarrows 2[Ag(CN)_3]^=$$

Reactions of Cyanide Ion

Hydrolysis. Alkali and alkaline earth cyanides are considerably hydrolyzed in water. As a result they are strongly basic and smell of HCN.

$Hg(CN)_2$ requires special mention. In water it is almost unionized. It is not decomposed by strong bases or by boiling with Na_2CO_3. Ag^+ does not precipitate AgCN. CN^- can be detected only after removal of Hg^{++} by H_2S.

Cobaltous ion in large excess precipitates CN^- from neutral or slightly basic solution as light brown $Co(CN)_2$. The precipitate tends to be colloidal and in analysis may not be seen until after centrifuging.

Benzidine and cupric acetates in absence of other oxidants and reductants are reported to detect 0.00025 mg of HCN. Benzidine is oxidized to a blue compound, probably according to the following reactions:

$$Cu^{++} + 2HCN = \underline{Cu(CN)_2} + 2H^+$$
$$\underline{2Cu(CN)_2} \rightarrow \underline{Cu_2(CN)_2} + \overline{(CN)_2}$$
$$\overline{(CN)_2} + 2H^+ + 2e^- \rightleftarrows 2HCN$$

the benzidine being oxidized by $(CN)_2$.

Alkali polysulfide oxidizes CN^- to NCS^-,

$$CN^- + S_2^= = NCS^- + S^=.$$

After the reaction has been completed, the solution is acidified with HCl and the H_2S boiled out. Addition of Fe^{+3} will then form red $[Fe(NCS)_6]^{-3}$.

Permanganate ion is reduced by CN^- but not by HCN.

$$CN^- + 2OH^- \rightleftarrows CNO^- + H_2O + 2e^-$$

In the test for Group II anions, if the C_{H^+} is too small, a large amount of cyanide may reduce some MnO_4^-.

ANIONS OF GROUP VIII

Thiosulfuric Acid and Its Ion

Properties. Free thiosulfuric acid is unstable and consequently is unknown. The acid has been shown to decompose in three ways.[8]

$$H_2S_2O_3 \rightarrow H_2SO_3 + \underline{S}$$
$$2H_2S_2O_3 \rightarrow H_2S + H_2S_3O_6$$
$$2H_2S_2O_3 \rightarrow H_2O + H_2S_4O_5$$

These reactions indicate equilibrium between two forms.



Practically the only commercial salt is $Na_2S_2O_3 \cdot 5H_2O$, the so-called "hypo" used in photography. $Na_2S_2O_3$ is made by boiling Na_2SO_3 with sulfur.

$$SO_3^= + \underline{S} \rightleftarrows S_2O_3^=$$

Thiosulfate ion is likely to be found in *yellow* alkali sulfide solutions.

$$2S^= + 2O_2 + H_2O \rightarrow S_2O_3^= + 2OH^-$$
$$2S_2^= + 3O_2 \rightarrow 2S_2O_3^=$$

The more soluble solid sulfides such as CaS after long exposure to air frequently contain considerable thiosulfate.

Complex ions. Most thiosulfates are soluble in water. BaS_2O_3 is sparingly soluble, $Ag_2S_2O_3$ and PbS_2O_3 are nearly insoluble. All

[8] Bassett and Durrant, J. Chem. Soc., **1937**, 1401-1408.

these are soluble in excess of $S_2O_3^=$ owing to formation of complex anions such as $[Ag(S_2O_3)_2]^{-3}$, and the like.

Reactions of Thiosulfate Ion

Dilute mineral acids decompose thiosulfate with formation of free S and liberation of SO_2.

Silver nitrate precipitates from nearly neutral solution white $Ag_2S_2O_3$. The white salt rapidly decomposes, forming yellow and brown mixtures and finally black Ag_2S. The decomposition is almost instantaneous in strongly acid solution [Group VIII (and also Group III) reaction].

Potassium permanganate in dilute H_2SO_4 is reduced by thiosulfate with formation of $SO_4^=$. (The products may vary with concentrations and temperature.) Very dilute $KMnO_4$ probably forms $S_4O_6^=$, at least as a first product.

Ferric ion is reduced to ferrous ion by thiosulfate.

Hydrogen peroxide in dilute AcOH oxidizes $S_2O_3^=$ to $S_4O_6^=$.

$$2S_2O_3^= + H_2O_2 + 2H^+ \rightleftarrows S_4O_6^= + 2H_2O$$

In alkaline solution only $SO_4^=$ is formed.

$$S_2O_3^= + 4HO_2^- \rightleftarrows 2SO_4^= + 2OH^- + H_2O$$

Iodine dissolved in KI (I_3^-) oxidizes $S_2O_3^=$ to $S_4O_6^=$.

$$I_3^- + 2S_2O_3^= = S_4O_6^= + 3I^-$$

This is a much used reaction in volumetric quantitative analysis.

ELECTRON CHANGES IN FORMATION AND OXIDATION OF $S_2O_3^=$

	Electrons per Sulfur
$2S^= + 6OH^- \rightleftarrows S_2O_3^= + 3H_2O + 8e^-$	4
$2S_2O_3^= \rightleftarrows S_4O_6^= + 2e^-$	0.5
$3S_2O_3^= + 6OH^- \rightleftarrows 2S_3O_6^= + 3H_2O + 8e^-$	1⅓
$S_2O_3^= + 6OH^- \rightleftarrows 2SO_3^= + 3H_2O + 4e^-$	2
$S_2O_3^= + 6OH^- \rightleftarrows S_2O_6^= + 3H_2O + 6e^-$	3
$S_2O_3^= + 10OH^- \rightleftarrows 2SO_4^= + 5H_2O + 8e^-$	4

PRACTICE EXERCISE

Write balanced equations for the following reactions:

1. $S_2O_3^= + H^+ =$
2. $Ag^+ + S_2O_3^= + H_2O \rightleftarrows$

3. $MnO_4^- + S_2O_3^= \rightleftarrows$

4. $Fe[Fe(CN)_6] + S_2O_3^= + H^+ \rightarrow$

Thiocyanic Acid and Its Ion

Thiocyanogen $(NCS)_2$ was first isolated in 1919. It is stable only at low temperatures and forms bright yellow crystals which melt at about $-3°$. Above this temperature it decomposes. It is more stable in solution in alcohol or ether in which it dissolves largely. It is less soluble in CS_2 and in CCl_4.

Chemically $(NCS)_2$ resembles I_2 rather closely. The electrode potentials of both are evidently nearly the same since the reaction

$$I_2 + 2NCS^- \rightleftarrows (NCS)_2 + 2I^-$$

is readily displaced in either direction by excess of the ion.

Anhydrous HNCS is an unstable, colorless, oily liquid which solidifies at 5°. It has a very sharp penetrating odor much like that of HCl. It is stable at low temperature and in very dilute solution (not over 5%). It decomposes into HCN and a yellow solid, the so-called isoperthiocyanic acid, $H_2N_2C_2S_3$. (Compare hydrorubianic acid, note 2, page 316.)

Acidic strength. HNCS is a very strong acid, comparable to HCl, HBr, and HI. Most thiocyanates are soluble in water, exceptions being those of Ag^+, Hg^{++}, and Cu^{++}. $Pb(NCS)_2$ is sparingly soluble.

Reactions of Thiocyanate Ion

Silver nitrate precipitates white silver thiocyanate (AgNCS), insoluble in dilute HNO_3, sparingly soluble in NH_3 solution. AgNCS is slightly more soluble in water (1.3×10^{-4} mg/ml) and in NH_3 solution (2.2 mg/ml in $2N$ NH_3) than is AgBr.

Potassium permanganate in dilute H_2SO_4 is reduced by thiocyanate ion, with formation of cyanate ion (NCO^-) and sulfate ion.

Ferric ion forms a deep red coloration as a result of the formation of $[Fe(NCS)_6]^{-3}$.

Zinc reduces thiocyanate in dilute sulfuric acid solution to H_2S. (Compare with test for $S^=$ in insoluble sulfides.)

Na_2CO_3 in hot $3N$ solution transposes water-insoluble thiocyanates, with the exception of AgNCS.

Sulfuric acid, if moderately concentrated and hot, oxidizes NCS^- to $SO_4^=$ and HCN.

PRACTICE EXERCISE

Write balanced equations for the following reactions:

1. $Ag^+ + NCS^- =$
2. $\underline{AgNCS} + NH_3 \rightleftarrows$
3. $\underline{AgNCS} + HS^- \rightleftarrows$
4. $Fe^{+3} + NCS^- \rightleftarrows$
5. $MnO_4^- + NCS^- + H^+ =$
6. $\underline{Zn} + H^+ + NCS^- =$

The Hydrohalic Acids and Their Ions

The properties of the halides made use of in analysis are: (1) the solubilities in water and in ammonia of their silver salts; and (2) the readiness with which they are oxidized, that is, their effectiveness as reductants as shown by their molar electrode potentials. These properties are more readily comprehended by comparison of the various hydrogen halides. In Table 21 is collected this information, along with other useful data. Although in analysis fluoride is not grouped with the other halides, it is included in the table for purposes of comparison.

Iodine

Occurrence. Iodine is one of the less abundant elements. It is present as I^- in sea water to the extent of about $3.5 \times 10^{-5}\%$, about the same as F^-. The commercial sources are the mother liquors from NaCl crystallizations and the ash of marine plants such as kelp. In the mother liquor of Chile saltpeter it occurs as IO_3^-. This constitutes an important source. Iodine is a constituent of thyroxine, a secretion of the thyroid gland. In iodine-deficient regions goiter is a frequent disease.

Properties. Iodine is the only halogen which is solid at room temperature. It melts at 113.5° but sublimes far below this temperature. Even at 25° its vapor pressure is sufficient to make its characteristic odor easily perceptible. It is nearly insoluble in water but dissolves in CS_2, $CHCl_3$, and CCl_4 with a violet color and in alcohol, acetone, ether, and solutions of iodides with a brown

color. The violet color is due to I_2 molecules, the brown color to solvated molecules such as $I_2(C_2H_5OH)_x$ or I_3^- (in iodide). Very minute amounts give a deep blue color to hydrosols on which they are adsorbed, such as starch paste or the basic acetate of La^{+3}.

TABLE 21
PHYSICAL PROPERTIES OF SOME HALIDES

Halogen	Fluorine	Chlorine	Bromine	Iodine
M.p. anhydrous HX.....	−83°	−112°	−88°	−50.7°
B.p. anhydrous HX.....	+19.6°	−85°	−67.1°	−35.8°
Apparent ionizn. of HX in 0.1 N soln. (from conductivity).....	10%	92.6%	93.5%	95%
Concn. and b.p. of constant boiling mixture of HX with water.....	35.4% (120°)	20.25% (110°)	48% (126°)	57% (127°)
Approx. normality of coml. "concentrated" acid.....	27	12	9	.....
Soly. of Ag^+ salt mg/ml..	Soluble	1.87×10^{-3} (25°)	7.9×10^{-5} (20°)	3×10^{-7} (21°)
$C_{Ag^+} \times C_{x^-}$ in satd. soln..	.....	1.56×10^{-10}	7.7×10^{-13}	1.5×10^{-16}
Soly. of AgX in 2 N NH_3 mg/ml.....	.....	21.5	2.0	0.03
Insoluble salts.....	Alk. earths, Pb^{++}, BiO^+	Ag^+, Hg_2^{++}, Pb^{++}, BiO^+, SbO^+	Same	Same
Molar electrode potentials:				
$2X^- \rightleftarrows X_2 + 2e^-$.....	+2.85 v.	+1.358 v.	+1.065 v.	+0.535 v.
$X^- + 3H_2O \rightleftarrows XO_3^- + 6H^+ + 6e^-$....	.....	+1.45 v.	+1.44 v.	+1.09 v.

Reactions of Iodide Ion

Silver ion precipitates pale yellow AgI, insoluble in dilute HNO_3 and nearly insoluble in NH_3 solution but turned white by it because of formation of $AgNH_3I$. AgI is decomposed by Zn and dilute H_2SO_4.

$$2\underline{AgI} + 2\underline{Zn} + H^+ + HSO_4^- = 2\underline{Ag} + 2I^- + 2Zn^{++} + \overline{\overline{H}}_2 + SO_4^-$$

Alkali sulfides decompose AgI to form the more insoluble Ag_2S and I^-. AgI dissolves in CN^- and also in $S_2O_3^-$ as a result of formation of complex anions such as $[Ag(CN)_2]^-$ and $[Ag(S_2O_3)_2]^{-3}$.

Ferric ion in weakly acid solution oxidizes iodide to iodine (difference from Br^-). Iodine is then detected by extraction with CCl_4. In presence of NCS^-, red $[Fe(NCS)_6]^{-3}$ is also formed. In this case I_2 is removed by shaking with CCl_4 until the red color of $[Fe(NCS)_6]^{-3}$ is clearly visible in the water layer.

Permanganate ion, if very dilute, oxidizes I^- to I_2. More concentrated MnO_4^- added in small excess oxidizes I_2 to IO_3^- (colorless) (test for anion Group II).

$$I_2 + 6H_2O \rightleftarrows 2IO_3^- + 12H^+ + 10e^-$$

Cyanoferriate ion oxidizes I^- to I_2. When ferric ferricyanide is used, colloidal or solid iron blues will be formed (test for anion Group II-A).

All strong and medium strong oxidants such as HNO_2, $Cr_2O_7^=$, Cl_2, Br_2, and H_2O_2 oxidize I^- in acid solution to I_2 and IO_3^-. Thus I^- is a rather strong reductant.

Na_2CO_3 in boiling $3N$ solution does not transpose AgI, HgI_2, or BiOI.

PRACTICE EXERCISE

Write balanced equations for the following reactions:

1. $AgI + S^= =$
2. $AgI + CN^- \rightleftarrows$
3. $AgI + S_2O_3^= \rightleftarrows$
4. $I_2 + S_2O_3^= \rightarrow S_4O_6^=$
5. $I^- + I_2 \rightleftarrows$
6. $I^- + MnO_4^- = IO_3^-$
7. $I^- + H_2O_2 = I_2$
8. $I^- + Cl_2 \rightleftarrows$
9. $I^- + Cr_2O_7^= =$
10. $I^- + Fe^{+3} \rightleftarrows$

Bromine

Occurrence. Bromine constitutes about $2 \times 10^{-3}\%$ of sea water. It is now obtained commercially from this source. It is also obtained from the mother liquors of NaCl crystallizations.

Properties. Bromine is a dark brown liquid which boils at 59° and solidifies at −7.3°. Solid bromine has a slightly metallic luster like that of iodine.

Solubility. Bromine is more soluble in water (36 mg/ml at 20°) than iodine. It is, however, less soluble than I_2 in CS_2 and CCl_4. In direct sunlight a solution of Br_2 in water slowly evolves O_2 (similarity to Cl_2).

$$Br_2 + H_2O \rightleftarrows HBrO + HBr$$
$$HBrO \rightarrow HBr + \tfrac{1}{2}O_2$$

Bromine is a strong oxidant, although it is weaker than Cl_2.

Reactions of Bromide Ion

Silver ion precipitates yellowish white AgBr, insoluble in dilute HNO_3 and only sparingly soluble in NH_3 solution (2 mg/ml of $2N$ NH_3). Like AgI it dissolves readily in solutions of CN^- or $S_2O_3^=$. It is not transposed by boiling $3N$ Na_2CO_3. It is decomposed by alkali sulfide solutions and by Zn and dilute H_2SO_4.

Ferric ion does not oxidize Br^- to Br_2 (difference from I^-).

Ferricyanide ion is not reduced by Br^- (difference from I^-).

Permanganate ion in dilute acid oxidizes Br^- to Br_2. If a sufficient C_{H^+} is present, Mn^{++} is formed. If C_{H^+} is too small, MnO_2 will be formed. When the mixture is shaken with CCl_4 to extract Br_2, a film of MnO_2 sometimes prevents the droplets of CCl_4 from coalescing. This gives a slight yellow color to the CCl_4 layer and thus makes it difficult to identify a small amount of Br_2 (test for anion Group II).

Fluorescein, a yellow dye, is changed by Br_2 to brilliant red tetrabromofluorescein. Feigl states this reaction detects 0.002 mg of Br_2. It is useful when the CCl_4 layer is mixed with MnO_2 or when the yellow tint is too pale to prove certainly the presence of Br^-. I_2 would form iodocosin of the same red color but should have been completely removed.

Chlorine water in not more than equivalent amount oxidizes Br^- to Br_2. Excess of Cl_2, however, oxidizes Br_2 to colorless bromine chloride, BrCl.

Oxidants such as HNO_2, $Cr_2O_7^=$, H_2O_2, in dilute acid solution, do not oxidize Br^- (difference from I^-).

Chlorine

Occurrence. Chlorine is one of the more abundant elements. It constitutes about 2% of sea water. By evaporation of sea water, enormous beds of NaCl have been formed. In the Stassfurt deposits carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$, is an important layer.

Properties. Chlorine solidifies at $-101.6°$ and boils at $-34.6°$. It is less soluble in water than Br_2 (about 6 mg/ml at 25°). It is one of the strongest oxidants and when hot attacks nearly all metals.

Reactions of Chloride Ion

Silver ion precipitates white AgCl, insoluble in dilute HNO_3 but largely soluble in NH_3 solution (difference from AgNCS, AgBr, AgI). It is not transposed by hot $3N$ Na_2CO_3 solution. It is decomposed by alkali sulfide, by CN^-, and by $S_2O_3^{=}$. It dissolves in high C_{Cl^-} because of formation of complex anions such as $[AgCl_3]^=$.

Permanganate ion in dilute acid solution does not oxidize Cl^- to Cl_2 (difference from Br^- and I^-).

Concentrated H_2SO_4 even when hot does not oxidize Cl^- or HCl gas to Cl_2 (difference from Br^-, which forms HBr and Br_2, and I^-, which forms I_2). Bromides reduce H_2SO_4 to SO_2. Solid iodides reduce $36N$ H_2SO_4 mainly to H_2S.

Powerful oxidants, such as $KMnO_4$, $NaBiO_3$, $K_2Cr_2O_7$, MnO_2, and PbO_2, liberate Cl_2 from $12N$ HCl or from solid chlorides in concentrated acids.

PRACTICE EXERCISE

ACTION OF OXIDANTS ON HALIDES

Reagent	Cl^-	SCN^-	Br^-	I^-
1. $Fe^{+3} + H^+$				
2. $MnO_4^- +$ small H^+				
3. $FeFe(CN)_6$				
4. H_2SO_4 $36N$ hot				
5. $Cr_2O_7^- +$ dilute acid				
6. $Cr_2O_7^- +$ conc. acid				
7. $HNO_2 +$ small H^+	•			
8. HNO_3 $16N$ hot				

In the table write "no action" if none occurs. If reaction occurs, write only reduction product of oxidant and oxidation product of reductant, for example, only H_2S and I_2.

GROUP IX: IONS NOT PRECIPITATED IN GROUPS IV–VIII

$(ClO_3^-, BO_2^-, NO_2^-, NO_3^-, H_3CCOO^-)$

Chloric Acid and Its Ion

Chloric acid, $HClO_3$, in unstable. Its aqueous solution can be concentrated by evaporation in vacuum to about 40%. Such a solution decomposes when heated above 40°. $HClO_3$ is completely ionized in aqueous solution. $KClO_3$ and $NaClO_3$ are the commonest commercial salts. They are stable but decompose on ignition with evolution of O_2 and formation of Cl^- and perchlorate.

$$4KClO_3 = 3KClO_4 + KCl$$
$$KClO_4 = 2O_2 + KCl$$

Chlorates are powerful oxidants and it is *dangerous* to pulverize them in mixture with organic matter, thiosulfates, sulfur, or cyanides. Violent explosions will occur. Chlorates are used chiefly in safety matches, fireworks, and explosives. All chlorates are soluble in water.

Reactions of Chlorate Ion

Concentrated H_2SO_4 decomposes solid chlorates:

$$3HClO_3 \rightarrow 2\overline{ClO_2} + HClO_4 + H_2O$$

Chlorine dioxide, ClO_2, is a greenish gas, in appearance and odor closely resembling Cl_2. When warmed above 100° it decomposes violently into O_2 and Cl_2. If but *very small* amounts of chlorate and acid are used, the crackling noises which are produced by the reaction are characteristic.

