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QUANTITATIVE ANALYSIS
BY
ELECTROLYSIS

BY

ALEXANDER CLASSEN

WITH THE COÖPERATION OF H. CLOEREN

REVISED ENGLISH TRANSLATION OF THE
FIFTH GERMAN EDITION

BY

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PREFACE.

THE first edition of this book appeared in 1882 and contained, for the most part, only those methods which had been worked out in the author's laboratory. Examples were also given of the applicability of electrolytic methods in the analysis of technical products. Successive editions contained the innovations and improvements that were made in the years 1882 to 1897 until, in the fourth edition, a section was introduced which contained theoretical considerations based upon the then new theory of solutions. During the last decade, however, the development of electrochemical methods not only on the practical side but also as a result of the development of physical chemistry, especially electrochemistry, has placed electro-analysis upon a scientific foundation. The advances in both practical and theoretical directions have been so marked that it has become necessary to revise the book thoroughly and the present edition may be regarded as practically a new book.

Among other things the book now includes many new rapid electrolytic methods, the determination and separation of the halogens as well as the metals of the alkali and alkaline earth groups, and a special part concerned with the analysis of technical products. For carrying out the rapid methods, the outfit in use in the author's laboratory at Aachen is described. This was the first of its kind in Germany and shortly after its installation was used as a model for many other laboratories.

A. CLASSEN.

TRANSLATOR'S PREFACE

THE earliest English edition of this book was prepared by W. H. Herrick and a later edition was by B. B. Boltwood. Owing to the rapid progress made in the development of electrolytic methods of chemical analysis since 1882, there remains little of the present text, which is exactly like that of previous translations. Previous editions, moreover, have followed the German text closely. The present edition, however, is a revision, without further reference to the German text, of the translation made six years ago. Some new procedures have been added, the order of treatment has been changed and the theoretical explanations modified. It is more important to understand exactly what is known to take place during electrolysis than it is to apply any particular theory to the phenomena. On the other hand, a simple application of the modern electronic theory seems to clarify rather than befog the vision of the beginner. An attempt, therefore, has been made to apply this theory a little more closely than has been done in most of the other well-known books on the subject.

In preparing this revised text, the writer wishes to acknowledge his indebtedness to his assistants, E. E. Richardson and S. G. Simpson, who have read the proofs and offered various suggestions.

WILLIAM T. HALL.

CAMBRIDGE, April, 1919

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QUANTITATIVE ANALYSIS BY ELECTROLYSIS

PART I.

INTRODUCTION.

In an ordinary gravimetric analysis, the substance to be weighed is formed by precipitation from a solution by means of a chemical reagent. In an electro-analysis the substance to be weighed is deposited by the passage of an electric current through the solution. In gravimetric analysis there are usually several different compounds into which the metal or the acid may be converted. The principal requirements to be satisfied by gravimetric analysis are: (1) the precipitate shall contain only the metal or acid to be determined in the form of a known compound, *i.e.*, it must be chemically pure; (2) it must contain the whole of the metal or acid in question, or, in other words, the precipitation must be complete, and (3) the precipitate must be of such a nature that it can be transformed easily into a substance of known composition from which the quantity of the element in question can be computed and in which it remains unchanged during the weighing. If, moreover, the precipitate possesses (4) a high molecular weight, and (5) if the precipitate settles quickly so that it can be filtered promptly, it possesses two desirable properties which are not, however, indispensable.

The electrolytic methods of chemical analysis are up to the present time restricted mainly to the determination and separation of metals, and as regards the deposits obtained a few characteristics may be mentioned. In most cases the deposits consist of the metal itself rather than one of its compounds. Only a few metals, such as lead, manganese, molybdenum and uranium, are obtained in the form of oxides. As with an ordinary gravimetric analysis, it is necessary that the deposit shall (1) be chemically pure and (2) contain all the element. As regards the third requisite of quantitative analysis, which concerns the accurate weighing, it is almost always true that the metallic or oxidic deposits are easily converted by washing and drying into a weighable condition. The choice of a compound of high molecular weight is naturally out of the question, but as regards the time factor it is to-day possible to carry out an electro-analysis so quickly that it is finished in less than an hour, or so slowly that the deposition can be completed during the night.

Just as in carrying out an ordinary gravimetric analysis it is necessary, for accurate work, to understand the exact behavior of the reagents and to know that they are sufficiently pure and present in sufficient quantity, so in the case of an electrolytic method it is necessary to know exactly how the electric current behaves toward the solutions, the effect of different strengths of current, and how it is possible to obtain and maintain the prescribed current during every operation.

It is necessary, therefore, to find out, on the basis of the theory of electricity, what happens when an electric current is passed through any given solution.

If the wires from the positive and negative poles of a suitable source of current are each connected with separate pieces of platinum foil and the two pieces of foil are suspended a slight distance apart in a sugar solution or in chloroform, it will be found, by placing a galvanoscope or ammeter in the circuit between one of the poles and the wire that leads to the liquid, that only a very weak electric current is flowing.