Alkali nitrite in dilute acid reduces chlorate to Cl^-.

$$ClO_3^- + 3HNO_2 \rightleftarrows Cl^- + 3NO_3^- + 3H^+$$

This is the basis of the method for detecting ClO_3^- in the centrifugate from the Group III precipitate. Since the HNO_3 solution already contains Ag^+, addition of a nitrite will cause precipitation of AgCl. Care must be taken not to mistake a precipitate of

$AgNO_2$ for one of AgCl. The solubility of $AgNO_2$ is 4.2 mg/ml at 25°. It dissolves on addition of much water or a little HNO_3, while AgCl is not affected.

Manganous ion in syrupy H_3PO_4 forms, on heating, violet $[Mn(PO_4)_2]^{-3}$. This reaction is given also by CrO_4^-, NO_2^-, and by large NO_3^-. $[Fe(CN)_6]^{-3}$ precipitates brown $Mn_3[Fe(CN)_6]_2$.

Other reductants which reduce ClO_3^- to Cl^- are hot 12 *N* HCl, H_2S in 0.3 *N* H^+, H_4MnCl_6, H_2SO_3, $S_2O_3^=$, Fe^{++}, and many metals (for example, Zn, Fe, Al, in dilute H_2SO_4).

PRACTICE EXERCISE

Write balanced equations for the following reactions:

1. $ClO_3^- + HNO_2 =$
2. $ClO_3^- + Mn^{++} + H_3PO_4 \rightarrow$
3. $H_4MnCl_6 + ClO_3^- \rightarrow$
4. $Fe^{++} + ClO_3^- + H^+ =$
5. $H_2SO_3 + ClO_3^- =$
6. $H_2S + ClO_3^- =$

Boric Acid and Its Ions

Occurrence. In the earth's lithosphere boron appears only as borate, usually of Na^+, Mg^{++}, or Ca^{++}. Large deposits occur in salt beds from evaporated sea waters. Boric acid also is found in certain silicate rocks in small amounts, for example, the tourmalines, where BO_2^- replaces SiO_2 to some extent in the crystal lattice.

Properties. Boron stands just above aluminum in Periodic Group III, but in its properties and many of its compounds it resembles carbon much more than it does aluminum. It forms a large number of compounds with H, hydroborons or boranes, analogous to the hydrocarbons. The simplest one is not BH_3, as would be expected, but B_2H_6, analogous to C_2H_6, ethane. Just as NH_3 tends to become NH_4^+ by coordination, so boron tends to acquire a coordination number of 4 as in $[BF_4]^-$, fluoroborate ion.

Acidic strength. Boric acid, HH_2BO_3 or HBO_2, is one of the weakest of the acids, ionizing in solution to about the same extent as HCN and $HAsO_2$. It is a monobasic acid. The free acid is a white solid, sparingly soluble in cold water but largely soluble in

boiling water. Borax, the commonest salt, is a tetraborate, $Na_2B_4O_7 \cdot 10H_2O$. Alkali borates are largely hydrolyzed in solution.

$$B_4O_7^{=} + 3H_2O \rightleftarrows 2BO_2^{-} + 2H_3BO_3$$
$$BO_2^{-} + H_2O \rightleftarrows HBO_2 + OH^{-}$$

Reactions of Borate Ions

Calcium, barium and cadmium borates are either more soluble than stated in the literature or tend to form supersaturated solutions. For example, although $Ca(BO_2)_2 \cdot 6H_2O$ is stated to dissolve in water to the extent of about 2 mg per ml, Sneed and Duschak report that 13.5 mg per ml of BO_2^- are required to give a precipitate in Group IV with $(AcO)_2Ca$. We have never observed borate precipitating in any of the Sneed and Duschak groups (our system IV–VIII).

Sodium carbonate in hot $3N$ solution transposes all water-insoluble borates.

$$\underline{Ca(BO_2)_2} + CO_3^{=} + H_2O \rightleftarrows H_2BO_3^{-} + \underline{CaCO_3}$$

Ammonium ion, which is nearly as strong an acid as **boric acid,** can displace HBO_2 from its salts. Hence water-insoluble **borates** dissolve in hot concentrated ammonium salt solutions.

$$\underline{Ca(BO_2)_2} + 2NH_4^{+} \rightleftarrows 2HBO_2 + Ca^{++} + 2NH_3$$

Silver ion added to a *concentrated* solution of borax precipitates white $AgBO_2$; if to a *very dilute* solution, brown Ag_2O precipitates.

Turmeric paper, spotted with an HCl solution of a borate and dried on the steam plate, turns pink to red which becomes greenish black when touched with 1% NaOH solution. Strong oxidants, such as chlorate, chromate, nitrite, $[Fe(CN)_6]^{-3}$, and I^-, bleach the turmeric. When any of these are present, other tests must be used. If interfering ions are absent, this is the most sensitive of all the tests. If any interfering ion is present, one of the following flame tests is to be used.

Flame tests. Borate salts do not color a Bunsen flame but boric acid and its volatile compounds, such as BF_3 and methyl and ethyl borates, $BO_3(CH_3)_3$, $BO_3(C_2H_5)_3$, impart to it a green color. The tests are carried out as follows.

1. *Boric acid esters.* A little of the solid material to be tested is mixed with a few drops of $36N$ H_2SO_4 in a crucible. A little methyl

or ethyl alcohol is stirred in and the alcohol vapors ignited. A green-edged flame appears if borate is present. This test may not detect very small amounts. Ba and Cu salts also give a green flame and C_2H_5Cl, formed if a large amount of chloride is present, may likewise give a green flame.

2. *Boron fluoride.* A little of the solid unknown is thoroughly ground with a little CaF_2. Enough 36 *N* H_2SO_4 is added to make a thick paste. When some of this paste is brought on a glass rod to about $\frac{1}{4}''$ from the side of the flame, a green color, due to very volatile BF_3, *gradually* appears in the flame. This test detects the boron in tourmaline. Cu and Ba salts cannot volatilize *outside* the flame.

Nitrous Acid and Its Ion

The only common commercial nitrites are those of K^+ and Na^+. All nitrites are soluble in water except $AgNO_2$. The alkali nitrites, prepared by heating the corresponding nitrates, usually contain small amounts of nitrate. Nitrite ion is a strong complex former. Of importance in analysis is $[Co(NO_2)_6]^{-3}$ of which the K^+ salt is insoluble.

Nitrous acid is a moderately weak acid its K_{ion} at room temperature being 4.5×10^{-4}. When set free from its salts by a more highly ionized acid, it decomposes ordinarily according to

$$3HNO_2 \rightleftarrows 2\dot{N}O + NO_3^- + H^+ + H_2O$$

When a solid alkali nitrite is thrown into very cold dilute H_2SO_4, a blue color is visible, presumably resulting from N_2O_3 or N_4O_6. N_2O_3 decomposes into NO and NO_2 and then

$$HNO_2 + \dot{N}O_2 = \dot{N}O + NO_3^- + H^+.$$

When NO_2 is dissolved in cold water, nitrous and nitric acids are formed.

$$2\dot{N}O_2 + H_2O \rightleftarrows HNO_2 + NO_3^- + H^+$$

Reactions of Nitrite Ion

Silver ion precipitates white $AgNO_2$ from moderately concentrated solutions. $AgNO_2$ is soluble in water to the extent of 4.2 mg

per ml at 25°. It is much more soluble in dilute HNO_3, since HNO_2 tends to form. Mistaking $AgNO_2$ for AgCl is a frequent error in testing for ClO_3^-.

Permanganate ion oxidizes HNO_2 to NO_3^- (test for anion Group II).

Cyanoferriate ion oxidizes HNO_2 to NO_3^- (test for anion Group II-A).

Chloromanganoate ion reduces HNO_2 to NO (test for anion Group I).

Ammonium ion in excess reduces NO_2^- to N_2 on boiling. This reaction is useful in detecting nitrate in nitrites.

$$2NH_4^+ \rightleftarrows \overline{N_2} + 8H^+ + 6e^-$$
$$2NO_2^- + 8H^+ + 6e^- \rightleftarrows \overline{N_2} + 4H_2O$$
$$NH_4^+ + NO_2^- = \overline{N_2} + 2H_2O$$

Strong reductants reduce HNO_2 to NO.

$$HNO_2 + H^+ + e^- \rightleftarrows \overline{NO} + H_2O$$

Such reductants are $[MnCl_6]^{-4}$, I^-, Fe^{++}, H_2S.

Strong oxidants oxidize HNO_2 to NO_3^-.

$$HNO_2 + H_2O \rightleftarrows NO_3^- + 3H^+ + 2e^-$$

Such oxidants are MnO_4^- and ClO_3^-.

Aluminum, zinc, or Devarda's alloy in a strong base reduce NO_2^- to NH_3.

$$NO_2^- + 5H_2O + 6e^- \rightleftarrows NH_3 + 7OH^-$$
$$\underline{Zn} + 3OH^- + H_2O \rightleftarrows [HZn(OH)_4]^- + 2e^-$$
$$\underline{Al} + 6OH^- \rightleftarrows [Al(OH)_6]^{-3} + 3e^-$$

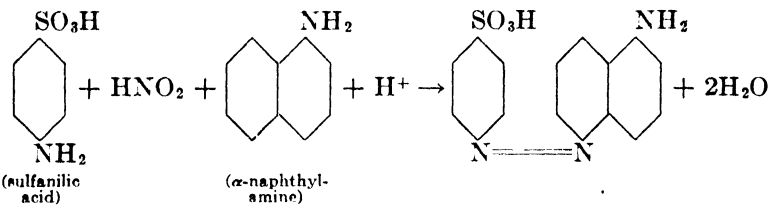
Sulfanilic acid and α-naphthylamine forms a red dye with nitrite ion in AcOH solution. The test is carried out by placing on a spot plate 1 drop of AcOH and 1 drop of aqueous unknown or "prepared solution," and by adding 1 drop of sulfanilic acid and then 1 drop of α-naphthylamine solution. A red color shows the presence of NO_2^-. Nitrates do not interfere with this test.

The red color is due to formation of a diazo dye.

The reaction essentially is

$$-NH_2 + HNO_2 + H^+ \rightarrow (-N{=}N-) + 2H_2O$$

(diazo group)



Nitric Acid and Its Ion

Properties. Commercial HNO_3 has a specific gravity of 1.42 and contains 68% by weight HNO_3. This solution, the constant boiling mixture, boils at 120.5° under 1 atm. pressure. It is about 15*N*. In dilute solution HNO_3 is completely ionized.

Nitric acid as oxidant. In dilute acid solution NO_3^- is an oxidant of about the same strength as Br_2 but the rate of reduction is so slow that it is reduced at an appreciable rate only by a few of the strongest reductants, such as Zn or Sn. Concentrated HNO_3, especially if hot, is a very powerful oxidant and oxidizes most of the metals.

Reduction products of HNO_3. Nitrogen forms compounds in all apparent valences from −3 to +5. Examples are: NH_3, N_2H_4 (hydrazine), NH_2OH (hydroxylamine), N_2, N_2O, NO, HNO_2, NO_2, HNO_3. When HNO_3 is used as an oxidant, its reduction products vary with the concentration of the acid and the temperature and also with the nature of the reductant. Usually a single reduction product is formed chiefly, but traces of several others are to be found in the solution. It follows that no redox reaction involving HNO_3 is to be considered strictly quantitative.

In general hot concentrated acid will be reduced mostly to NO_2, 7–9*N* acid to NO. Zn, Mg, and Sn reduce 1*N* acid to NH_4^+.

Electron changes in reduction of nitrate:

$$NO_3^- + 2H^+ + e^- \rightleftarrows \overline{NO_2} + H_2O$$
$$NO_3^- + 3H^+ + 2e^- \rightleftarrows HNO_2 + H_2O$$
$$NO_3^- + 4H^+ + 3e^- \rightleftarrows \overline{NO} + 2H_2O$$
$$2NO_3^- + 10H^+ + 8e^- \rightleftarrows \overline{N_2O} + 5H_2O$$
$$2NO_3^- + 12H^+ + 10e^- \rightleftarrows \overline{N_2} + 6H_2O$$
$$NO_3^- + 8H^+ + 6e^- \rightleftarrows NH_3OH^+ + 2H_2O$$

$$2NO_3^- + 17H^+ + 14e^- \rightleftarrows N_2H_5^+ + 6H_2O$$
$$NO_3^- + 10H^+ + 8e^- \rightleftarrows NH_4^+ + 3H_2O$$

Solubility. All nitrates except a few basic salts are soluble in water. As a result nitrates, if present, can usually be found in the water extract of any solid unknown material.

Reactions of Nitrate Ion

$MnSO_4$ in syrupy H_3PO_4 when slowly heated with a large $C_{NO_3^-}$ forms $[Mn(PO_4)_2]^{-3}$ violet.

Chloromanganous acid (12 *N* HCl saturated with $MnCl_2$), when heated with a nitrate becomes dark brown because of formation of $[MnCl_6]^{-3}$. Small concentrations of NO_3^- react rather slowly, and the test should be allowed to stand at least 10 minutes. Even then a negative result does not *prove* absence of a minute amount of NO_3^-. A blank containing the reagent alone and similarly heated must always be compared with the unknown.

Ferrous sulfate and concentrated H_2SO_4 form $Fe(NO)^{++}$ (dark brown) with both NO_3^- and NO_2^-. This is the "brown ring test."

$$NO_3^- + 3e^- + 4H^+ \rightleftarrows \overline{\overline{N}}O + 2H_2O$$
$$Fe^{++} + \overline{\overline{N}}O \rightleftarrows [FeNO]^{++} \text{ (brown)}.$$

The reaction mixture must be kept as cold as possible because $Fe(NO)^{++}$ is easily decomposed on warming.

This test is not reliable in presence of CrO_4^-, ClO_3^-, I^-, Br^-, $Fe(CN)_6^{-4}$, and $Fe(CN)_6^{-3}$. CrO_4^- and ClO_3^- may oxidize all the Fe^{++} to Fe^{+3}, which does not form a complex with NO. I^- and Br^- are oxidized by conc. H_2SO_4 to I_2 and Br_2, which might form brown rings. $[Fe(CN)_6]^{-3}$ will interfere by forming Turnbull's blue with Fe^{++}. $[Fe(CN)_6]^{-4}$ will also interfere, since Fe^{++} salts always contain more or less Fe^{+3}, which would form Prussian blue.

Aluminum, zinc, or Devarda's alloy[4] in NaOH or KOH reduce NO_3^- and NO_2^- to NH_3, readily detected by moist red litmus paper. Most compounds containing nitrogen are reduced to NH_3 and must be removed.

$$NO_3^- + 6H_2O + 8e^- \rightleftarrows NH_3 + 9OH^-$$

NH_4^+ salts react at once with the alkali to form NH_3. CN^-, NCS^-, $[Fe(CN)_6]^{-4}$ and $[Fe(CN)_6]^{-3}$ are all reduced with formation

[4] The approximate composition of Devarda's alloy is Al, 45%; Zn, 5%; Cu, 50%. Copper, by forming a couple, lowers the overvoltage of zinc and aluminum.

of NH_3 but much more slowly than NO_2^- or NO_3^-. NH_4^+ can be removed by boiling the test solution after addition of NaOH until red litmus is no longer changed. CN^-, NCS^-, $[Fe(CN)_6]^{-4}$ and $[Fe(CN)_6]^{-3}$ are removed by precipitating with Ag_2SO_4, centrifuging, and using the centrifugate for the test.

Reduction of nitrate to nitrite. If the sulfanilic acid α-naphthylamine test for nitrite is negative, an exceedingly sensitive test for nitrate can be made in the same solution by adding a few fragments of Devarda's alloy. If NO_3^- is present the red color caused by HNO_2 will gradually develop.

$$NO_3^- + 3H^+ + 2e^- \rightleftarrows HNO_2 + H_2O$$

$CrO_4^=$ forms a dark precipitate with α-naphthylamine, which obscures the reaction. If $CrO_4^=$ is present, remove it with $(AcO)_2Ba$ before making the test.

This test can be used to detect nitrates in nitrites by boiling the test solution with saturated NH_4Cl until a drop gives no color with sulfanilic acid and α-naphthylamine.

$$NO_2^- + NH_4^+ \rightarrow N_2 + 2H_2O$$

NO_3^- is not affected. After all NO_2^- has been removed, addition of a little Devarda's alloy will show whether NO_3^- was present.

Acetic Acid and Its Ion

Acetic acid is formed in the bacterial fermentation of organic matter. Vinegars are impure dilute solutions of acetic acid. Acetic acid is the second of a long series of aliphatic organic acids, formic HCOOH, acetic H_3CCOOH, propionic H_5C_2COOH, and so on.

Properties. The anhydrous acid boils at 118° and freezes at 16.6°. It is frequently called "glacial" acetic acid. It is miscible with water in all proportions. In 0.1 *N* solution acetic acid is only 1.34% ionized.

Solubility. All metal acetates are soluble in water except those of Ag^+ and Hg_2^{++}, which are sparingly soluble. Some basic acetates are only slightly soluble.

Tests for Acetate Ion

Various tests for acetate have been proposed, none of which are very sensitive. Among these are:

Warm 1:1 H_2SO_4 displaces from solid acetates acetic acid detectable in the steam as a vinegar-like odor.

Ethyl alcohol or **isoamyl alcohol,** when added to the reaction mixture of the preceding test, forms an ester of acetic acid, having a characteristic odor. The odor of the ethyl ester (usually described as "fruity") is not easy to distinguish from that of ethyl alcohol. The odor of the isoamyl ester resembles that of bananas and is more easily distinguished from that of the alcohol.

Lanthanum nitrate, when heated with a faintly ammoniacal solution containing acetate ion and a very little colloidal iodine, is hydrolyzed. The hydroxide or basic acetate of lanthanum formed is dyed bright blue by the iodine just as is starch paste. So many anions and cations interfere with this test that it is worthless in practice.

Ferric ion forms with concentrated solutions of acetate ion deep red $[Fe(AcO)_6]^{-3}$ very similar in appearance to $[Fe(NCS)_6]^{-3}$ but not very stable. On dilution the red color vanishes. As a test for AcO^- this reaction is not at all sensitive.

Acetone test. The most sensitive and reliable test for acetate appears to be the formation of acetone in the decomposition of solid acetates by heat and its detection by sodium nitroprusside as described under "Test for acetate," page 407.

$$(H_3CCOO)_2Ca \rightarrow CaCO_3 + (H_3C)_2CO$$

Silicic Acid and Silicates

Occurrence. Silicon is the most abundant of all the elements except oxygen. It never occurs as the free element but always combined with oxygen as SiO_2, quartz, or as silicates in many of which AlO_2^- partially replaces SiO_2. In these forms it is estimated to constitute more than 85% of the earth's lithosphere.

Granite, a widely distributed rock, is a mixture of quartz, feldspar (Na, K, Ca, aluminosilicate), and mica (K, Na, Li, Mg, Fe, aluminosilicate).[5]

Solubility. Quartz and many silicates are insoluble in acids. A few silicates in which the cations are almost exclusively alkali and

[5] For classification and composition of silicate minerals consult W. M. Latimer and J. H. Hildebrand, *Reference Book of Inorganic Chemistry*, p. 241, Macmillan, 1929.

alkaline earth elements can be decomposed by hot $12N$ HCl. All silicates can be decomposed by either of the following methods:

1. Treatment with HF and fuming with H_2SO_4 or $HClO_4$.

$$\underline{MeSiO_3} + 2HF_2^- + 4H^+ \rightleftarrows \overline{SiF_4} + 3H_2O + Me^{++}$$

$$3\overline{SiF_4} + 3H_2O \rightleftarrows 2H_2[SiF_6] + \underline{H_2SiO_3}$$

Hot concentrated H_2SO_4 or $HClO_4$ by absorbing H_2O prevents the second reaction from taking place.

2. Fusion with Na_2CO_3.

Acid-insoluble silicates are changed to Na_2SiO_3, and metal carbonate or oxide and the fused mass can then be decomposed by acid. Silica forms colloidal or gelatinous $[(H_2O)_2Si(OH)_4]$ (amphoteric) like $[(H_2O)_3Al(OH)_3]$ gel. On evaporating and dehydrating at about 120°, some 99% of the gel becomes very slowly soluble in dilute acid and can be removed. For exact analysis three or four evaporations and dehydrations are necessary to remove the SiO_2 sufficiently.

Both of the above methods require the use of platinum vessels. For this reason silicates are not included in elementary courses in analysis.

Some of the newer alloys contain a little silicon as silicide, for example, Cu_2Si. When such alloys are treated with HNO_3, gelatinous silica, resembling alumina, is formed. It must be dehydrated and removed before one begins the detection of the metals.

$$\underline{Cu_2Si} + 2H_2O \rightleftarrows \underline{SiO_2} + 2Cu^{++} + 4H^+ + 8e^-$$

$$3\underline{Cu_2Si} + 8NO_3^- + 20H^+ + 2H_2O$$

$$= 3\underline{(H_2O)_2Si(OH)_4} + 8\overline{NO} + 6Cu^{++}$$

Confirmation of Silica Gel

Metaphosphate beads do not dissolve silica gel. When microcosmic salt, $NaNH_4HPO_4 \cdot 4H_2O$ is taken up in a loop of the platinum wire and heated in the flame, sodium metaphosphate is formed as a colorless glass.

$$\underline{NaNH_4HPO_4 \cdot 4H_2O} = \underline{NaPO_3} + \overline{NH_3} + 5\overline{H_2O}$$

If a little of the silica gel is taken up on the bead and the latter reheated, a clot of SiO_2 (skeleton) can be seen moving about in the molten bead. Alumina would dissolve and leave the bead clear.

CHAPTER 19

INTRODUCTORY STUDY OF ANIONS

REACTIONS OF CARBONATE ION (GROUP IV)

Study pages 340, 341.

Experiment 1. Use of phenolphthalein as an indicator in removing $CO_3^=$. Read note 1, page 398.

Place 2 drops of $3N$ sodium carbonate reagent and 18 drops of water in a centrifuge tube. Add a *capillary* drop of phenolphthalein indicator, stir, and record color. Counting the drops, add $0.1N$ AcOH until only a faint pink color remains and then add an equal number of drops of the acid. Is a gas evolved during this latter addition of acid? Test the solution with red litmus paper. Is the solution basic or acid to this indicator? If the solution has become acidic, add $0.1N$ NH_3 until the solution has become faintly basic. Use this solution for experiment 2.

Write an equation for the reaction during the first addition of acid and another equation for the reaction during the second addition of acid.

Experiment 2. Action of the group reagent. To the solution from experiment 1 add 2 drops of calcium acetate, $(AcO)_2Ca$, and stir thoroughly. Is a precipitate formed? (Test for Group IV.) Centrifuge any precipitate and discard centrifugate. In another tube add $(AcO)_2Ca$ directly to 2 drops of $CO_3^=$ test solution. Centrifuge and compare volume of the two precipitates. Account for difference in volume.

In the systematic analysis for anions, *nearly* neutralizing a Na_2CO_3 solution containing the anions is an essential preliminary to the group precipitations. In consequence, carbonate must be detected by a special test on the *original* material. This experiment shows, however, that at least a little $CO_3^=$ may be precipitated in Group IV.

From a study of Table 10 (page 264) state what the result would be if $(AcO)_2Ba$ was used in place of $(AcO)_2Ca$.

If an unknown solution has been treated as directed in experiment 1, will much $CaCO_3$ be in the Group IV precipitate?

Experiment 3. Action of H^+ (test for carbonate). To one-half of the combined precipitates from experiment 2 add 6 drops of water and 3 drops of $3N$ HCl. What is the gas given off? How could you prove your answer?

When semimicro quantities are taken, our observations indicate that, of all the anions forming volatile compounds when acidified with HCl, only carbonate effervesces. Due to the smaller solubility of CO_2 as compared with SO_2, H_2S, and HCN, this gas appears as small bubbles in the solution while the other gases seem to be liberated only at its surface.

Experiment 4. Sensitive test for carbonate. Place the other half of the precipitates from experiment 2 in the Erlenmeyer flask, equipped as directed under "Tests on gases," (page 189) and proceed as directed on page 405, "Test for carbonate."

REACTIONS OF OXALATE ION (GROUPS II, II-A, AND IV)

Study pages 344, 345.

Experiment 1. Action of the group reagent. Place 2 drops of $C_2O_4^=$ test solution and 18 drops of water in a centrifuge tube. Add $(AcO)_2Ca$ reagent as long as precipitate continues to form. Centrifuge. Discard centrifugate. Wash twice with $3N$ AcOH using 6 drops each time. Discard washings. Reserve precipitate for experiment 2.

Experiment 2. Action of large C_{H^+}. To the washed precipitate from experiment 1 add 6 drops of $3N$ H_2SO_4 and 3 drops of water. Warm and stir. Cool the solution and use for experiment 4.

Experiment 3. Action of weak acids. To 10 drops of water add 4 drops of $6N$ AcOH, 2 drops of $C_2O_4^=$ test solution, and then 2 drops of $(AcO)_2Ca$ reagent. Is CaC_2O_4 soluble in AcOH?

Experiment 4. Action of permanganate (reagent for Group II).[1] Place 3 drops of distilled H_2O in a test tube. Make acid with 6 drops of $3N$ H_2SO_4 and add dropwise very dilute $0.01N$ $KMnO_4$ solution until a permanent pink color remains. This solution is a "blank" for comparison. Record the number of drops of $KMnO_4$ required. Now to the solution from experiment 2 ($H_2C_2O_4$ in H_2SO_4) add the same number of drops of $0.01N$ $KMnO_4$ that was added to the H_2SO_4 solution (blank) above and then one drop more. Does the solution have a permanent pink color? If not, add more drops

[1] The electron partial equations for redox reactions in Groups I, II, and II-A are tabulated at page 393.

of 0.01 *N* $KMnO_4$ until a permanent pink color is obtained or until 5 drops have been added. Now heat the solution nearly to boiling (80°) and add dropwise 0.1 *N* $KMnO_4$ until a permanent pink color remains. Record the number of drops of 0.01 *N* and of 0.1 *N* MnO_4^- that were bleached by 1 mg of $C_2O_4^=$. (Confirmation of oxalate ion.)

5 drops (0.25 ml) of 0.1 *N*
(as oxidant) should equal about 1 mg $C_2O_4^=$.
5 drops (0.25 ml) of 0.01 *N*
(as oxidant) should equal about 0.1 mg $C_2O_4^=$

Experiment 5. Action of ferric ferricyanide (reagent for Group II-A). To 2 ml of distilled water add 2 drops of 1 *N* $Fe(NO_3)_3$ solution, 1 drop of *freshly prepared* saturated solution of potassium ferricyanide ($K_3Fe(CN)_6$), and 4 drops of 3 *N* HCl. Mix thoroughly and divide between two test tubes. To one add 2 drops of water; to the other add 2 drops of $C_2O_4^=$ test solution. Observe and record any color change as compared with the blank.

REACTIONS OF PHOSPHATE ION (GROUPS III-A AND IV)

Study pages 341–344.

Experiment 1. Action of the group reagent. To 2 drops of $HPO_4^=$ test solution add 18 drops of water, stir, then add $(AcO)_2Ca$ as long as precipitate forms. Centrifuge. Wash and reserve precipitate ($CaHPO_4$) for experiment 2. How would phosphate ion react with Ba and Cd acetates in neutral solution?

Experiment 2. Action of small C_{H^+}. To the precipitate from experiment 1 add 3 drops of 6 *N* AcOH. Warm and stir until precipitate all dissolves. Reserve solution for experiment 3.

Experiment 3. Benzidine acetate test. Place 2 drops of the $H_2PO_4^-$ solution from experiment 2 in a test tube. Dilute to 1 ml. Use this solution to carry out the benzidine acetate test (page 410). Note possibility of interferences.

Experiment 4. Ammonium molybdate test. To 1 ml of $(NH_4)_2MoO_4$ and 3 drops of 3 *N* HNO_3 add 2 drops of $HPO_4^=$ test solution and warm to 60°. Repeat the test, using 2 drops of $HAsO_4^=$ ion test solution instead of $HPO_4^=$. If no precipitate forms at 60° heat to 100° and observe results.

Experiment 5. Action of $AgNO_3$ in acid and in neutral solution (reagent for Groups III and III-A). To two drops of $HPO_4^=$ test solution add 16 drops of water, 2 drops 3 *N* HNO_3, and 3 drops silver

nitrate reagent. Is a precipitate formed? (Test for Group III.) Now add *very dilute* NH_3 (2 drops $6N$ NH_3 and 8 drops H_2O) drop by drop, stirring thoroughly after each addition until a precipitate forms (test for Group III-A). Note and record color of precipitate formed. Reserve precipitate for experiment 6.

Experiment 6. Solubility of Ag_3PO_4 in small C_{H^+} and in NH_3. To the precipitate from experiment 5 add 3 drops $6N$ AcOH. Reprecipitate the Ag_3PO_4 by adding $6N$ NH_3. Then add more NH_3 and note that it dissolves the Ag_3PO_4.

REACTIONS OF FLUORIDE ION (GROUP IV)

Study pages 346–348.

Experiment 1. Action of the group reagent. To 2 drops of fluoride ion test solution in a centrifuge tube add 18 drops of water and 2 drops of $(AcO)_2Ca$. Centrifuge. Wash and reserve precipitate for experiment 2.

Experiment 2. Action of small C_{H^+}. To the precipitate from experiment 1 add 3 drops of $6N$ AcOH. Warm and stir. Does the precipitate dissolve? Wash and reserve residue for experiment 4.

Experiment 3. Zirconium alizarin sulfonate test. On each of four depressions of the spot plate place 1 drop of $3N$ HCl and 1 drop each of zirconyl nitrate and "Alizarin red S" solution. Note color of the mixture. Allow to stand for 2 minutes. To one depression add 1 drop of fluoride test solution. Stir thoroughly. Note and record the time necessary to change the pinkish-red color of the reagent to a greenish yellow. To another add 1 drop of fluoride test solution containing 1 mg F^- per ml. To the third one add a little solid CaF_2. To the fourth test portion add 1 drop of distilled water (blank). Note that $SO_4^=$, $HPO_4^=$, and $C_2O_4^=$ interfere (page 347).

Experiment 4. Etching test. Place the residue from experiment 2 in a crucible and ignite strongly to *completely remove water*, which is detrimental to the test. Carry out the etching test very exactly as directed on page 409.

REACTIONS OF SULFATE ION (GROUP V)

Study pages 348, 349.

Experiment 1. Action of the Group IV reagent. To 2 drops of sulfate ion test solution in a centrifuge tube add 17 drops of water and 2 drops of $(AcO)_2Ca$. If no precipitate forms use the solution

for experiment 2. Compare the solubility of $CaSO_4$ with that of the Ca salts of $CO_3^=$, $C_2O_4^=$, $HPO_4^=$, and F^-, page 329.

Experiment 2. Action of the Group V reagent. To the solution from experiment 1 add 2 drops of $(AcO)_2Ba$. Stir thoroughly Centrifuge and reserve precipitate ($BaSO_4$) for experiment 3.

Experiment 3. Action of large C_{H^+}. To the precipitate from experiment 2 add 3 drops of $3N$ HCl. Warm and stir thoroughly. Does the precipitate appear to be dissolving? (Test for sulfate ion.) Would you expect barium sulfate to precipitate in an acid solution?

REACTIONS OF SULFITE ION (GROUPS II, II-A, IV, AND V)

Study pages 349–351.

Experiments 1, 2. Repeat experiments 1 and 2, sulfate, using sulfite ion test solution instead of sulfate ion. Reserve precipitates from experiments 1 and 2 for use in the following experiments.

Experiment 3. Action of permanganate. Carry out the test for Group II anions as directed for oxalate (page 380), but use one half of precipitate from experiment 2 ($BaSO_3$) treated with 6 drops of $3N$ H_2SO_4 instead of oxalate solution.

Experiment 4. Action of ferric ferricyanide. Carry out the test for Group II-A reductant anions (page 401), using the other half of the precipitate from experiment 2 ($BaSO_3$) dissolved in 2 drops of $3N$ HCl.

Experiment 5. Confirmatory test for SO_2 (sulfite ion). Using 1 drop (0.5 mg) of the $SO_3^=$ test solution, carry out the zinc nitroprusside test (page 409).

REACTIONS OF CHROMATE ION (GROUPS I, III-A, AND V)

Study pages 351, 352.

Experiments 1, 2. Repeat experiments 1 and 2, sulfate, using chromate ion test solution instead of sulfate ion.

Experiment 3. Action of large C_{H^+}. To the precipitate from experiment 2 ($BaCrO_4$) add 3 drops of $3N$ HNO_3. Note and record color changes. Reserve solution for experiment 4.

Experiment 4. Ether–hydrogen peroxide test. To the solution from experiment 3 add 4 drops ethyl ether. *Shake, cool under the tap*, then add 1 or 2 drops of H_2O_2 solution and shake quickly. A blue color in the ether layer is $CrO(O_2)_2$ (confirmatory test for $CrO_4^=$).

Experiment 5. Action of manganous sulfate in phosphoric acid. In one of two micro crucibles place one drop of chromate ion test solution. Add 1 drop of saturated $MnSO_4$ solution and 4 drops of syrupy H_3PO_4. In the other crucible prepare a blank by adding 1 drop distilled water and the same number of drops of $MnSO_4$ and H_3PO_4 that were added to the chromate. Now *slowly* heat the crucibles *just* to boiling (see note) and allow them to cool. Violet-colored $[Mn(PO_4)_2]^{-3}$ is a test for certain strong oxidant anions.

Note: If *overheated*, oxidation by *air* may form $[Mn(PO_4)_2]^{-3}$ (metaphosphate bead test for Mn).

Experiment 6. Action of chloromanganous acid (reagent for Group I). Add 1 drop of chromate ion test solution to 2 drops of H_4MnCl_6 solution. Heat carefully and let stand 10 minutes if a color does not develop sooner. A brown color compared to a blank that is run at the same time, using 1 drop of distilled water instead of test solution, indicates oxidant anions.

Experiment 7. Action of $AgNO_3$ in acid and in neutral solution. To 2 drops of $CrO_4^{=}$ test solution add 16 drops of water, 2 drops of $3N$ HNO_3 and 3 drops of silver nitrate reagent. Is a precipitate formed? Now add $1N$ NH_3 solution dropwise with thorough stirring after each drop until a precipitate forms. Note and record color of precipitate. Add excess NH_3 until the precipitate redissolves.

REACTIONS OF SULFIDE ION (GROUPS II, II-A, III, AND VI)

Study pages 353–355.

Experiment 1. Action of the group reagent. To 2 drops of $S^{=}$ test solution add $(AcO)_2Cd$ dropwise with stirring until precipitation is complete. Warm and stir (test for Group VI). Centrifuge and discard centrifugate. Wash the precipitated CdS and use for experiment 2.

Experiment 2. Test for hydrogen sulfide (sulfide ion). Use part of the CdS precipitate from experiment 1. Carry out the test as directed on page 411.

Experiment 3. Action of permanganate. Carry out the Group II test for reductant anions as directed for oxalate, experiment 4, using 1 drop of test solution diluted to contain 1 mg sulfide ion per ml.

Experiment 4. Action of ferric ferricyanide. Carry out the Group II-A test for reductant anions as directed for oxalate, experiment 5, using 1 drop of the test solution diluted to contain 1 mg $S^{=}$ per ml.

Experiment 5. Action of silver nitrate (reagent for Group III). Place in a test tube 2 drops of sulfide ion test solution and 18 drops of water. Add 3 drops $3N$ HNO_3 and 1 drop of $AgNO_3$.

REACTIONS OF CYANOFERROATE (FERROCYANIDE) ION (GROUPS II, II-A, III, AND VI)

Study pages 355, 356.

Experiment 1. Action of the group reagent. Repeat experiment 1, sulfide, using cyanoferroate test solution instead of sulfide ion.

Experiment 2. Action of ferrous and ferric ions. Review experiments 5 and 6, iron, page 283, and state the action of Fe^{++} and of Fe^{+3} on cyanoferroate ion.

Experiment 3. Action of permanganate. Carry out the Group II test for reductant anions as in experiment 4, oxalate, using ferrocyanide test solution.

Experiment 4. Action of ferric ferricyanide (reagent for Group II-A). From results of experiment 2 predict what would happen if you added $[Fe(CN)_6]^{-4}$ to $FeFe(CN)_6$ reagent.

Experiment 5. Action of silver nitrate (reagent for Group III). Place in a test tube 2 drops of ferrocyanide test solution. Add 3 drops $3N$ HNO_3 and 1 drop of $AgNO_3$. Note color of precipitate.

REACTIONS OF CYANOFERRIATE (FERRICYANIDE) ION (GROUPS I, III, AND VI)

Study pages 356, 357.

Experiments 1, 2, 3. Repeat experiments 1, 2, and 5, ferrocyanide, using ferricyanide test solution.

REACTIONS OF ARSENITE ION (GROUPS II, III-A, AND VI)

Study pages 357, 358.

Review experiment 2, arsenic, page 293.

Experiment 1. Repeat experiment 1, sulfide, using arsenite test solution instead of sulfide ion.

Experiment 2. Action of $AgNO_3$ in acid and in neutral solution (reagent for Groups III and III-A). To 2 drops of AsO_2^- test solution and 15 drops of water add 3 drops of HNO_3 and 3 drops of $AgNO_3$. Does a precipitate form? Now add $1N$ NH_3, drop by drop, until a precipitate forms. After you have observed and recorded the physical characteristics of this precipitate, add excess NH_3. What happens?

Experiment 3. Bettendorf test. Place in one test tube 2 drops of a 2 mg per ml solution of AsO_2^- and in another 2 drops of a 2 mg per ml solution of $HAsO_4^=$. Carry out the Bettendorf test (page 293). Note and record the time required for a yellow or brown color to appear in each tube.

Experiment 4. Action of permanganate. Carry out Group II test for reductant anions as in experiment 4, oxalate, page 380, using 2 drops of AsO_2^- test solution.

REACTIONS OF ARSENATE ION (GROUPS III-A AND VI)

Study pages 358, 359.

Review experiment 1, arsenic cations, page 293.

Experiments 1, 2. Repeat experiments 1 and 2, arsenite, using arsenate test solution instead of arsenite ion.

Experiment 3. Compare experiment 3, arsenite, above. Is it possible to distinguish between AsO_2^- and $HAsO_4^=$ by the Bettendorf test?

Experiment 4. Ammonium molybdate test. Review experiment 4, phosphate, page 381.

REACTIONS OF CYANIDE ION (GROUPS II[?], III, AND VII)

Study pages 359–361.

Experiment 1. Action of the group reagent. To 2 drops of CN^- test solution add 18 drops of water and then $4N$ $Co(NO_3)_2$ solution dropwise as long as a precipitate forms. Then add 2 drops more. Centrifuge and wash precipitate.

Experiment 2. Benzidine acetate–cupric acetate test. Place the precipitate from experiment 1 in the Erlenmeyer flask equipped as described under "Tests on gases," page 189. Test for cyanide as directed on page 404. Test paper turning blue is test for HCN (cyanide ion).

Experiment 3. Action of $AgNO_3$ (reagent for Group III). Place in a centrifuge tube 2 drops of CN^- test solution and 18 drops

of water. Add $AgNO_3$ reagent, stirring after each drop is added. When a *permanent* precipitate is formed add 3 drops of $3N$ HNO_3.

REACTIONS OF THIOSULFATE ION (GROUPS II, II-A, III, AND VIII)

Study pages 361–363.

Dilute 2 drops of thiosulfate test solution to 1 ml. Use one half the solution for experiment 1.

Experiment 1. Action of large C_{H^+}. To one half the above solution add $3N$ HCl. Stir and warm. What is the precipitate formed? What gas is given off?

Experiment 2. Action of silver nitrate. To the remainder of the diluted test solution add 2 drops $AgNO_3$ solution. Observe carefully and record results.

Experiment 3. Action of permanganate. Carry out the Group II test for reductant anions, experiment 4, oxalate, page 380, using 1 drop of $S_2O_3^=$ test solution.

Experiment 4. Action of ferric ferricyanide. Carry out the Group II-A test for reductant anions, experiment 5, oxalate.

REACTIONS OF THIOCYANATE ION (GROUPS II, II-A, III, AND VII)

Study pages 363, 364.

Experiment 1. Action of the group reagent. Place in a centrifuge tube two drops of thiocyanate (NCS^-) test solution. Dilute to 1 ml; add 3 drops of $3N$ HNO_3 and sufficient $AgNO_3$ for complete precipitation. Centrifuge; wash the precipitate thoroughly, and use it for experiment 2.