If, however, the pieces of platinum foil, called the *electrodes*, are suspended in dilute sulphuric acid, in dilute caustic soda, or in a solution of sodium chloride, the instrument will then show the passage of a stronger electric current. The solutions of these substances conduct electricity. On the basis of their behavior toward the current, all soluble substances (and with these only shall we concern ourselves) can be divided into those which are good conductors and those which are not. Those substances which, in aqueous solution, conduct electricity are called *electrolytes;* to this class belong most acids, most bases, and nearly all salts, whether organic or inorganic in nature, and it is with these that electro-analysis is concerned.

The first question that arises is this: What changes take place in the solution of an electrolyte when an electric current is passed through it?

If a sufficiently strong current is passed between platinum electrodes through a dilute, aqueous solution of sulphuric acid, or through a solution of potassium hydroxide, it will be found that oxygen gas is liberated at the positive pole (the *anode*) and hydrogen gas at the negative pole (the *cathode*). In the electrolysis * of a solution of potassium sulphate, oxygen is likewise liberated at the anode and hydrogen at the cathode. Moreover, in this case, blue litmus paper will show the presence of acid in the vicinity of the anode and red litmus paper will enable one to detect alkali in the vicinity of the cathode, although the original solution of potassium sulphate was neutral. Here, as in the electrolysis of all other electrolytes, a decomposition has taken place in the liquid owing to the action of the electric current.

For a long time it was assumed that the action of the electric current was to decompose the molecules of electrolyte. Thus, for example, sulphuric acid, H_2SO_4, was supposed to be broken down into the components H_2 and SO_4, the hydrogen was liberated at the cathode, while the acid radical, SO_4, which cannot exist by itself, reacted with water so that sulphuric acid was again formed and oxygen evolved at the anode:

$$SO_4 + H_2O = H_2SO_4 + O.$$

The oxygen, according to this view, is not the product of the direct action of the current upon the acid but is formed by the action of the group SO_4, which is incapable of existing in a free state, upon water; oxygen, therefore, represents a *secondary product* of the action of the electric current.

The same view applied to the decomposition of potassium sulphate leads to these conclusions: the primary products of the action of the current upon this salt are K_2 and SO_4; the potassium, owing to its chemical nature, reacts with water as fast as it is set free

$$K_2 + 2\,H_2O = 2\,KOH + H_2,$$

so that potassium hydroxide and hydrogen appear at the cathode;

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* *Electrolysis* signifies, in general, the decomposition of an electrolyte by the influence of an electric current irrespective of whether the substance itself is in solution or in a melted condition. The decomposition of the electrolyte in solution for the purpose of analysis is appropriately called *electro-analysis*.

at the anode the SO_4 reacts with water, as explained above, and forms H_2SO_4 with evolution of oxygen.

This view is not correct, according to the views which prevail to-day concerning the nature of aqueous solutions.

According to the theory of *electrolytic dissociation*, proposed by Arrhenius in 1887 and since verified by careful study of the physical properties of solutions, it is assumed that components of the electrolyte, which formerly were thought to be formed by the initial action of the electric current, already exist as such in an aqueous solution.

It is not necessary, here, to discuss the basis of this theory of electrolytic dissociation or *ionization*; it is now generally taught in the study of inorganic chemistry. It will be well, however, to review the theory as far as it pertains to the understanding of the mechanism of the changes that take place during electro-analysis.

Faraday, who first designated the positive electrode as the anode and the negative electrode as the cathode, noticed that the components of the electrolyte migrated toward one or the other of the electrodes, and therefore called these components *ions* (wanderers). The component which moves toward the anode (+ pole) is called the *anion* and that which moves toward the cathode (− pole) is called the *cation*. The anion, since it is attracted to the positive pole, must be regarded as the electronegative constituent of the electrolyte, and the cation, since it is attracted to the negative pole, must be regarded as the electropositive constituent. The new thing in the theory of Arrhenius consists merely, as stated above, in assuming that the ions already exist in aqueous solutions and do not result from the action of the electric current upon the solution. In an aqueous solution of sodium chloride, for example, it is assumed that sodium and chloride ions are present. To bring this hypothesis into harmony with the well-known fact that free sodium cannot exist in contact with water, and furthermore to explain the fact that the ions are attracted by the electrically charged electrodes, it is necessary to ascribe properties to the ions which are not attributed to elementary atoms. It is assumed that the ions are atoms, or groups of atoms, which are charged with electricity, and in the sodium-chloride solution the sodium ions are charged with positive electricity while the chloride ions bear an equal charge of negative electricity. The ionic condition is expressed by writing small + signs above the symbols of positively charged ions (cations) and small − signs above negatively charged ions (anions);* thus the ionic condition of dissolved sodium chloride is expressed by Na^+ and Cl^-. The charges of opposite sign must be equal, for the entire solution is electrically neutral.

By assuming the existence of ions, charged respectively with positive and negative electricity, it is perfectly clear why the ions migrate when subjected to the action of an electric current; the source of the current charges the positive electrode (anode) with positive electricity and this anode attracts the negatively charged ions (anions) and repels the positively charged cations; the latter are attracted by the negatively charged cathode, which on its part repels the positively charged anions and sends them toward the anode.