Experiment 2. Action of ammonia. To the precipitate from experiment 1 add 3 drops of $15N$ NH_3; slime the precipitate thoroughly, using a glass rod. Centrifuge. Has any of the precipitate dissolved? How can you find out? Whether or not the precipitate has dissolved completely, add 3 drops of colorless NH_4HS reagent and again slime thoroughly. Centrifuge and discard the precipitate. *Boil* the NH_3 out of the solution and centrifuge out any sulfur. Use this solution for experiment 3.

Experiment 3. Action of ferric ion. To the *boiled* solution from experiment 2 add 6 drops of $3N$ HNO_3, 3 drops of CCl_4, and enough

$Fe(NO_3)_3$ reagent to permanently color the solution. Shake thoroughly and examine CCl_4 layer for color. Use the water layer for experiment 4.

If the sulfide ion was not completely removed in experiment 2, a white precipitate upon addition of Fe^{+3} would be sulfur due to

$$2Fe^{+3} + H_2S = 2Fe^{++} + \underline{S} + 2H^+.$$

Experiment 4. Action of permanganate (reagent for Group II). To the water layer of experiment 3 add $KMnO_4$ dropwise until the red color of $[Fe(NCS)_6]^{-3}$ disappears and the pink color of dilute MnO_4^- is permanent. Reserve for experiment 5.

Experiment 5. Test for complete removal of thiocyanate. To the solution from experiment 4 add 1 drop of H_2O_2 and then 1 drop $AgNO_3$. Has all of the NCS^- been destroyed? What two ions has it formed?

Oxidation of $Fe(NCS)_6^{-3}$ by MnO_4^- frequently causes some MnO_2 to form. This is instantly reduced by H_2O_2. Some H_2O_2 contains Cl^-. The reagent should be tested for Cl^- before using here.

REACTIONS OF IODIDE ION (GROUPS II, II-A, III, AND VIII)

Study pages 364–366.

Experiment 1. Repeat experiment 1, thiocyanate, using iodide ion test solution instead of thiocyanate ion. Use precipitate for experiment 2.

Experiment 2. Repeat experiment 2, thiocyanate, using the precipitate from experiment 1. Use solution for experiment 3.

Experiment 3. Repeat experiment 3, thiocyanate, using the boiled solution from experiment 2 (test for iodide ion). Remove the water layer to a crucible and boil gently until I_2 is completely volatilized. Add another drop of $Fe(NO_3)_3$ if necessary. Solution should be yellow and not brown. Test the solution by experiment 4 for complete removal of I_2.

Experiment 4. Test for complete removal of iodine. To the solution from experiment 3 add $KMnO_4$ dropwise until the pink color of dilute MnO_4^- is permanent. Test for I_2 by shaking the solution with 4 drops of CCl_4. Was all the I_2 removed in experiment 3?

REACTIONS OF BROMIDE ION (GROUPS II, III, AND VIII)

Study pages 366–368.

Experiment 1. Repeat experiment 1, thiocyanate, using bromide ion test solution instead of thiocyanate ion. Use precipitate for experiment 2.

Experiment 2. Repeat experiment 2, thiocyanate, using the precipitate from experiment 1. Use solution for experiment 3.

Experiment 3. Repeat experiment 3, thiocyanate, using the boiled solution from experiment 2. Use both water and CCl_4 layers for experiment 4.

Experiment 4. Repeat experiment 4, thiocyanate, using the solution (both water and CCl_4) from experiment 3 (test for bromide ion). Use the CCl_4 solution for experiment 5 and the water solution for experiment 6. Would the presence of NCS^- and I^- interfere with the detection of Br^-?

Experiment 5. Sensitive test for bromine. Spot a piece of filter paper with 1 drop of fluorescein reagent. Now add to the spot 1 capillary drop of the CCl_4 solution of Br_2. A pinkish-red ring will be formed if Br_2 is present (confirmation of Br^-). Any MnO_2 present will remain at the center of the spot.

Experiment 6. Test for complete removal of bromine. Place the clear water solution from experiment 4 in a crucible and boil to remove any Br_2 not removed by CCl_4. Test for Br_2 by shaking the solution with 4 drops of CCl_4. Continue boiling until no more Br_2 is present. Add 2 drops of $AgNO_3$. Has all of the Br^- been oxidized?

REACTIONS OF CHLORIDE ION (GROUPS III AND VIII)

Study page 368.

Experiment 1. Repeat experiment 1, thiocyanate, using chloride ion test solution instead of thiocyanate ion. Use precipitate for experiment 2.

Experiment 2. Action of ammonia. To the precipitate from experiment 1 add 3 drops of $15N$ NH_3. Stir thoroughly. Does the precipitate dissolve? Add 3 drops of NH_4HS reagent. Stir thoroughly. Centrifuge and discard the precipitate. Boil the NH_3 out of the solution and centrifuge out any sulfur. Use this solution for experiment 3.

Experiment 3. Action of permanganate. To the boiled solution from experiment 2 add 6 drops $3\,N$ HNO_3, 3 drops of CCl_4, and then add $KMnO_4$ until the pink color of MnO_4^- is permanent. Does MnO_4^- oxidize Cl^-? Use the water solution for experiment 4.

Experiment 4. Confirmatory test for chloride. To the solution from experiment 3 add a drop of H_2O_2 to reduce $KMnO_4$ and any MnO_2. Add $AgNO_3$ dropwise until precipitation is complete. White AgCl proves chloride.

Test the reagent H_2O_2 for Cl^- before using. If Cl^- is found in it, run a blank using the same number of drops of H_2O_2 as were used in the unknown. Subtract the amount of Cl^- in the blank from that found in the unknown.

REACTIONS OF CHLORATE ION (GROUP I)

Study pages 369, 370.

Experiment 1. Action of silver nitrate. Place in a centrifuge tube 2 drops of chlorate ion test solution. Dilute to 1 ml. Add 3 drops of $3\,N$ HNO_3 and 2 drops $AgNO_3$. Use solution for experiment 2. Is $AgClO_3$ insoluble in dilute HNO_3?

Experiment 2. Action of nitrous acid. To the clear solution from experiment 1 add 3 drops of HNO_3 and 1 to 2 drops of chloride-free KNO_2. What is the precipitate? Prove that it is not $AgNO_2$.

Experiment 3. Action of manganous ion and phosphoric acid. With 1 drop of chlorate ion test solution carry out the test as directed for experiment 5, chromate, page 384.

Experiment 4. Action of chloromanganous acid. With 1 drop of chlorate ion test solution carry out group test for oxidants as in experiment 6, chromate, page 384.

REACTIONS OF NITRITE ION (GROUPS I[?], II, II-A)

Study pages 372–374.

Place in a test tube 2 drops of nitrite ion test solution and 18 drops of water. What is concentration of NO_2^- in mg per ml? Use this solution for the following experiments.

***Experiment 1.**[2] **Action of manganous ion and phosphoric acid.** Using 1 drop of NO_2^- test solution (10 mg/ml), perform test for oxidant anions as in experiment 5, chromate, page 384. Repeat

[2] Experiments so marked may be omitted in shorter courses.

the test, using 1 drop of the dilute solution (1 mg/ml). Would you rely on this test to find or to prove absent a small amount (0.5 to 1.0 mg per ml) of NO_2^-?

Experiment 2. Action of chloromanganous acid. Perform the test for Group I anions as directed in experiment 6, chromate, using 1 drop of 10 mg/ml test solution. Repeat, using 1 drop of the 1 mg/ml solution.

Experiment 3. Action of permanganate. Carry out the Group II test for reductant anions as in experiment 4, oxalate, page 380, but use 2 drops of the dilute solution of nitrite ion.

Experiment 4. Action of ferric ferricyanide. Carry out the Group II-A test for reductant anions as in experiment 5, oxalate, but use 2 drops of the dilute solution of nitrite ion.

Experiment 5. Sulfanilic acid–α-naphthylamine test. Carry out the sulfanilic acid–α-naphthylamine test for nitrite, page 406. *A blank must be run.*

Experiment 6. Brown-ring test. For interferences see page 375. In a test tube place a few drops of an aqueous solution or of the "prepared solution" which has been acidified with 3 *N* H_2SO_4. For this experiment use 1 drop of NO_2^- test solution. Add an equal volume of concentrated H_2SO_4 and cool the mixture as much as possible by holding in a stream of tap water. Then with a pipet, and holding the test tube as nearly horizontal as possible, run down the side of the test tube about 0.5 ml of freshly prepared saturated solution of $FeSO_4 \cdot 7H_2O$ or of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ so that the solution does not mix with the acid layer. If nitrate or nitrite is present, a brown ring will form at the junction of the two layers, the time required being proportional to the amount present. The mixture must be kept as cold as possible because $Fe(NO)^{++}$ is easily decomposed on warming. Interfering anions (except ClO_3^-) can be removed before applying the test by adding saturated Ag_2SO_4 solution as long as a precipitate continues to form. Centrifuge and discard the precipitate.

Experiment 7. Repeat experiment 6, using 6 *N* AcOH instead of conc. H_2SO_4.

***Experiment 8. Reduction of nitrite to ammonia.** Place 1 drop of nitrite ion test solution and 8 drops of NaOH in the Erlenmeyer flask, equipped with wedge point pin and red litmus paper, as in test for ammonium ion (page 308). Test for NH_3 in the solution by gently warming the solution. Litmus paper turning blue proves NH_3 in the mixture. If present, remove as directed on page 308.

To the solution free from NH_3 add a few fragments of Devarda's alloy. Litmus paper turning blue indicates reduction of nitrite ion to NH_3. (Other nitrogen-containing compounds are also reduced to NH_3.)

***Experiment 9. Destruction of Nitrite Ion by Ammonium Ion (test for nitrate in nitrite).** In a crucible place 2 drops of NO_2^- test solution (10 mg/ml). Add 6 drops of saturated NH_4Cl solution and heat *slowly* just to dryness. Take up with 6 drops of water. Test 1 drop of the solution for NO_2^- as in experiment 5. If the test is positive, repeat the evaporation to dryness. Take up with 6 drops of water and repeat the test. If necessary evaporate a third time or until 1 drop gives no test for NO_2^-. When a drop gives no test for NO_2^-, add to this test mixture on the spot plate a fragment of Devarda's alloy. Any color appearing now is due to NO_3^- which has been reduced to HNO_2.

REACTIONS OF NITRATE ION (GROUP I[?])

Study pages 374–376.

Place in a test tube 2 drops of nitrate ion test solution and 18 drops of water. Use this solution for experiments 1 to 3.

Experiment 1. Action of manganous ion and phosphoric acid. Using 1 drop of nitrate ion test solution (10 mg/ml), NO_3^-, perform this test as directed in experiment 5, chromate, page 384. Repeat the test, using 1 drop of the dilute solution (1 mg NO_3^-/ml). Would you rely on this test to find or to prove absent a small amount (0.5 to 1 mg per ml) of nitrate?

Experiment 2. Action of chloromanganous acid. Perform the group test for oxidant anions as directed in experiment 6, chromate, page 384, using, instead, 1 drop of test solution of nitrate ion. Repeat the test, using 1 drop of the solution made above (1 mg/ml NO_3^-). Would you rely on this test to find or to prove absent a small amount of nitrate?

Experiment 3. Repeat experiment 5, nitrite, using 1 drop of the dilute nitrate ion solution instead of nitrite ion. Use test mixture for experiment 4.

Experiment 4. Reduction of nitrate to nitrite. If the sulfanilic acid–α-naphthylamine test in experiment 3 was negative, add a fragment of Devarda's alloy. A red color should gradually develop.

Experiment 5. Repeat experiments 6 and 7, nitrite, using 1 drop of nitrate ion test solution instead of nitrite ion.

Experiment 6. Repeat experiment 8, nitrite, using 1 drop of nitrate ion test solution instead of nitrite ion.

REACTIONS OF BORATE ION (NO GROUP REAGENT)

Study pages 370–372.

Experiment 1. Turmeric paper test. Using 1 mg BO_2^- per ml acidified with HCl, perform the turmeric paper test (page 405).

Experiment 2. Flame tests. Using a little solid borate salt in each case, perform the two flame tests on page 371.

REACTIONS OF ACETATE ION (NO GROUP REAGENT)

Study pages 376, 377.

Formation of acetone and its action on alkaline nitroprusside. Perform the test for acetate ion as described on page 407 on each of the following materials:

1. 5 mg of solid $(AcO)_2Pb$.
2. 5 mg of solid AcONa.
3. 4 drops of AcO^- test solution.

REDOX REACTIONS IN GROUPS I, II, AND II-A

Group I.	Reductants	$[MnCl_6]^{-4} \rightleftarrows [MnCl_6]^{-3} + e^-$
		$Mn^{++} + 2H_2PO_4^- \rightleftarrows [Mn(PO_4)_2]^{-3} + 4H^+ + e^-$
	Oxidants	$ClO_3^- + 6H^+ + 6e^- \rightleftarrows Cl^- + 3H_2O$
		$HCrO_4^- + 7H^+ + 3e^- \rightleftarrows Cr^{+3} + 4H_2O$
		$[Fe(CN)_6]^{-3} + e^- \rightleftarrows [Fe(CN)_6]^{-4}$
		$HNO_2 + H^+ + e^- \rightleftarrows \overline{NO} + H_2O$
		$NO_3^- + 4H^+ + 3e^- \rightleftarrows \overline{NO} + 2H_2O$
Group II.	Oxidant	$MnO_4^- + 8H^+ + 5e^- \rightleftarrows Mn^{++} + 4H_2O$
	Reductants	$[Fe(CN)_6]^{-4} \rightleftarrows [Fe(CN)_6]^{-3} + e^-$
		$HSO_3^- + H_2O \rightleftarrows SO_4^- + 3H^+ + 2e^-$
		$3S_2O_3^- + 5H_2O \rightleftarrows 2SO_4^- + S_4O_6^-$ (tetrathionate) $+ 10H^+ + 10e^-$
		$HAsO_2 + 2H_2O \rightleftarrows H_2AsO_4^- + 3H^+ + 2e^-$
		$HC_2O_4^- \rightleftarrows 2\overline{CO_2} + H^+ + 2e^-$ (hot solution only)
		$3H_2O + I^- \rightleftarrows IO_3^- + 6H^+ + 6e^-$
		$2Br^- \rightleftarrows Br_2 + 2e^-$
		$NCS^- + 5H_2O \rightleftarrows SO_4^- + NCO^- + 10H^+ + 8e^-$
		$H_2S + 4H_2O \rightleftarrows SO_4^- + 10H^+ + 8e^-$
		$HNO_2 + H_2O \rightleftarrows NO_3^- + 3H^+ + 2e^-$

Group II-A. Oxidant $[Fe(CN)_6]^{-3} + e^- \rightleftarrows [Fe(CN)_6]^{-4}$; $Fe^{+3} + e^- \rightleftarrows Fe^{++}$

Reductants which reduce Fe^{+3} more rapidly.	$H_2S \rightleftarrows S + 2H^+ + 2e^-$	Turnbull's blue
	$HSO_3^- + H_2O \rightleftarrows SO_4^- + 3H^+ + 2e^-$	
	$2S_2O_3^- \rightleftarrows S_4O_6^-$ (tetrathionate) $+ 2e^-$	
Reductants which reduce $[Fe(CN)_6]^{-3}$ more rapidly.	$2I^- \rightleftarrows I_2 + 2e^-$	Prussian blue
	$HNO_2 + H_2O \rightleftarrows NO_3^- + 3H^+ + 2e^-$	

REMOVAL OF INTERFERING CATIONS

Make a "transposed solution" of each of the following salts *separately* as directed on page 397. Notice carefully colors of insoluble residues. Test each prepared solution for the anion (not carbonate) supposed to be in it, following directions below for each salt. Centrifuge out precipitates and estimate and record amount of anion in the 1 ml of solution.

1. $BaSO_4$. Acidify 1 ml with HCl, add $(AcO)_2Ba$ reagent until precipitation is complete.

2. $MgNH_4PO_4$. Acidify 1 ml strongly with HNO_3 and test for phosphate ion with $(NH_4)_2MoO_4$.

3. $Ca_3(PO_4)_2$. Proceed as in 2.

4. CaF_2. Neutralize 1 ml as directed on page 398 and add $(AcO)_2Ca$ reagent. Wash any precipitate thoroughly; extract any $CaCO_3$ present with AcOH. Test any residue for F^- with zirconium alizarin sulfonate.

5. $CuCrO_4$. Neutralize 1 ml as directed on page 398. Does a precipitate form on neutralization? What does it appear to be? Judging by the color of the solution, has much $CrO_4^=$ gone into solution?

6. $Al(H_2O)_6Cl_3$. Neutralize 1 ml as above. What is the precipitate that forms? Should large C_{Cl^-} be in the solution?

7. As_2S_3. Neutralize 1 ml as above. What is the precipitate that forms? Centrifuge and discard it. To the clear centrifugate add $(AcO)_2Cd$ as long as any precipitate forms. Centrifuge, wash, and treat precipitate with 3 *N* HCl. What is the yellow residue? Explain its formation.

8. ZnS. Neutralize with AcOH and test for $S^=$ as directed on page 411.

9. $Fe_4[Fe(CN)_6]_3$. Acidify 1 ml with HCl and test for $Fe(CN)_6^{-4}$.

10. HgI_2. Acidify 1 ml of the solution with HNO_3 and test for I^-.

Theory of the Transposed Solution

Since the carbonates or hydroxides of all cations except Na^+, K^+, and NH_4^+ are insoluble in water and the Na salts of all anions are soluble, boiling with conc. Na_2CO_3 should remove most cations and bring most anions into solution. At 100° Na_2CO_3 is considerably hydrolyzed.

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

Since both $CO_3^=$ and OH^- are present, carbonate, hydroxide, or basic salt of a given cation may precipitate, depending upon which of the three is least soluble. Since a large excess of Na_2CO_3 is used, $CO_3^=$ is rarely used up and the HCO_3^- remains unacted upon.

$$\underline{NH_4Fe(SO_4)_2 \cdot 12H_2O} + 3CO_3^= + OH^- \rightleftarrows \underline{FeOOH} + 2SO_4^= + 3HCO_3^- + \overline{NH_3} + 11H_2O$$

$$\underline{ZnCrO_4} + CO_3^= \rightleftarrows \underline{ZnCO_3} + CrO_4^=$$

Ammonium salts are completely decomposed.

$$NH_4^+ + CO_3^= + H_2O = \overline{NH_3} + H_2O + HCO_3^-$$

Amphoteric hydroxides are dissolved only a little, since C_{OH^-} cannot become very large.

$$\underline{AlOOH} + OH^- + H_2O \rightleftarrows Al(OH)_4^-$$

$$\underline{\overline{CuCO_3}} + 3OH^- + H_2O \rightleftarrows \underset{\text{(blue)}}{Cu(OH)_4^=} + HCO_3^-$$

The blue color produced by cupric salts is probably due mostly to $[Cu(CO_3)_2]^=$.

On neutralizing the Na_2CO_3 solution, the amphoteric hydroxide reprecipitates and is removed.

Sulfides of Cation Group II-B, except HgS, may form thioanions.

$$\underline{As_2S_3} + 6OH^- \rightleftarrows [AsS_2O]^{-3} + [AsSO_2]^{-3} + 3H_2O$$

$$\underline{\overline{SnS_2}} + 2OH^- \rightleftarrows [SnS_2O]^= + H_2O$$

On neutralizing the solution, the sulfides reprecipitate.

As shown in Chapter 8, page 112, the extent to which an insoluble salt is transposed by Na_2CO_3 depends on the ratio $\frac{K_{s.p.}\ \text{salt}}{K_{s.p.}\ \text{carbonate (or hydroxide)}}$. For example, $BaSO_4$ is only partially transposed,

$$\underline{BaSO_4} + CO_3^{=} \rightleftarrows \underline{BaCO_3} + SO_4^{=},$$

because $BaSO_4$ is considerably less soluble than $BaCO_3$. On the other hand, $PbCrO_4$, which has about the same solubility as $BaSO_4$, is almost completely transposed because $PbCO_3$ (or basic carbonate) is very much less soluble than $PbCrO_4$.

CHAPTER 20

SYSTEMATIC ANALYSIS OF ANIONS

In general the cations, except Na^+, K^+, and NH_4^+, interfere with anion analysis and should be removed before proceeding. As shown in the preceding chapter, most material is decomposed when boiled or fused with Na_2CO_3. The cations are precipitated and the anions pass into solution. This solution, referred to in various texts as the "transposed solution," the "prepared solution," or the "sodium carbonate solution," is the test solution most frequently used in anion analysis.

According to the nature of the material to be analyzed, a transposed solution may or may not have to be made. Four cases have to be considered.

REMOVAL OF INTERFERING CATIONS: THE TRANSPOSED SOLUTION

Cases 1 and 2. Material completely soluble in water. Dissolve 50 mg of the solid material in 2.5 ml of water. To a drop of the aqueous solution add a drop of $3N$ Na_2CO_3 and stir thoroughly. (1) If *no* precipitate results, interfering cations are absent and the solution is ready for analysis. (2) If Na_2CO_3 forms a precipitate, treat 2 ml of the solution with 1 ml of $3N$ Na_2CO_3 and heat as directed under case 4.

Case 3. Material partly soluble in water. The water-soluble part may be extracted and tested separately and the thoroughly extracted insoluble part treated with Na_2CO_3 as in case 4. This method has the advantage of later indicating to some extent which anions were combined with which cations. It has the disadvantage of requiring *two* anion analyses instead of one. Of course, the material may be treated *at once* with Na_2CO_3 without previous extraction with water.

Case 4 (and 3). Material entirely or partly insoluble in water. Make the transposed solution by placing 50 mg of the solid in a small Erlenmeyer flask, adding 2.5 ml of $3N$ Na_2CO_3, and keeping it at a *gentle* boil for five minutes. Note whether NH_3 is evolved. Each minute replace the water that has boiled away and stir the mixture

thoroughly. Transfer the hot mixture to a 15 ml centrifuge tube and centrifuge. Add water to make the solution 2.5 ml. (*Save the residue* until the cation analysis has been made. It may be needed!)

Substances not transposed by sodium carbonate. The following substances are not much affected by the Na_2CO_3 treatment:

1. All phosphates, except those of Na^+, K^+, and NH_4^+.
2. Most sulfides, except those of As, Sb, and Sn^{+4}, which are amphoteric.
3. Mineral fluorspar, CaF_2. The freshly precipitated salt is much more soluble.
4. Halides of Ag^+, that is, AgCl, AgBr, AgI, and AgSCN.
5. Most mineral silicates.

Since in certain cases these anions may not pass into the Na_2CO_3 solution but remain entirely in the carbonate-hydroxide residue, this residue must always be preserved until the anion analysis has been made. In many cases a consideration of solubilities will show that it will not be necessary to analyze the residue for all the possibilities. For example, if a solid unknown is entirely soluble in dilute HNO_3, it cannot contain a halide of silver. Directions and methods for testing this insoluble residue will be found on page 413.

Neutralization of the "prepared solution." Add to the clear Na_2CO_3 solution in a clean Erlenmeyer flask 1 capillary drop of phenolphthalein (see note 1). Then add 6 *N* AcOH 1 drop at a time with vigorous shaking after each drop. Count the drops until the pink color just disappears. Spot a strip of filter paper with a capillary drop of $(AcO)_2Pb$. Continue the dropwise addition of AcOH with vigorous swirling of the liquid to remove CO_2 until as many more drops have been added as were required to decolorize the indicator. Expose the test paper to the escaping gases while the second and third drops of acid (after phenolphthalein was bleached) are added. As little as 0.5 mg of $S^=$ in the solution can be detected as H_2S at this point (see note 2). In nearly all cases the solution will be basic to litmus. Now using litmus paper as indicator and 1 *N* AcOH, cautiously bring the solution just to the basic side of neutrality (see note 3). If the solution becomes acid, make it *just* basic by using 1 *N* NH_3.

Notes: 1. Phenolphthalein is pink to $CO_3^=$ and colorless to HCO_3^-. If, of the 1.5 molal $CO_3^=$, x moles have reacted with cations or with water, x moles of HCO_3^- have been formed and $1.5 - x$ molar $CO_3^=$ remains. When the AcOH is added,

$$CO_3^= + AcOH = AcO^- + HCO_3^-.$$

When all CO_3^- has become HCO_3^-, the phenolphthalein becomes colorless But since

$$HCO_3^- + H_2O \rightleftarrows \overline{CO_2} + OH^- + H_2O,$$

the solution, though neutral to phenolphthalein, is still distinctly basic to litmus. Since if *any* CO_3^- reacted with cations there must be more HCO_3^- than CO_3^- in the solution, as many drops of AcOH can safely be added after the phenolphthalein becomes colorless as were required to decolorize it. The solution will still be basic to litmus. After all CO_3^- has become HCO_3^-, each drop of AcOH causes evolution of CO_2. After half or more of the HCO_3^- has been neutralized, it is safer to finish with 1 *N* AcOH so as not to let the solution reach distinct acidity. CO_2 should be removed as completely as possible by swirling the liquid, but the solution must not be heated nor allowed to become acid, since this might result in loss of H_2SO_3, HCN, or HNO_2.

2. HS^- is a much weaker acid than HCO_3^- and will be changed to H_2S before all HCO_3^- is neutralized. The evolution of large amounts of CO_2 appears to remove H_2S completely from the solution at this point unless an unusual amount of sulfide is in the solution. It has been found rather easy to detect the H_2S if the test is made *exactly* at the point directed. Small amounts of S^- are likely to give no precipitate of CdS in Group V. Larger amounts usually give some precipitate, although part of the S^- will have been lost during neutralization of the sodium carbonate solution. It is to be remembered that only if alkali sulfides are present in an aqueous solution is much S^- likely to be found in the "prepared solution." As a rule S^- must be sought in the insoluble residue from this solution.

3. The solution neutralized as above directed will still contain a little CO_2. This may cause precipitation of a little $CaCO_3$ in Group IV. However, the amount will not be sufficient to cause serious confusion.

SYSTEMATIC ELIMINATION OF ANION GROUPS

Study (pages 331–339) two examples of correct use of the A.E.S.

Color and *p*H (test A). Observe and record whether an unknown aqueous solution, the aqueous extract of a solid unknown, or the "prepared solution" is colored or colorless. In a colorless solution $CrO_4^=$ and $[Fe(CN)_6]^{-3}$ are certainly absent. Determine whether an unknown aqueous solution or the water extract of a solid unknown is neutral, basic, or acidic. This preliminary test is to be indicated on the A.E.S. by "A."

Note: A basic aqueous solution indicates the presence of alkali salts of weak acids. An acidic aqueous solution may occasionally be due to hydrolysis of a salt of a weak base and a strong acid. In an aqueous unknown solution it may be due to the presence of free acids such as H_2SO_3 or $H_2C_2O_4$. A neutral solution is not to be taken as proving absence of weak acids or bases. A solution of $AcONH_4$ is neutral, although it is

the salt of a weak base and a weak acid. Two hydrolyses, one producing H^+, the other OH^-, might neutralize each other. This test is of chief importance in determining the measures necessary for neutralizing an aqueous solution for the precipitation of Groups IV to VIII when no "prepared solution" has to be made.

Preliminary Group Tests

Indicate on the A.E.S. each of the following group tests by the number assigned below to the test. For example, if in test I *no* color is observed, place I in the "Certainly Absent" column opposite ClO_3^- and $CrO_4^=$ and place a check in the "Try Other Tests" column opposite NO_3^-, NO_2^-, and $[Fe(CN)_6]^{-3}$.

Tests for Group I (oxidant anions). Either or both of the two tests below may be used. Except as to NO_2^-, the results should be alike. Enter either or both tests on the A.E.S. as I.

1. Anions which oxidize chloromanganous acid. Add 1 drop of test solution to 2 drops of H_4MnCl_6 solution. Heat carefully and let stand 10 minutes. A brown color compared to a blank that is run at the same time, using 1 drop of distilled H_2O instead of test solution, indicates the presence of ClO_3^-, $CrO_4^=$, $[Fe(CN)_6]^{-3}$, NO_3^-, or NO_2^-. This test is more reliable for NO_2^- than is test 2. Small NO_3^- may react slowly. *A negative result is not absolute proof of absence of small NO_2^- and NO_3^-.*

2. Alternate test. In a micro crucible place 1 drop of test solution, either original aqueous or "prepared solution." (If test solution is strongly basic, acidify with H_3PO_4.) In another crucible (the blank) place 1 drop of distilled water. To each add 1 drop saturated $MnSO_4$ solution and 4 drops of syrupy H_3PO_4. Heat both at the same time slowly to boiling then let the crucibles cool. Violet-colored $[Mn(PO_4)_2]^{-3}$ indicates ClO_3^-, $CrO_4^=$, or (NO_3^-). Large amounts of NO_2^- may give the test. $[Fe(CN)_6]^{-3}$ causes, before heating, precipitation of brown $Mn_3[Fe(CN)_6]_2$. If this precipitate forms, pipet off the clear liquid to another crucible and add more $MnSO_4$.

Care must be exercised not to overheat the crucibles because in presence of fuming H_3PO_4 air will form the violet anion.

Test for Group II (anions that reduce MnO_4^- in acid solution). Place 3 drops of distilled H_2O in a test tube. Make acid with 6 drops of dilute H_2SO_4 and add dropwise very dilute ($N/100$) $KMnO_4$ solution until a permanent pink color remains. Now in another test tube place 3 drops of test solution, 6 drops of dilute

H_2SO_4, and 1 more than the number of drops of 0.01 N $KMnO_4$ that was added to the blank. Bleaching of the $KMnO_4$ indicates the presence of one or more of the following reducing anions: $[Fe(CN)_6]^{-4}$, $SO_3^{=}$, $S_2O_3^{=}$, AsO_2^{-}, $C_2O_4^{=}$, I^-, Br^-, NCS^-, $S^=$, NO_2^-. Stir or shake for 2 minutes after each addition. Reduction by some anions may be slow. If $KMnO_4$ is bleached, add three more drops of dilute $KMnO_4$. If the solution is still colorless, add dropwise 0.1N $KMnO_4$ solution until a permanent pink color remains. 3 drops of CCl_4 are now added and the mixture shaken vigorously. A brown-yellow CCl_4 layer indicates presence of bromide. Colorless CCl_4 layer proves absence of Br^-. If the $KMnO_4$ is not bleached, heat and note the results. If bleaching takes place *only upon heating*, the presence of $C_2O_4^=$ only is indicated. A negative test shows absence of *all* anions of this group except CN^- which, if *very* dilute, may not act on $KMnO_4$. CN^- must *always* be looked for in Group VII.

Test for Group II-A (anions that reduce Fe[Fe(CN)$_6$] reagent). To 2 ml of distilled water add 2 drops of 1 N $Fe(NO_3)_3$ solution, 1 drop of *freshly prepared* saturated solution of $K_3Fe(CN)_6$, and 4 drops of 3 N HCl. Mix thoroughly and divide between two test tubes. To one add 1 drop of the test solution. Blue or green color (see note), as compared with that of the blank, indicates $S^=$, NO_2^-, $SO_3^=$, I^-, $S_2O_3^=$, $[Fe(CN)_6]^{-4}$, ($C_2O_4^=$). A red coloration, $[Fe(NCS)_6]^{-3}$, indicates NCS^-. $C_2O_4^=$ if large may give a green color that does not become blue. This is probably due to formation of $[Fe(C_2O_4)_3]^{-3}$. Too large C_{H^+} makes the reagent greenish instead of brown. It also slows up the redox reactions.

Note: A mixture of a little soluble iron blue and excess $[Fe(CN)_6]^{-3}$ may give a green color. The reagent itself may become blue after standing 5 to 10 minutes.

Test for Group III (anions whose silver salts are insoluble in dilute HNO_3). Place 5 drops of the aqueous known or unknown solution or of the transposed solution in a centrifuge tube and add 3 drops of 3 N HNO_3. Test solution with litmus to be sure solution is distinctly acid. Now add dropwise $AgNO_3$ solution as long as a precipitate continues to form. Note appearance of black or yellowish tints. Black Ag_2S would indicate presence of $S^=$ or $S_2O_3^=$. Centrifuge and add 1 drop of $AgNO_3$ to insure complete precipitation and reserve the clear centrifugate for a test for chlorate. A precipitate indicates Cl^-, Br^-, I^-, NCS^-, CN^-, $S^=$, $S_2O_3^=$, $[Fe(CN)_6]^{-3}$,

$[Fe(CN)_6]^{-4}$. Note color of precipitate. Which of these ions form Ag^+ salts that are not white? *Record results* on A.E.S.

Na_2CO_3 usually contains a trace or more of Cl^-. The reagent must be tested and its content of Cl^- allowed for here and in Group VIII.

Test for chlorate ion. Make this test *only* if oxidizing acids were found present in Group I. Heat one half of the clear centrifugate from Group III and add 1 drop of chloride-free KNO_2. If a white precipitate forms, stir vigorously and centrifuge. A white precipitate insoluble in excess of HNO_3 but soluble in dilute NH_3 is AgCl and proves ClO_3^-. *Record result on A.E.S.* as test III.

Test for Group III-A (anions whose silver salts are colored and soluble in HNO_3 but insoluble in neutral solution). To the remaining half of the clear centrifugate from Group III add 3 drops of $AgNO_3$, then add *capillary* drops of $1N$ NH_3, stirring thoroughly after addition of each drop (see note). Continue the dropwise addition of NH_3 until a precipitate forms or until the solution becomes *just* basic to litmus. A reddish precipitate indicates $CrO_4^=$ and/or $HAsO_4^=$. A yellow precipitate would indicate $HAsO_2$ and/or $HPO_4^=$. If the solution is *very nearly* neutral, absence of precipitate proves absence of *all* these ions from the solution tested. *Record results on A.E.S.*

White silver salts of other anions may precipitate. No inference as to their identity is possible at this point.

Note: The silver salts of Group III-A anions are soluble in excess of NH_3.

Precipitation Group Tests

A Na_2CO_3 extract of a solid unknown (the transposed solution) was made faintly basic to litmus at the time of preparation and is ready for these precipitation tests.

Test for Group IV. Place 1 ml of the *cool* solution which is just basic to litmus (see note 1) in a centrifuge tube and add dropwise from a pipet $2N$ $(AcO)_2Ca$ solution as long as a precipitate continues to form. Centrifuge, add 1 drop of $(AcO)_2Ca$ to ensure complete precipitation, and reserve the clear centrifugate for Group V. Wash the precipitate with 2 to 3 drops cold water, stirring up the precipitate thoroughly, and collect this wash water with the original centrifugate. Wash the precipitate at least twice more with about 2 drops of water at a time.

The precipitate may be ($CaCO_3$) (see note 2), $CaHPO_4$, CaC_2O_4, CaF_2, ($CaSO_3$), ($Ca(AsO_2)_2$). Compounds in parentheses may or may not precipitate according to amount present. Reserve a precipitate for later examination. *Record results on A.E.S.*

Notes: 1. As stated on page 330, the solution should be cold and only *slightly* basic to litmus to prevent AsO_2^- and $HAsO_4^=$ from precipitating.

2. If a solution has been neutralized as previously directed, very little $CaCO_3$ should be precipitated. The original solid or solution should be used to test for $CO_3^=$.

Test for Group V. To the filtrate from Group IV that must be just basic to litmus add $2N$ $(AcO)_2Ba$ dropwise as long as precipitate forms. Centrifuge, then add 1 drop of $(AcO)_2Ba$ to test for complete precipitation. Reserve solution for Group VI. Wash precipitate thoroughly with water containing a drop of $(AcO)_2Ba$. Precipitate may be $BaSO_4$, $BaSO_3$, $BaCrO_4$, (BaS_2O_3, $BaHAsO_4$). Reserve a precipitate for later examination. *Record results on A.E.S.*

Test for Group VI. To the filtrate from Group V made just basic to litmus (see note 1) and heated nearly to boiling add $2N$ $(AcO)_2Cd$ dropwise as long as precipitate forms. Centrifuge and reserve solution for Group VII. Wash a precipitate thoroughly with water containing a drop of $(AcO)_2Cd$. Precipitate may be CdS (see note 2), $Cd_2[Fe(CN)_6]$, $Cd_3[Fe(CN)_6]_2$, $Cd(AsO_2)_2$, $CdHAsO_4$. No precipitate with Cd^{++} does not *prove* absence of AsO_2^- or $HAsO_4^=$, since these ions may have been precipitated by Ca^{++} or Ba^{++}. A more reliable test is given later. Reserve a precipitate for later examination. *Record results on A.E.S.*

Notes: 1. It is well to recheck at this point the reaction of the solution to litmus. Reactions may have caused considerable change of *p*H.

2. Only if the "prepared solution" contained a large $C_{S^=}$ (see p. 399).

Test for Group VII (only if Group III test was positive). To the filtrate from Group VI, made *just* basic to litmus, add $4N$ $Co(NO_3)_2$ solution dropwise as long as a precipitate forms, then 2 drops in excess. Centrifuge (see note 1) whether a precipitate is visible or not and reserve the solution for Group VIII. Wash a precipitate once with water containing 2 drops of $Co(NO_3)_2$. A precipitate must always be confirmed (see note 2).

Notes: 1. $Co(CN)_2$, yellowish-brown, strongly tends to be colloidal. It is less soluble and less dispersed in high $C_{Co^{++}}$. For these reasons a large

excess of precipitant must be used; the solution must be centrifuged even when no precipitate is visible, and a precipitate must be washed with water containing considerable Co^{++}.

2. Blue $CoOHNO_3$ sometimes precipitates.

Confirmation of CN^-. Transfer the precipitate to the Erlenmeyer flask, which has been fitted with a cork carrying the wedge-point pin. In the loop of the pin place a strip of filter paper spotted with 1 drop of $(AcO)_2Cu$ and 1 drop of benzidine acetate. To the precipitate add 6 drops of $3N$ H_2SO_4 and close the flask. Warm the solution gently. A blue color on the filter paper proves CN^-.

Test for Group VIII (only if the Group III test was positive). The filtrate from Group VII is made strongly acid to litmus with $3N$ HNO_3, and $AgNO_3$ is added until precipitation is complete. Heat to boiling. Centrifuge and discard liquid. Wash the precipitate with a few drops of water containing HNO_3. Precipitate may be *Ag_2S* (black) from $S_2O_3^-$, *AgNCS, AgI, AgBr, AgCl.* Note carefully color of precipitate. A black precipitate here is *proof* of $S_2O_3^-$.

TESTS FOR INDIVIDUAL ANIONS

These individual tests are to be made only if the A.E.S. shows that preceding tests have *not proved* the ion absent.

Tests in HCl Solution

Test for carbonate (HCl_I).

1. If the unknown is an aqueous solution, put 4 drops in a small centrifuge tube and add $3N$ HCl dropwise until the solution is decidedly acidic.

2. If an unknown solid is to be tested, place about 5 mg in a centrifuge tube, add dropwise about 4 drops $3N$ HCl, warm, and stir.

In either 1 or 2 observe carefully, holding the tube between the eye and a window, whether a fine stream of gas bubbles is formed (*a*) at contact of the HCl with the solution or (*b*) with the solid (see note 1). A colorless, *odorless* gas evolved in bubbles (see note 2) is practically always CO_2 from carbonate. This characteristic test for CO_3^- is given by amounts larger than a trace. If doubtful, confirm by more sensitive test (page 405). A permanent gelatinous precipitate from a water soluble unknown would suggest possible presence of $[Si(OH)_6]^-$, $[Sn(OH)_6]^-$, $[Sb(OH)_6]^-$. Formation of

colloidal sulfur would be a result of $S_2O_3^=$ or of the interaction of SO_2 with H_2S.

Notes: 1. Many alkali salts of weak acids such as $NaAsO_2$ and basic oxides such as MgO may have taken up CO_2 from the air and give a feeble test for $CO_3^=$. In such a case careful observation is required to see the exceedingly minute stream of bubbles. From a solid surface adsorbed air is likely to be released at irregular intervals in rather large bubbles. This bears little resemblance to the *regular* evolution of CO_2.

2. Of the volatile weak acids that can be formed here (H_2CO_3, H_2SO_3, HCN, HNO_2, H_2S) carbonic is by far most frequently met and is practically the only one to form bubbles, as the others are much more soluble in water. SO_2 and HCN have characteristic odors. HNO_2 decomposes, giving yellow-brown NO_2. In semimicro analysis lack of odor and color is not very reliable proof of absence, since quite small amounts may be present.

Sensitive test for $CO_3^=$.

1. *Unknown an aqueous solution.* Place 10 drops in Erlenmeyer flask equipped for gas tests (page 189). Add bromine water dropwise, with thorough shaking until the solution has a permanent yellow color. This is to oxidize any $SO_3^=$ which may be present to $SO_4^=$. (SO_2 would form $CaSO_3$.) In a depression of the spot plate mix 3 drops of $2N$ $(AcO)_2Ca$ and 3 drops of $6N$ NH_3. Dip the carefully cleaned loop of the wedge-point pin into the mixture so that a film is formed within the loop. To the solution in the flask add 5 drops of $3N$ H_2SO_4 and quickly stopper the flask with the cork carrying the test film. Set on the hot plate for two minutes. If the film becomes milky from the formation of $CaCO_3$, the presence of $CO_3^=$ is proved.

Notes: 1. If the pin is not freshly cleaned, the film may become blue because of formation of $Cu(NH_3)_4^{++}$. A clean pin will not give this color.

2. The CO_2 present in air will produce a turbidity in the test film but only after some time. In the test for very small amounts of carbonate a blank should always be run.

2. *Unknown a solid mixture.* Place about 5 mg in the Erlenmeyer flask and proceed as directed in 1 above.

Preparation of an HCl solution for tests $HCl_{II\,V}$. Place in a centrifuge tube 10 drops of either transposed solution or an original unknown solution, if a transposed solution was unnecessary (see page 397). Add $3N$ HCl dropwise until the solution is decidedly acidic. Notice carefully color and texture of any precipitate. Centrifuge and use the clear liquid for tests HCl_{II} to HCl_V.

Tests for borate (HCl_{II}). Place 1 drop of the HCl solution on turmeric paper, place the paper on a watch glass, and dry *thoroughly*

on the steam plate. Pinkish-red color turning green-black where touched with a 1% solution of NaOH (1 drop 6*N* NaOH + 19 drops H_2O) proves borate. Strong oxidants (see note) may interfere. Note whether these have been indicated and, if so, use the flame tests on page 371.

Note: Oxidants, ClO_3^-, CrO_4^-, $[Fe(CN)_6]^{-3}$, NO_2^- bleach turmeric. I^- also interferes.

Test for sulfate (HCl_{III}). To 1 drop of the HCl solution add 1 drop $BaCl_2$. A white precipitate, $BaSO_4$, insoluble in HCl, proves sulfate.

Tests for ferrocyanide, ferricyanide, and thiocyanate (HCl_{IV}). Place in each of two depressions of the spot plate 1 drop of the HCl solution. To one add 1 drop $FeCl_3$ solution. A blue solution or precipitate is Prussian blue and proves $[Fe(CN)_6]^{-4}$ present. A red solution (see note) would be $[Fe(NCS)_6]^{-3}$. To the other test drop add 1 drop of a freshly prepared solution of $FeSO_4 \cdot 7H_2O$. A blue solution or precipitate is Turnbull's blue and proves $[Fe(CN)_6]^{-3}$ present.

Note: A blue precipitate or suspension might obscure this color. Even if NCS^- is not detected here, it will be found in Group VIII.

Tests for arsenite and arsenate (HCl_V). Boil 5 drops of HCl solution to remove any SO_2 that may be present. Centrifuge to remove any turbidity. Saturate the clear cold solution with H_2S. If there is an immediate formation of a yellow precipitate (As_4S_6), the presence of AsO_2^- is shown. Centrifuge, again pass H_2S into the solution to make sure all AsO_2^- has been removed. To the clear solution add an equal volume of conc. HCl, heat to boiling, and pass in H_2S. Formation (which may be slow) of a yellow precipitate consisting of As_4S_6, and S indicates arsenate (see note).

Note: Study action of H_2S on arsenious and arsenic acid, page 224. In case of doubt as to presence or absence of As, try the Bettendorf test, page 293. Consider the different time required for $HAsO_2$ and for H_3AsO_4 to be reduced to As^0. Consider also indications given by Group III-A test.

Remaining Anions of Group IX

Test for nitrite (IX-A). In each of two depressions of a spot plate place 2 drops of 6*N* AcOH. To one (the blank) add 1 drop of water, to the other 1 drop of aqueous unknown or "prepared solution." Stir thoroughly. Add to each 1 drop of sulfanilic acid and

then 1 drop of α-naphthylamine solution. An immediate red color (see note) shows the presence of NO_2^-. This test is said to detect 0.00001 mg of HNO_2. Record on A.E.S. as IX-A.

Note: A *brown precipitate* would indicate a large amount of NO_2^-. In this case greatly dilute a drop of the test solution and repeat test on one drop of this very dilute solution.

Test for nitrate (IX-B). If the above test was *negative*, a test for NO_3^- can be made in the same solution by adding two or three fragments of Devarda's alloy. A red color slowly spreads out from the metal if NO_3^- is present. ClO_3^- does not interfere. This test is said to detect 0.00005 mg of HNO_3. $CrO_4^=$ forms a black precipitate with α-naphthylamine and obscures the test. Record on A.E.S. as IX-B.

$CrO_4^=$ if present could be reduced to Cr^{+3} by H_2S in HCl solution and S and H_2S removed before making the test.

Detection of nitrate in presence of nitrite. Proceed as directed in experiment 9, page 392.

Test for acetate (IX-C). 1. *Unknown a solution.* In a crucible place approximately 20 mg of solid $CaCO_3$. Add 1 ml of the solution to be tested. Evaporate carefully just to dryness. To the residue add 10 drops ethyl alcohol, mix thoroughly, and again evaporate to dryness. Proceed as directed in 2.

2. *Unknown a solid mixture.* Mix together intimately 20 mg of *dry* original solid unknown (see note 1) and 20 mg of calcium carbonate. Transfer the mixture to a 15 ml pyrex centrifuge tube. Tap the tube to pack the powder at the bottom. Then cover with a layer of $CaCO_3$ about 3 mm thick. Fold a piece of filter paper one inch square to form a cone. This is done by taking a corner of the square and folding it across the paper so that a triangle is formed. Again fold the paper so that the 2 points of the triangle are together. Open the cone and place in it 2 drops of a freshly prepared saturated solution of sodium nitroprusside.

Insert the pointed end into the centrifuge tube and press the cone down into the tube so that it forms a fairly close-fitting plug. Holding the tube in a *horizontal* position with a test tube holder, heat the powder until drops of water are visible on the inner walls of the tube. Continue heating the powder until it darkens. Now *carefully* warm the walls of the tube so that the collected moisture is driven up toward the plug. *Do not* heat the tube within one-half inch of the plug. Remove the plug, open it, and moisten the paper with

capillary drops of 1 *N* NaOH. A brownish-red color proves acetate (see note 2). Always compare the test paper with another spotted with 1 capillary drop of sodium nitroprusside and 1 capillary drop of 1 *N* NaOH. If the first test is negative, repeat the test using a larger sample.

Notes: 1. If the solid appears moist, indicating highly hydrated salts, the test portion should be treated with 1 ml of ethyl alcohol and the latter removed by evaporation to dryness.

2. This test, which cannot be trusted to detect much less than 1 mg of AcO^-, depends on formation of acetone, $H_3C—CO—CH_3$, when metal acetates are heated. For example,

$$Ca(C_2H_3O_2)_2 = CaCO_3 + C_3H_6O.$$

Presence of moisture in the reaction mixture, for example hydrated salts, seems to interfere with the reaction. Alcohol is used for its dehydrating effect.

The nature of the reaction of acetone on $Na_2[Fe(CN)_5NO]$ and NaOH is not known.

SUMMARIZING RESULTS

The information gathered from all the preceding tests should now be summarized on the A.E.S. Every anion included in the course must be checked at least once on this sheet. When this has been done, a thoughtful study should show that *in no case* will more than the following tests now have to be made.

1. Test of Ca precipitate for F^-, $C_2O_4^=$, $HPO_4^=$, $SO_3^=$. (A given precipitate may contain *none* of these ions since Ca^{++} might precipitate some other ions if they were present in large amounts.)

2. Test of Ba precipitate for $SO_3^=$. If in doubt about $CrO_4^=$, confirm it by formation of blue $CrO(O_2)_2$.

3. Test of Ag precipitate (Group VIII) for I^-, NCS^-, Br^-, Cl^-.

4. Confirmation of doubtful HCl_I test for $CO_3^=$ by the more sensitive test (page 405).

TESTS SHOWN NECESSARY BY THE A.E.S. SUMMARY

Group IV Precipitate

Tests for fluoride. (*a*) In each of two depressions of the spot plate place 1 drop of 3 *N* HCl, 1 drop of zirconyl nitrate solution, and 1 drop of "alizarin red S" solution. Allow to stand 2 minutes.

Note the color of the mixture. To one (the blank) add a drop of water. To the other add a small portion of the calcium group precipitate. Stir thoroughly. Color changing from pinkish-red to greenish-yellow proves fluoride.

(*b*) Place a portion of the calcium group precipitate in a micro crucible and ignite strongly to entirely remove water, which interferes with the following test.

Clean two micro slides with alcohol to remove grease. Make a circle with the finger (see note) around an area 1 to 2 mm^2. On this clean area place a *small* amount of the powdered strongly ignited precipitate. On the clean face of the other slide place a capillary drop of conc. H_2SO_4. Remove most of it with the pipet. Bring the two slides together with the acid spot over the precipitate. Keeping the slides pressed together, hold them 6 to 8 inches above a flame for three minutes. Wash thoroughly and examine for etching. If both slides are etched so as to form similar patterns, F^- is *proved*. Put a drop of HCl on the etched spots and wash thoroughly to ensure that a solid residue is not mistaken for etching. Try a second time if the first test is negative.

Note: The purpose of the circle is to have the CaF_2 and H_2SO_4 confined within a small area. The thin film of oil deposited by the finger presumably prevents the CaF_2 from spreading out when moistened by the acid. It also serves to form a seal between the plates and thus confines the liberated HF to a small area.

Experience has shown that the etching test is actually considerably more sensitive when conducted as prescribed above than it is when the film of oil is omitted.

Test for sulfite (*to be made only if the A.E.S. indicates its possible presence*). In a depression of a spot plate place 2 drops of saturated zinc sulfate solution, one drop of $6N$ NH_3, and one drop of saturated nitroprusside solution. Mix thoroughly. Suspend a strip of filter paper from the loop of the wedge-point pin. Dip the filter paper into the zinc nitroprusside paste.

Place in the Erlenmeyer flask a portion of the Ca precipitate. Add three drops of $3N$ H_2SO_4 and insert the cork carrying the test paper. Warm gently (solution must not boil). Test paper turning pink to red according to the amount of SO_2 proves $SO_3^=$.

This test can be made directly on any unknown solution or finely powdered solid mixture if $S^=$ and/or $S_2O_3^=$, when present, are previously precipitated by $HgCl_2$. If either or both these ions are present, place in the Erlenmeyer flask 5 drops of unknown solution

or 5 to 10 mg of finely powdered solid mixture. Add 2 or 3 drops of $HgCl_2$ test solution, stir thoroughly, and let stand a few minutes. Then add H_2SO_4 and proceed as above. The HgS need not be removed.

Separation of phosphate and sulfite from oxalate and fluoride. To the rest of the calcium precipitate add 1 drop of $6N$ AcOH and note carefully whether tiny bubbles of carbon dioxide escape (indication of carbonate, not however in the unknown in case a transposed solution was used). Continue dropwise addition of AcOH until 5 drops have been added and warm gently for a few minutes. Centrifuge. Residue may be CaF_2, CaC_2O_4, or $CaSO_3$. Solution may contain $H_2PO_4^-$, HSO_3^-.

Test for phosphate. *Warning: Do not touch test paper with fingers!* On a piece of *silica-free* ("HF-washed") filter paper place, in the following order, a drop of the AcOH solution of the calcium precipitate, a drop of $(NH_4)_2MoO_4$, and a drop of benzidine acetate. Using forceps, hold paper for three minutes over a test tube containing $15N$ NH_3. (Caution—Do not let the paper touch the tube.) A blue color indicates phosphate. Large amounts of arsenate and silicate may give the color, but they are unlikely to be in the calcium precipitate. Both react in the cold much more slowly than H_3PO_4 to form complex ions with $HMoO_4^-$.

Test for oxalate (*to be made only if the A.E.S. indicates its possible presence*). Wash the residue insoluble in acetic acid with $3N$ acetic acid, warming and stirring. Remove wash liquid and test it for reductant anions with $0.01N$ $KMnO_4$, comparing it with 6 drops of $3N$ acetic acid as a blank. Continue washing with fresh portions of $3N$ AcOH until the wash liquid uses no more $0.01N$ $KMnO_4$ than was required for the blank.

Dissolve washed residue in *hot* $3N$ H_2SO_4. Add one drop $0.01N$ MnO_4^-. If the drop is bleached, continue dropwise addition with constant stirring until 2 more drops have been added than are used in a blank (page 400). If the solution is still colorless, add $0.1N$ MnO_4^- dropwise until a faint pink color persists.

Five drops of $0.1N$ MnO_4^- is equivalent to 1.1 mg of $C_2O_4^-$, from which relation the weight of $C_2O_4^-$ in 1 ml of unknown solution can be calculated.

Group V Precipitate

Test for sulfite (*to be made only if the A.E.S. indicates its possible presence*). Whether or not SO_3^- was found in the Ca precipitate,

test a small portion of the Ba precipitate exactly as directed above for the calcium precipitate.

Test for chromate (*to be made only if the A.E.S. indicates its possible presence*). To a small part of the barium group precipitate add 2 drops of dilute nitric acid and 2 drops of ether. Shake, cool under the tap, then add 2 drops of H_2O_2 solution and quickly shake. A blue color in the ether layer is due to $CrO(O_2)_2$ and proves $CrO_4^=$.

Group VI Precipitate

This precipitate will have to be tested only for $S^=$, since the other anions of the group will have been detected by previous tests.

Test for sulfide (*to be made only if the A.E.S. indicates its possible presence and if the Cd group precipitate is at all yellow*). Place in the Erlenmeyer flask, equipped as usual for gas tests, a portion of the cadmium precipitate. Suspend in the loop of the pin a strip of filter paper. Spot the paper with a drop of $(AcO)_2Pb$ reagent. Add to the precipitate 3 drops of $3N$ H_2SO_4 and close flask. Warm on a steam plate. Brown or black spot on the test paper *proves* $S^=$.

Group VIII Precipitate

[Ag_2S (from $S_2O_3^=$), $AgNCS$, AgI, $AgBr$, $AgCl$]

Note from the A.E.S. which of this group of anions have already been detected (see note 1).

Dissolution of the silver salts and removal of silver. The well-washed Group VIII precipitate is slimed very thoroughly with 2 to 5 drops $15N$ NH_3 solution, then 5 drops of colorless NH_4HS is added and it is thoroughly slimed again (see note 2). Centrifuge. The solution may then contain I^-, Br^-, Cl^-, or NCS^-.

Boil in a crucible until NH_3 is removed. Centrifuge out any precipitate. Transfer the solution to a 2 ml test tube and add 3 drops $3N$ HNO_3, 1 drop of $Fe(NO_3)_3$ solution, and 3 drops of CCl_4. Shake vigorously for 1 minute. Proceed as directed in Table 22.

Notes: 1. The use of CCl_4 in Group II test should have detected Br^-. If present, NCS^- should have been detected in test HCl_{IV} unless the red color was hidden by an iron-blue. From these tests and from the tint of the Group VIII precipitate it may be possible to omit more or less of the procedure outlined in Table 22. For example, if in Group II CCl_4 was not at all colored and if in HCl_{IV} no NCS^- was indicated, a white Group VIII precipitate which dissolves readily in NH_3 is almost certainly only AgCl.

TABLE 22
SEPARATION OF HALIDES

<table>
<tr><td rowspan="3">Purple CCl_4 layer proves *iodide*

Red water layer proves NCS^-</td><td colspan="2">*Water layer*, I_2, $[Fe(NCS)_6]^{-3}$, Br^-, Cl^-. Remove to a crucible[a] and boil gently until I_2 is all volatilized. Add more $Fe(NO_3)_3$ if necessary. Solution should be yellow, showing excess of ferric ion. Return to test tube and shake again with 1 drop of CCl_4 to make certain that all I_2 has been removed. Add 4 drops of 3 N HNO_3 and 3 drops of CCl_4, then 0.1 N $KMnO_4$ dropwise until a permanent pink color remains.[b] Shake vigorously.</td></tr>
<tr><td rowspan="2">*CCl_4 layer* (brown-orange) proves *bromide.* Confirm a doubtful color with fluorescein.</td><td>*Water layer*, Br_2, SO_4^-, NCO^-, Cl^-. If Br_2 is present, remove to a crucible[a] and boil until all Br_2 is removed. The color of the soln. must still be pink. Test again for Br_2 with CCl_4.</td></tr>
<tr><td>When Br_2 is all removed, reduce excess $KMnO_4$ and any MnO_2 by adding a drop or two of H_2O_2. Add $AgNO_3$ dropwise until precipitation is complete. White AgCl proves *chloride.*[c] Some H_2O_2 contains Cl^-. Test the laboratory solution before using here.</td></tr>
</table>

[a] I_2 is 85 times and Br_2 is 26 times as soluble in CCl_4 as in water. It is not desirable to remove these halogens completely by shaking the aqueous solution with CCl_4. After presence of the halogen has been detected by the use of CCl_4, the rest of it is more quickly and easily removed by boiling the solution as directed. Fe^{+3} oxidizes I^- to I_2 but does not affect Br^- and Cl^-.

[b] In acid solution $KMnO_4$ oxidizes NCS^- to SO_4^- and NCO^- more readily than it oxidizes Br^- to Br_2. If C_{H^+} is too small, MnO_4^- is reduced to MnO_2 instead of to Mn^{++}. If CCl_4 is shaken with the water layer, it is likely to form globules which are prevented from coalescing by a skin of MnO_2. A mass of globular CCl_4 may assume a brown color somewhat like that due to Br_2. In case of doubt the fluorescein test can always be applied. The formation of MnO_2 indicates that more HNO_3 should be added. Cl^- is oxidized by MnO_4^- to Cl_2 only in very high C_{H^+}.

[c] In the analysis of solid mixtures a small amount of Cl^- is nearly always found. This may be due to traces of Cl^- present (1) in the reagents used and (2) in the original solid mixture. When the amount of Cl^- found in Group VIII is so small as to suggest either of these origins, it is well, provided that $[Fe(CN)_6]^{-4}$, $[Fe(CN)_6]^{-3}$, and CN^- are absent, to extract a few mg of the original solid unknown with 3 N nitric acid and to the clear solution add 0.1N $KMnO_4$ until a permanent pink color remains. Reduce excess MnO_4^-, and any MnO_2 formed, with H_2O_2. Then add 1 drop of $AgNO_3$. Frequently no AgCl will be obtained, showing that Cl^- in Group VIII came from reagents and not from the material analyzed.

2. AgI is nearly insoluble in $15N$ NH_3, but it turns white in the NH_3 because of the formation of $AgNH_3I$. AgBr and AgNCS are sparingly soluble in $15N$ NH_3, while AgCl dissolves readily and largely. If the Group VIII precipitate dissolves readily and completely in the NH_3, it is probably only AgCl, although it might contain a trace of Br^-. This should have been detected in Group II.

Silver halides, when shaken and centrifuged, tend to form curds. By "sliming" is meant disintegrating these curds into very fine portions so that the reagents may come in contact with all the precipitate. Unless this is done, NH_4HS will form Ag_2S on the outside of the curds and the halide will not be dissolved or decomposed. This is particularly likely to happen in the case of AgI. The larger the Group VIII precipitate the greater is the necessity for thorough sliming.

Analysis of the Residue from the Prepared Solution

As stated on page 398, most *sulfides* (except those of As, Sb, and Sn^{+4}) and most phosphates (except those of K^+, Na^+, and NH_4^+) are little transposed by boiling with $3N$ Na_2CO_3. *Silver halides* are not detectably affected. Mineral CaF_2, fluorspar, is little transposed, the precipitated salt somewhat more.

It follows then that the residue from the "prepared solution" must be reserved and frequently examined for such of the above four ions as have not been found.

Test for phosphate. Treat a few mg of the Na_2CO_3 residue with hot $3N$ HNO_3. (If it dissolves completely, no silver or mercurous halides are present.) Add 2 to 3 drops of the *clear* solution to 1 ml of $(NH_4)_2MoO_4$ solution and heat to 60°. Yellow $(NH_4)_3[P(Mo_3O_{10})_4]\cdot H_2O$ proves $HPO_4^=$. Since all phosphates are more or less soluble in hot $3N$ HNO_3, all water-insoluble salt mixtures can be tested directly for $HPO_4^=$ by extracting with HNO_3 and testing as above. $(NH_4)_3[As(Mo_3O_{10})_4]\cdot H_2O$, also yellow, precipitates only at 100° if $HPO_4^=$ is not present, but it frequently coprecipitates with $HPO_4^=$ at 60°. However, the larger part of any arsenate will have been transposed by Na_2CO_3.

Test for sulfide. All sulfides give off H_2S when treated with Zn and $3N$ HCl. The H_2S is detected by paper spotted with $(AcO)_2Pb$. This test can be made on an original solid as well as on the Na_2CO_3 residue. The interference of NCS^-, $S_2O_3^=$, and $SO_3^=$, all of which are reduced to H_2S by Zn and H^+, must be considered.

Test for fluoride. Perform the tests for fluoride (page 408) on the original solid or on the Na_2CO_3 residue.

Test for silver halides. The residue from the "prepared solution" should never be examined for these compounds until

Ag^+ or Hg_2^{++} has been found in the cation analysis. Silver halides are not frequently met in analysis.

If the halides are treated with Zn and hot $3N$ H_2SO_4, such reactions as the following occur *slowly:*

$$2\underline{AgI} + 2\underline{Zn} + 2H^+ = 2Zn^{++} + 2\underline{Ag} + \overline{H_2} + 2I^-$$

$$\underline{Ag_2S} + \underline{Zn} + 2H^+ = 2\underline{Ag} + \overline{H_2S} + Zn^{++}$$

When the reactions are complete, a black residue is to be removed.

In the solution I^-, Br^-, and Cl^- may be treated as directed for separation and detection of these ions (Table 22, page 412).

CHAPTER 21

SYSTEMATIC QUALITATIVE ANALYSIS

A systematic qualitative analysis consists of a series of procedures which may be classified under five main divisions:

I. Preliminary Examination of the Material.
II. Preparation of Material for Analysis.
III. Systematic Analysis for Anions.
IV. Systematic Analysis for Cations.
V. Critical Examination of the Results of I, II, III, and IV for Obvious Inconsistencies.

I. PRELIMINARY EXAMINATION

The unknown material may be (1) a solution; (2) a nonmetallic, salt-like material; (3) a metal or alloy.

1. Unknown material a solution.

(*a*) Test it with litmus paper. Record whether solution is acid, basic, or neutral.

(*b*) Observe and record color.

(*c*) Notice whether solution is clear. If precipitate is present, centrifuge and analyze solid and solution separately.

2. Unknown material a solid and salt-like.

(*a*) Spread out the material in a thin layer and with a lens, if one is available, observe and record whether sample appears homogeneous or is obviously a mixture.

(*b*) Record form (crystalline or amorphous) and color of each distinguishable ingredient. These observations will be of great importance in division V.

Two instances will emphasize this point. (1) An unknown solid consists of blue crystal fragments and a white amorphous powder. On analysis only SO_4^{--} and Cu^{++} are found. These results of Divisions III and IV seem to be incompatible with the observations made in Division I until it is considered that $CuSO_4 \cdot 5H_2O$ is blue while anhydrous $CuSO_4$ is white.

(2) An unknown solid clearly consists of three distinct amorphous powders; one yellow, another bright red, a third purplish brown. On analysis no anions are found and only one cation, Pb^{++}. The observations

of Division I are not incompatible with those of III and IV, for three different oxides of lead have the colors observed in the mixture.

3. Unknown material a metal or an alloy. Note and record color, density, hardness, and brittleness.

II. PREPARATION OF MATERIAL FOR ANALYSIS

Mechanical reduction of particle size. Solid material should always be ground to the finest possible powder before determining the action of solvents. There are two good reasons for this precaution: (1) the material may not be homogeneous and, unless it is thoroughly mixed by grinding, a portion taken for analysis may not include all the ingredients; (2) the rate of action of a solvent on solid material is largely dependent upon the size of the particles. Beginners frequently err in assuming that slowly dissolving large particles are insoluble and needlessly proceed to try another solvent.

III. SYSTEMATIC ANALYSIS FOR ANIONS

Proceed as directed on pages 397–414, *et seq.* Reserve the residue from the transposed solution until after the analysis for cations has been completed.

IV. SYSTEMATIC ANALYSIS FOR CATIONS

A solution for anion analysis is invariably a Na_2CO_3 solution. For the bringing of cations into aqueous solution suitable for analysis, reagents must be used to convert water-insoluble substances into others which are water-soluble. Experience has shown that for the majority of substances acids are preferable to bases for this purpose.

HCl is always preferred to HNO_3 as a solvent because the latter, when hot and concentrated, is a strong oxidant and may oxidize the unknown so that the resulting solution may contain entirely different ions from the original solid. Possible reactions with hot conc. HNO_3: (1) formation of SnO_2, Sb_2O_{4-5}; (2) oxidation of $S^{=}$ or S to $SO_3^{=}$ or $SO_4^{=}$ (see note), arsenites to arsenates, I^- and Br^- to I_2 and Br_2.

Note: Roasting sulfides with constant stirring before cation analysis is often useful. Elemental and sulfide sulfur is burned off as SO_2, leaving oxides which are soluble in acid if the roasting temperature is not too high.

Relative merits of HCl and HNO_3 as solvent. Hot concentrated HCl dissolves dioxides such as MnO_2, PbO_2, CoO_2, NiO_2, which are

insoluble in HNO_3. It does not dissolve the most insoluble sulfides. It forms acid-insoluble compounds with Ag^+ and Hg_2^{++}. When an HCl solution is evaporated to dryness to remove excess of acid, nearly all $HAsO_2$ present is volatilized as $AsCl_3$ and a little $HgCl_2$ may be lost.

Concentrated HNO_3 is a powerful oxidant and dissolves many sulfides that are insoluble in HCl. In this process, however, some $SO_4^=$ is always formed which will precipitate Ba^{++}, Sr^{++}, and Pb^{++}, and may partially precipitate Ca^{++}, if any of these ions are present. It also oxidizes Hg_2^{++} to Hg^{++}, $HAsO_2$ to H_3AsO_4, Fe^{++} to Fe^{+3}, and Sn^{++} and Sb^{+3} to the acid-insoluble oxides SnO_2 and Sb_2O_{4-5}.

On account of the possible presence in alloys of certain "metalloids," C, Si, P, As, and S which with HCl would form volatile CH_4, SiH_4, PH_3, AsH_3, H_2S, an oxidizing solvent such as HNO_3 or Br_2 must be employed. See following chapter.

Aqua regia as solvent. This solvent has the disadvantage of forming AgCl and $PbCl_2$. It may also form $BaSO_4$, $SrSO_4$, and $CaSO_4$ if sulfides are present. When aqua regia is required, the solid should be heated with $12\,N$ HCl, and $16\,N$ HNO_3 should be added a few drops at a time. No more of this acid should be used than is required to complete the dissolution of the material.

Dissolution of Solids

Preliminary tests for solubility in various solvents. These tests are made by placing about 1 mg of unknown in a small test tube with 5 drops of water. Stir thoroughly, then, if undissolved material remains, heat the mixture to boiling, with constant stirring. Observe and record whether the unknown dissolves completely, partly, or apparently not at all. If the material is partly or wholly insoluble in water, repeat the experiment, using fresh material and the next solvent in the following order: (1) dilute HCl, (2) conc. HCl, (3) dilute HNO_3, (4) conc. HNO_3, (5) aqua regia, until complete dissolution is attained.

Some substances dissolve very slowly. As long as a substance seems to be dissolving, the presumption is that it will all dissolve in time if sufficient solvent is used. Many water-soluble salts are insoluble in concentrated acids, for example, NaCl in concentrated HCl; $Ba(NO_3)_2$ in concentrated HNO_3. Whenever a *crystalline* solid is seen to form during attempts to dissolve a solid in acid, it

is very likely to be a water-soluble salt. Addition of a little water will frequently cause it to dissolve.

The analyst frequently secures valuable information by careful observation of the action of the various solvents. For example: If an unknown is soluble in water, all salts insoluble in water can be eliminated at once.

New water-insoluble substances may be seen to form during the treatment with water, for example,

$$Sr(NO_3)_2 + Na_2CO_3 \rightarrow \underline{SrCO_3}$$
$$Bi(NO_3)_3 + 2H_2O \rightarrow \underline{Bi(OH)_2NO_3} + 2H^+$$

If an unknown is partially soluble in water, it is frequently time saving to completely extract the water-soluble part and analyze it separately from the insoluble portion. This frequently obviates unpleasant difficulties. Consider:

$$\underline{Ag_2CO_3} + KI \rightarrow \underline{AgI}.$$

An acid-insoluble compound results that would have been easily avoided had the water-soluble KI been completely extracted before treating with acid.

When testing the solubility of a solid unknown in acids the analyst should observe whether volatile compounds are formed. In such a case *very cautiously* note the odor, color, and so on. The following compounds give rise to characteristic odors, colors, or reactions with acid.

1. Nitrites—brown choking fumes of NO_2.
2. Sulfides—odor of H_2S, formation of sulfur.
3. Sulfites—odor of burning sulfur (SO_2).
4. Thiosulfates—SO_2 + free sulfur.
5. Carbonates—effervescent evolution of a colorless, odorless gas.

Preparation of a solution for cation analysis. From the information obtained in the analysis for anions and that obtained from the preliminary tests of solubility, decide which solvent is to be used. Dissolve 20 mg of the homogeneous sample in 1 ml of this solvent and proceed as directed on page 307, *et seq.*

Acid-insoluble substances. Occasionally material contains substances that are not decomposed by any of the acid solvents. Of such substances those most likely to be encountered are the following:

1. Silicates and silica, SiO_2 (absence assumed in this course).
2. Sulfates of Pb^{++}, Ba^{++}, Sr^{++}, Ca^{++}.
3. Halides of silver.
4. Ignited sulfates: $Cr_2(SO_4)_3$, $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$.
5. Native or ignited oxides: iron ores (Fe_2O_3 and Fe_3O_4), Cr_2O_3, SnO_2, and Sb_2O_4.

6. CaF_2.

7. The iron blues, carbon, and sulfur.

Treatment of acid-insoluble material. An acid-insoluble residue is best submitted to individual tests of small portions after one has considered the anions found present. For example:

$PbSO_4$ can be extracted with hot $3N$ $AcONH_4$ and the solution tested for Pb^{++}.

$PbSO_4$, $SrSO_4$, and $CaSO_4$ are readily transposed by boiling with $3N$ $NaCO_3$ solution. About 75% of $BaSO_4$ is similarly transposed. Ignited anhydrous sulfates become acid-soluble after boiling with Na_2CO_3. Hence it is frequently advantageous to extract repeatedly part of the residue from the transposed solution for anions with hot $3N$ HCl. If the HCl extract is cooled under the tap, $PbCl_2$ may crystallize out. The residual liquid may be tested for Pb^{++}, Al^{+3}, Fe^{+3}, Cr^{+3}, Ba^{++}, Sr^{++}, and Ca^{++}.

Of the insoluble silver salts only ferrocyanide and ferricyanide are transposed by boiling with Na_2CO_3. AgCl, AgBr, and AgI are best decomposed by Zn and dilute H_2SO_4. See page 414.

V. CRITICAL EXAMINATION OF THE RESULTS OF I, II, III, AND IV

After finding what anions and what cations are in the material, the analyst should review the observations recorded under I and II and be certain that the physical properties and the observed solubilities can be accounted for. In this connection should be remembered:

1. Reaction (metathesis) may occur between the ions of water-soluble salts when a solid is put into water, and a water-insoluble compound may form.

$$ZnSO_4 + Na_2CO_3 \rightarrow \underline{ZnCO_3}$$
$$Sr(NO_3)_2 + K_2SO_4 \rightarrow \underline{SrSO_4}$$
$$Ca(NO_3)_2 + H_2C_2O_4 \cdot 2H_2O \rightarrow \underline{CaC_2O_4}$$

2. From (1) it follows that a water-soluble salt mixture containing, for example, Hg^{++} cannot contain *any* anion that forms a water-insoluble compound with Hg^{++}. A water-soluble unknown which contains secondary phosphate ion can contain no cations except Na^+, K^+, or NH_4^+.

3. An unknown aqueous solution which is distinctly basic contains either a free base such as $Ba(OH)_2$ or the alkali salt of a weak acid, for example, $KHCO_3$.

4. An unknown aqueous solution which is *strongly* acid may contain free mineral acid added to prevent formation of insoluble basic salts. One that is *slightly* acid may contain hydrolyzed salts, such as $Al_2(SO_4)_3$, or anions which are weak acids, such as $H_2PO_4^-$, HSO_4^-, $HC_2O_4^-$.

5. Attention should be paid to the visible colors of a solid unknown but with consideration of the effect of color mixing, for example, yellow + blue = green; red + yellow = orange; red + blue = purple; white + black = gray.

CHAPTER 22

ANALYSIS OF NONFERROUS ALLOYS

INTRODUCTION

For purposes of rapid analysis it is useful to be able to recognize at sight the base-metal (principal constituent) of the various classes of alloys. The base-metals of some common alloys are:

1. Copper—brasses (Cu-Zn), bronzes (Cu-Sn).
2. Al-Mg—duralumin, magnalium, dowmetal.
3. Bismuth—fusible alloys.
4. Lead—type metal.
5. Tin—solders, bearing metals.
6. Zinc—bearing metal, white metal, zinc babbitt.
7. Nickel—nichromes, chromels.
8. Antimony—cheap cast ornamental objects.
9. Silver—coins, table ware, dental alloys.
10. Brittle alloys—phosphor-copper, and others (see note).

Note: Elements like Si and P can be added to alloys only in the form of metal silicides and phosphides. Since these elements are used in small and carefully controlled amounts, the compounds employed need to be reducible to powder form for exact weighing. For example, in making phosphor-bronze, copper phosphide would be used; in tin-base alloys, tin phosphide would be used. These metal phosphides are likely to be encountered.

The physical properties of the base metal are greatly modified by small additions of other elements and by variations in the amounts of the added elements. Note the stated composition of:

1. Four zeppelin alloys:

	Al	Zn	Cu	Fe	Si	Mn	Sn
Angles	90%	7.8%	0.7%	0.5%	0.4%	0.3%	0.1%
Braces	99	0.1	0.06	0.4	0.4	...	...
Channels	89	9.0	0.7	0.4	0.5	0.5	0.2
Rod	95	...	4.2	0.4	0.5	0.6	...

2. Two dowmetals:

	Mg	Cu	Cd	Mn	Al	Zn
D	88%	2.0%	1.0%	0.2%	8.3%	0.5%
T	92	3.8	2.0	0.2	...	...

3. Illium, a special alloy synthesized for Parr calorimeter bombs:

Ni	Cr	Cu	Mo	W	Fe	Mn	Al
63%	21%	6.5%	5%	2%	1%	1%	1%

Since physical and mechanical properties depend on the metals added to the base, very wide variations are to be expected. Navy brass contains 1% tin, which greatly increases its resistance to corrosion by sea water. Both brasses and bronzes frequently contain lead. So wide is the variation of amounts that it is sometimes difficult to classify an alloy as a brass or a bronze.

In alloy analysis the presence of minute amounts of some elements has to be kept in mind. Pure metals are not always used. Antimony and bismuth—copper also if it is not the electrolytic metal—may bring in a little arsenic. Zinc may carry lead, and lead may carry zinc. Iron is always possible either from contamination or as a constituent. Dental alloys or old fillings may contain mercury. Barium and calcium are being used in a few new special alloys but are rarely encountered. Outside of the light alloys, Mg or Al in small amounts may be encountered, since either is often used as a combined deoxidant and denitridant. Since these are likely to be adsorbed on precipitates, especially Group III, great care in this group must be observed.

DISSOLUTION OF ALLOYS

An oxidizing solvent must invariably be used. Since the metalloids are present as anions (arsenides, phosphides, silicides), a reducing solvent would cause their loss as volatile hydrides (AsH_3, PH_3, SiH_4). HNO_3 1:1 (equal volumes of 16N HNO_3 and water) is the usual solvent. It forms with the metalloids H_3AsO_4, H_3PO_4, H_2SiO_3. It also oxidizes tin and antimony to SnO_2 and Sb_2O_{4-5}, insoluble in 2N HNO_3 after having been evaporated to dryness. High Sn-Sb alloys have to be frequently stirred during dissolution in HNO_3 to remove the oxides adhering to particles of alloy and protecting them from the acid attack.

Aluminum-base alloys are scarcely attacked by HNO_3. Chromium-base or high Cr alloys are not attacked, or, if disintegrated, they may leave the Cr unaffected. For these, *bromine* (*not* its aqueous solution), together with 12N HCl, is used.

General procedures for dissolution of alloys. Try the action of 1:1 HNO_3 on a small fragment in order to decide whether the alloy should be treated by procedure A or procedure B.

Weigh out as accurately as possible 20 mg of sample and transfer it to a large crucible.

A. Al-base or Mg-base alloys (readily recognized by their lightness) and also high Cr alloys. Add to the alloy in a large crucible 2 drops of bromine (not bromine water!) then 1 ml of $12N$ HCl. Warm on a water bath, stirring with 1 mm glass rod (*not* a Pt wire!) until dissolution is complete. Notice carefully whether small black scales (graphite?) float to the *surface* of the liquid. If these remain unaffected by the solvents and are found to burn readily, report *carbon.* A *heavy* black residue may be a metal which has become passive (see note 1).

When dissolution is complete, evaporate to dryness over the water bath, add 5 drops of $16N$ HNO_3 and again evaporate on water bath to dryness (see note 2). Add 1 ml of $2N$ HNO_3, warm, and stir thoroughly. If a white insoluble residue remains, proceed according to Case 1. If a clear solution is obtained, go to Case 2.

Notes: 1. In some Cr alloys the Cr becomes passive. After centrifuging and washing, it can be brought into solution by heating in a crucible with $HClO_4$ until the acid fumes strongly. The metal dissolves to form $Cr_2O_7^=$ or CrO_3 (red) very slowly and only when the $HClO_4$ is fuming strongly.

2. This is done to precipitate and dehydrate SnO_2 and Sb_2O_{4-5}.

B. Other alloys. To 20 mg add 1 ml of 1:1 HNO_3 in a large crucible and warm on water bath. If a white precipitate forms, stir constantly with a glass rod to uncover particles of alloy. When metallic particles are no longer visible, evaporate *just* to dryness, add 4 drops conc. HNO_3, and evaporate again to dryness. Add 1 ml of $2N$ HNO_3, warm, and stir thoroughly. If a white insoluble residue remains, proceed according to Case 1. If a clear solution is obtained, follow Case 2.

ANALYSIS OF ALLOYS

Case 1. The Alloy Contains Tin and/or Antimony

If a white precipitate [SnO_2, Sb_2O_{4-5}, $Sn(H_2PO_4)_4$] has formed during dissolution of the alloy, transfer precipitate and solution to a small centrifuge tube.

Wash out the crucible with 1 ml of warm $2N$ HNO_3 a few drops at a time, transferring each washing to the centrifuge tube. Stir up the precipitate and liquid thoroughly, centrifuge, and return the liquid (solution 1) to the crucible. Wash the residue several times

with 4 drops of hot water containing NH_4NO_3, adding the first washing to the HNO_3 solution. Treat the washed residue (residue 1) as outlined in Table 23, and as directed in the procedures following it.

TABLE 23
DISSOLUTION AND ANALYSIS OF RESIDUE INSOLUBLE IN HNO_3

Residue 1. SnO_2, $Sn(H_2PO_4)_4$, Sb_2O_{4-5}, $SiO_2 \cdot xH_2O$. Extract repeatedly with warm NaOH and NaHS.		
Residue 2. Sulfides and hydroxides of Cation Groups II and III and Mg. Wash, dissolve in hot 2 *N* HNO_3. Centrifuge out *S*, etc., add *clear* soln. to soln. 1.	*Soln. 2.* SnS_3^-, SbS_3^{-3}, HPO_4^-. Acidify with 3 *N* HNO_3.	
	Ppt. 3. SnS_2, Sb_2S_3. Wash, extract water with alcohol. Add 5 drops 12 *N* HCl. Proceed as in Cation Group II-B, page 316.	*Soln 3.* H_3PO_4. Remove H_2S, test for H_3PO_4 with $(NH_4)_2MoO_4$.

Procedures. To the residue (residue 1) which may contain Sn, Sb, and the like, add 2 drops of 6 *N* NaOH and 6 drops of NaHS. Stir thoroughly, heat in a water bath, and stir frequently for several minutes. Centrifuge, remove the liquid (solution 2) to a small centrifuge tube, and at once acidify slightly with HNO_3. If any colored sulfide (precipitate 3) is formed, repeat the extraction of the residue with 1 drop of NaOH and 3 drops of NaHS at a time until the acidified extract no longer shows Sn or Sb.

Wash the residue (residue 2) until the washings are only slightly basic and dissolve it in a few drops of hot 2 *N* HNO_3. Centrifuge out any S and add the solution to solution 1.

SnO_2, and the like, will have adsorbed to a greater or less extent the ions of Groups II-A and III. Treatment with NaOH and NaHS changes these ions to hydroxides and sulfides. An insoluble, dark-colored residue will nearly always remain at this point.

Solution 2. Combine the acidified extracts containing Sb_2S_3, SnS_2, and also possibly $H_2PO_4^-$. Centrifuge out the sulfides (precipitate 3) and test the centrifugate (solution 3) for H_3PO_4.

Since $Sn(H_2PO_4)_4$ is insoluble in HNO_3, all the P in an alloy or only a part of it may precipitate here, according to the relative number of equivalents of Sn^{+4} and H_3PO_4 present. H_3PO_4 therefore must be tested for in

the insoluble residue and also in the HNO_3 solution of an alloy. The solution is acidified with HNO_3 instead of the HCl ordinarily used because the latter would interfere with the test for H_3PO_4 with $(NH_4)_2MoO_4$.

Solution 3. Evaporate the solution to a few drops, centrifuge out any sulfur, pour the clear solution into 2 ml of $(NH_4)_2MoO_4$ solution, and heat to 60°. Yellow $(NH_4)_3P(Mo_3O_{10})_4$ indicates P in the alloy as phosphide.

Precipitate 3. Wash the precipitate several times with water containing a little NH_4NO_3, add 1 ml of ethyl alcohol, stir thoroughly, and let stand 5 minutes to extract water. Then add 5 drops of 12*N* HCl and proceed as in Cation Group II-B, page 316. (Remember the Sn and Sb found here come from 20 mg of alloy.)

Analysis of the HNO_3 solution (solution 1). Add a few drops of the solution to 2 ml of $(NH_4)_2MoO_4$ and heat to 60° (see note 1). Bring the balance of the HNO_3 solution to a volume of exactly 2 ml. Take 1 ml for the remainder of the analysis. Add 1 drop of HCl to test for ions of Group I. If Group I is present, precipitate it completely. Transfer the solution and first washings to a centrifuge tube. Or, if Group I is not present, transfer 1 ml of the HNO_3 solution. Evaporate to 1 drop, add 3 drops of 12*N* HCl, and again evaporate almost to dryness. Take up with 1 ml of 12*N* HCl. Heat and pass in H_2S to precipitate H_3AsO_4 (see note 2). If As is present, make sure that *all* of it is precipitated. Evaporate the solution to 1 drop. Take up with 17 drops of water. Adjust C_{H^+} to 0.3*N*, using M.M.O. Saturate with H_2S and analyze any precipitate as usual for ions of II-A and for Hg^{++}. Test filtrate for all ions of Cation Groups III and IV, pages 318 and 325.

Notes: 1. $(NH_4)_3[P(Mo_3O_{10})_4]$ should always be precipitated in an HNO_3 solution. For this reason it is more convenient to test for H_3PO_4 at this point than in the 0.3*N* HCl solution at the beginning of the analysis of Group III. Usually no more than very minute amounts of H_3AsO_4 are in the solution. They will not react unless the solution is heated to boiling.

2. Since the oxidizing solvents always used for alloys will have oxidized P to H_3PO_4 and As to H_3AsO_4, the conditions for the rapid precipitation of As from its 5-valent state must always be observed in alloy analysis.

Case 2. The Alloy Contains Little or No Tin and/or Antimony

If the alloy dissolves without apparent residue, transfer the solution to a centrifuge tube and dilute to exactly 2 ml, using 2*N* HNO_3 as a diluent. Centrifuge. A very small precipitate may be a little SnO_2, Sb_2O_{4-5}, or $SiO_2 \cdot xH_2O$. Remove the liquid to another tube. Examine precipitate for Sn and Sb as directed in Case 1.

Test a few drops of the HNO_3 solution for H_3PO_4 with $(NH_4)_2MoO_4$. Evaporate or dilute the rest of the HNO_3 solution to exactly 2 ml and take 1 ml for the following analysis.

Test for Group I with HCl and remove it if present. Evaporate solution or the filtrate from Group I precipitate to 1 drop. Add 5 drops of 12 *N* HCl and again evaporate. Take up with 1 ml of 12 *N* HCl, precipitate H_3AsO_4 with H_2S, and make the solution 0.3 *N* in HCl as in Case 1 above. Then analyze for Cation Groups II (see note), III, and IV as in Case 1.

Note: Small amounts of Sb and Sn may be found in the HNO_3 solution.

APPENDIX

APPARATUS SET FOR EACH STUDENT

(Returnable if in good condition)

1 Beaker, Griffin, 100 ml (used as water bath)
11 Bottles without stopper, 30 ml
12 Bottles (homeopathic vials) 19 × 65 mm (1 dram)
4 Bottles, g.s., 1 oz. (tincture)
1 Brush, funnel
1 Clamp (micro test tube holder)
2 Centrifuge tubes, Pyrex, 15 ml
1 Rubber stopper, 1 hole, No. 0, to fit above
4 Centrifuge tubes, micro, 3 ml
2 Glass stirring rods 2 mm × 4″
2 Crucibles, high form, No. 0 (35 mm diam.)
2 Crucibles, wide form No. 0000, micro (18 mm diam.)
1 Cylinder, graduated, 10 ml, and 1 Fisher shock absorber for same
15 Dropper pipets 2¾″ long
1 Flask, Erlenmeyer, 25 ml
1 File, triangular
1 pr. forceps, iron
3 pieces soft glass tubing 7 mm × 20″
1 Micro burner and 3 ft. rubber tubing
6 Microscope slides
2 Plates, cobalt glass, 2″ × 2″
1 Plate, test (porcelain)
1 Platinum wire, 2″ (on glass tube)
1 Spatula, Monel, small (blade ¼″ wide)
1 Sponge
1 Stand, bottle—16 hole, block pine, shellacked, 17″ × 4.5″ × 2″; holes $1\frac{9}{16}$″ diam., 1″ deep
1 Stand, tube—42 hole, block pine, shellacked, 9″ × 5.5″ × 2″; 24 holes $\frac{7}{16}$″ diam., 1″ deep; 18 holes $\frac{1}{2}\frac{3}{2}$″ diam., 1″ deep
12 Test tubes, soft glass, 2″
1 Test tube, soft glass, 5″
1 Triangle, chromel, bent to support microcrucible
1 Triangle, pipestem
2 Watch glasses, 1½″ diam.
1 Water bath cover (galvanized iron 2¾″ × 2¾″, corners bent down to fit 100 ml beaker); hole $1\frac{5}{16}$″ diam. to take large crucible
1 Wire gauze 4″ × 4″

(Not Returnable)

15 Barnes combination cork and dropper nipples
5 Medicine dropper nipples

12 Corks, No. 3 (for vials)
1 Cork, No. 6, to fit 25 ml Erlenmeyer flask
2 doz. labels, No. 213 (1¼")
1 box matches
½ pkg. paper, filter, Reeve Angel No. 201, 9 cm
1 towel
1 vial litmus paper, red and blue
1 Oakville wedge-point pin
12 Unknown report forms
12 Anion elimination sheets

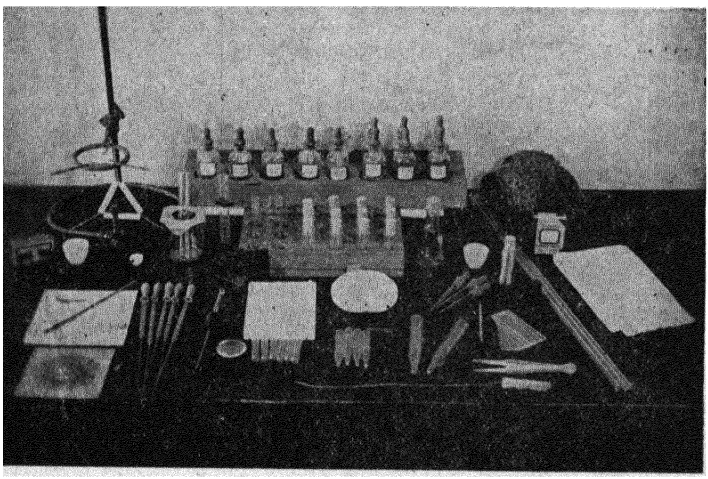


FIG. 7. STUDENT'S KIT FOR SEMIMICRO ANALYSIS.

SOLUTIONS AND REAGENTS

Test Solutions

Kept on side shelves in 120 ml bottles equipped with Barnes dropper-stopper pipets. Only "Reagent Grade" chemicals should be used. Test solutions for cations contain in 1 ml 10 mg of the *element;* those for anions contain in 1 ml 10 mg of the *anion.* The compounds used and the weight of each required to make 100 ml of solution are listed below.

Cations

Compound	Grams for 100 ml of Soln.	Compound	Grams for 100 ml of Soln.
$AgNO_3$	1.57	$SnCl_4 \cdot 5H_2O$ in 6 *N* HCl	2.95
$Hg_2(NO_3)_2 \cdot 2H_2O$ in 0.6 *N* HNO_3	1.40	$Al(NO_3)_3 \cdot 9H_2O$	13.90
$Pb(NO_3)_2$	1.60	$CrCl_3 \cdot 6H_2O$	5.10
$HgCl_2$	1.35	$FeCl_3 \cdot 6H_2O$	4.82
$Bi(NO_3)_3 \cdot 5H_2O$ in 3 *N* HNO_3	2.33	$Ni(NO_3)_2 \cdot 6H_2O$	5.00
$Cu(NO_3)_2 \cdot 3H_2O$	3.80	$Co(NO_3)_2 \cdot 6H_2O$	5.00
$Cd(NO_3)_2 \cdot 4H_2O$	2.78	$MnCl_2 \cdot 4H_2O$	3.60
As_2O_3 (Digest in 50 ml of 12 *N* HCl; then add 50 ml of water)	1.32	$Zn(NO_3)_2 \cdot 6H_2O$	4.55
		$BaCl_2 \cdot 2H_2O$	1.79
		$Sr(NO_3)_2 \cdot 4H_2O$	3.24
		$Ca(NO_3)_2 \cdot 4H_2O$	5.90
		$Mg(NO_3)_2 \cdot 6H_2O$	10.60
		$NaNO_3$	3.71
$SbCl_3$ in 3 *N* HCl	1.88	KNO_3	2.57
		NH_4Cl	2.94

Anions

Compound	Grams for 100 ml of Soln.	Compound	Grams for 100 ml of Soln.
$NaC_2H_3O_2$, anhydrous	1.39	$KF \cdot 2H_2O$	4.95
$Na_2HAsO_4 \cdot 7H_2O$	2.25	KI	1.31
$NaAsO_2$	1.20	$NaNO_3$	1.37
$Na_2B_4O_7 \cdot 10H_2O$	2.23	$NaNO_2$	1.50
NaBr	1.29	$(NH_4)_2C_2O_4 \cdot H_2O$	1.62
Na_2CO_3	1.76	$Na_2HPO_4 \cdot 12H_2O$	3.77
$NaClO_3$	1.28	$(NH_4)_2SO_4$	1.38
NaCl	1.65	$Na_2S \cdot 9H_2O$	7.52
K_2CrO_4	1.67	Na_2SO_3[a]	1.57
NaCN	1.90	KNCS	1.67
$K_3Fe(CN)_6$	1.55	$Na_2S_2O_3 \cdot 5H_2O$	2.21
$K_4Fe(CN)_6 \cdot 3H_2O$	1.98		

[a] Oxidizes rapidly; not reliable after 3 days.

Reagent Solutions

(Kept in liter bottles from which students fill their 30 ml bottles.)

Individual Students' Reagents

HCl	12 *N*	H_2SO_4	36 *N*
HNO_3	15 *N*	NH_3 soln.	15 *N*
HCl	3 *N*	NH_3 soln.	6 *N*
HNO_3	3 *N*	$AgNO_3$	0.1 *N*
H_2SO_4	3 *N*	Ca acetate	2 *N*
Acetic acid	6 *N*	Ba acetate	2 *N*
NaOH	6 *N*	Cd acetate	2 *N*

Desk-Shelf Reagents

(One set for each 8 students; 120 ml bottles equipped with Barnes dropper-stopper pipets)

H_2O_2	3%	$(NH_4)_2C_2O_4$	0.5 *N*
K_2CrO_4	1 *N*	$NH_4C_2H_3O_2$	3 *N*
$BaCl_2$	2 *N*	NH_4NO_3	5%
$KMnO_4$	0.1 *N* (as oxidant)	K_2SO_4	Saturated
$(NH_4)_2MoO_4$	0.65 *N*	Modified methyl orange indicator (M.M.O.)	
Cleaning powder			

Side-Shelf Reagents

(One set for each 24 students; 120 ml bottles equipped with Barnes dropper-stopper pipets)

Alcohol, amyl
Alcohol, ethyl, 95%
Ammonium carbonate, 4 *N*, 1.2 *N* in NH_3
Ammonium chloride, 3 *N*
Ammonium hydrosulfide, 3 *N* in 30 ml glass-stoppered bottles
Bromine, saturated solution in water
Bromine (for alloy analysis), 30 ml g.s. bottle
Carbon tetrachloride
Chloromanganous acid, 12 *N* HCl saturated with $MnCl_2 \cdot 4H_2O$
Chlorostannous acid, 0.5 *N*
Cobalt nitrate, 0.02% Co^{++} in 0.5 *N* HCl (for Zn test)
Cobalt nitrate, saturated (cyanide reagent)
Ethyl ether
Ferric nitrate, 1 *N* and 1 *N* in HNO_3
Lead acetate, 2 *N*
Nessler's reagent
Perchloric acid, 70% (in 30 ml glass-stoppered bottle)
Phosphoric acid, 90%
Potassium cyanide, 1 *N*
Potassium thiocyanate, 4 *N*
Potassium thiocyanatomercurate, 0.3 formal
Sodium carbonate, 3 *N*
Sodium cobaltinitrite
Sodium hydrosulfide, 1 *N* in 30 ml glass-stoppered bottles
Sodium nitrite (chloride-free), 2 *N*
Zinc acetate, 1% solution (for Cu test)
Zinc uranyl acetate

Solid Reagents

Aluminum, small granules
Ammonium chloride
Ammonium nitrate
Barium nitrate
Borax
Calcium chloride
Calcium fluoride
Devarda's alloy (small granules)
Ferrous ammonium sulfate
Magnesium powdered
Manganese dioxide
Potassium chlorate
Potassium chloride
Potassium ferricyanide
Potassium nitrite
Sodium acetate
Sodium bismuthate
Sodium carbonate
Sodium chloride
Sodium nitroprusside
Sodium thiosulfate
Stannous chloride
Strontium chloride
SiO_2–free test paper strips (HF washed filter paper)
Turmeric test paper
Zinc, 30 mesh (As free)
Zinc sulfate

Special Reagents

Aluminon. Ammonium salt of aurin tricarboxylic acid. Dissolve 0.5 g in 100 ml of water.

Ammonium hydrosulfide. Completely saturate $3N$ NH_3 with H_2S. During saturation the container should be packed to the neck in ice. To obtain a colorless product, air must be excluded. Therefore the container should be nearly full. Store in *completely filled* 30 ml glass-stoppered bottles sealed with paraffin.

For laboratory use, place in each of two 30 ml bottles 15 ml of $3N$ NH_3 and add the contents of a 30 ml bottle of the saturated product. Any of this reagent remaining at the end of a laboratory period should be discarded.

Ammonium molybdate. Approximately $0.65N$ in molybdate and $3N$ in HNO_3. Dissolve 6 g of commercial "ammonium molybdate" in 5.3 ml of $15N$ NH_3 and 15.4 ml of water. Let stand two days. Pour slowly with stirring into 24.5 ml of $15N$ HNO_3 diluted with 57.5 ml of water.

Benzidine acetate (for phosphate test). Dissolve 0.05 g of benzidine in 10 ml of glacial acetic acid and dilute to 100 ml.

Benzidine acetate (for cyanide test). 1 g benzidine and 1.85 ml $6N$ acetic acid. Dilute to 100 ml.

Cupric acetate (for cyanide test) 0.286 g in 100 ml water. Keep solutions separate.

Chlorostannous acid. $0.5N$. Dissolve 5.65 g $SnCl_2 \cdot 2H_2O$ in 25 ml of $12N$ HCl, adding a granule of tin. When *completely* dissolved, dilute slowly, with stirring, to 100 ml. Keep plenty of granulated tin in the reagent bottle.

Cobalt nitrate. 0.02% in Co^{++} ion, $0.5N$ in HCl. Dissolve 0.058 g of $Co(NO_3)_2 \cdot 6H_2O$ in 83.5 ml of water and 16.5 ml of $3N$ HCl.

Dimethylglyoxime. 1 g in 100 ml of 95% alcohol.

Fluorescein. Saturated solution in 1:1 alcohol-water.

Modified methyl orange. Dissolve 1 g methyl orange in 130 ml of 95% ethyl alcohol. Dissolve 1.4 g of xylenecyanole FF in 130 ml of 95% ethyl alcohol. (The dyes *must* be dissolved separately.) Mix the two solutions and dilute with water to 500 ml.

α-Naphthylamine. Boil 0.5 g with 100 ml of water. Filter if necessary. It *must* be colorless.

Nessler's reagent. Dissolve 8 g KI and 11.5 g HgI_2 in 45 ml of water. Make up to 50 ml and add 50 ml of $6N$ NaOH. Keep in a dark place.

α-Nitroso-β-naphthol. Saturated solution in 50% acetic acid. Not very stable. Must be tested frequently.

Phenolphthalein. Dissolve 0.1 g in 100 ml of 50% ethyl alcohol.

Phosphomolybdic acid. 5% solution in water. Precipitate ammonium phosphomolybdate. (Contrary to Feigl, the yield of acid appears to be larger if a *small* excess of $(NH_4)_2HPO_4$ is used.) Wash with 1 *N* HNO_3 until free of phosphate. Place the ammonium phosphomolybdate in hot aqua regia and heat until all dissolves. Evaporate to dryness. Dissolve the dry residue in water and recrystallize twice from water. Keep in a dark place.

Potassium thiocyanatomercurate. Approximately 0.3 formal. Dissolve 11.5 g KNCS in 100 ml of water. Add 8 g of $HgCl_2$ and stir until all is dissolved. Shake thoroughly. Let stand several days before using.

S and O reagent. Dissolve 0.001 g of *p*-nitrobenzene-azo-resorcinol in 100 ml of 2 *N* NaOH.

Sodium hydrosulfide. Completely saturate 1 *N* NaOH with H_2S exactly as directed for NH_4HS. Store same as NH_4HS.

Sodium rhodizonate. 0.4% solution in water. The solution is unstable and not reliable after a few hours.

Sulfanilic acid. Dissolve 0.5 g in 150 ml of 10% acetic acid.

Sodium cobaltinitrite (hexanitrocobaltiate). Dissolve 25 g $NaNO_2$ in a mixture of 50 ml of water and 13 ml of 6 *N* acetic acid. Add 2.5 g $Co(NO_3)_2 \cdot 6H_2O$. Let stand 24 hours. Filter and dilute with water to 100 ml.

Zinc uranyl acetate. Dissolve 10 g $UO_2(AcO)_2$ in 6 g of 5.2 *N* acetic acid, warming if necessary. Dilute to 50 ml. Mix 30 g of zinc acetate with 3 g 5.2 *N* acetic acid and dilute to 50 ml. Mix the two solutions. Add a pinch of NaCl, let stand 24 hours, then filter. (Neither of the salts dissolves completely until after mixing.)

Zirconyl nitrate (reagent for F^-). Dissolve 0.05 g in 10 ml of 12 *N* HCl and 50 ml of water.

Alizarin red S (reagent for F^-). Dissolve 0.05 g in 50 ml of water. Keep the two reagents separate.

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Natural numbers	0	1	2	3	4	5	6	7	8	9	Proportional Parts 1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

Natural numbers	0	1	2	3	4	5	6	7	8	9	Proportional Parts 1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9026	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4