The passage of the electric current through the solution from one electrode to the other is a purely physical change, involving merely the migration of the ions. The passage of electricity from the metallic electrode to the solution, however, always accomplishes an electrochemical change. This chemical change is an *oxidation* at the anode and a *reduction* at the cathode; the two processes always take place simultaneously.

The term oxidation originally implied increasing the oxygen content of a substance and reduction implied the removal of oxygen. In the typical oxidation of hydrogen by means of oxygen to form water, we now regard the hydrogen as representing the electro-positive constituent and the oxygen as representing the electro-negative constituent of the water. In the oxidation of hydrogen by oxygen, therefore, the former is changed from the electrically-neutral to the electro-positive condition and the latter from the neutral to the electro-negative state. In terms of the electrolytic theory, the term oxidation merely means an increase in the electro-positive charge on an atom, or, what amounts to the same thing, a decrease in the electro-negative charge. In the same way a reduction is merely a decrease in the electro-positive charge associated with an atom or an increase in the electro-negative charge.

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* Instead of designating the charges on the ions by small + and − signs, many authorities use dots and dashes. Thus the ions of NaCl are often written $Na^{\cdot}$ and Cl'.

Every species of ion present in a solution takes part in some degree in the movement toward the electrodes during electrolysis. At each electrode usually a single species of ions is oxidized or reduced. In a tenth-normal solution of sodium chloride in water, the salt molecules are ionized to the extent of nearly 85 per cent, but the water molecules are ionized into hydrogen cations and hydroxyl anions only to about 0.0000002 per cent at room temperature. Pure water is a poor conductor, but the salt solution is a good electrolyte. In the electrolysis of a salt solution between platinum electrodes, it is chiefly the movement of the sodium cations and chloride anions that interests us. At the electrodes, however, it is another matter. It is a great deal easier to discharge hydrogen ions at the cathode than to discharge sodium ions, even although only a few of the former are present at any instant. The moment the hydrogen ions originally present are discharged, however, more of them are formed from the ionization of the water which takes place at a very rapid rate. This increases the concentration of hydroxyl ions in the vicinity of the cathode because as each hydrogen atom is discharged, an equivalent weight of hydroxyl ions remains. These hydroxyl ions are in equilibrium with the sodium ions that have migrated to the cathode region.

It was formerly customary to assume, in explaining the electrolysis of a sodium chloride solution, that sodium was at first set free at the cathode and that the free sodium reacted with the water to form sodium hydroxide. This idea, however, is not substantiated by the facts.

The chemical reduction that takes place at the cathode during an electrolysis, whether it involves the deposition of a metal, the evolution of hydrogen gas, the loss in valence of some positively-charged element, or the gain in valence of some negatively-charged element, will always be that reduction which it is easiest to accomplish under the prevailing conditions. Theoretically, under suitable conditions, any oxidation and any reduction can be accomplished by means of electrolysis. The conductance of the solution is determined by the number of ions present, the charge each ion bears, and the mobility of the ion. The chemical nature of the ions, or at least the readiness with which they are oxidized and reduced, has nothing to do with the conductance of an electrolyte. At the electrodes, however, although the concentration of the ions does have an important effect, the chemical nature of the ions, especially as regards their readiness to be oxidized or reduced, is of great importance. It is easier to oxidize hydrogen ions from hydrogen chloride solution than from water because there are so many more hydrogen ions present from the ionization of the hydrogen chloride than from the ionization of water. But it is so much easier to reduce hydrogen ions than sodium ions from a salt solution that hydrogen gas is formed during electrolysis.

It is true, to be sure, that it is possible to get sodium amalgam formed at the cathode if the electrolysis is carried out with a mercury cathode. In this case the sodium ions are reduced, but the sodium is kept in metallic solution and is not set free in the pure state. By changing the conditions very slightly it is possible to change the nature of the chemical reactions that take place.

All that has been said thus far refers to the *qualitative* side of the action of the current upon an electrolyte. To understand the *quantitative* relations it is necessary to know something about the measurable factors of the current which play a part in electro-analysis, and to know how the measurements are made. These factors are *electromotive force* (potential), *current strength*, and *resistance* and they stand toward one another in the relation expressed by Ohm's law

$$\text{current strength} = \frac{\text{electromotive force}}{\text{resistance}},$$

or

$$\mathrm{I} = \frac{\mathrm{E}}{\mathrm{R}}.$$

This law holds, in the first place, for the passage of electricity through a solid conductor (*conductor of the first class*); it holds equally well, as we shall soon see, for the passage of electricity through the solution of an electrolyte (*conductor of the second class*). The distinction between these two classes of conductors arises from the fact that in metallic conductors (carbon is classed with these) there is no permanent alteration of the substance produced by the passage of the current, whereas in the case of liquid, non-metallic conductors, a transformation of substance takes place, as we have already seen; a heating effect is noticeable when the current passes through either kind of a conductor.

The unit employed for measuring the current strength, or intensity, is called the *ampere* and it represents a current which will deposit 1.118 mgms. of silver in a second from a solution containing about 15 gms. of pure silver nitrate in 85 cc. of distilled water.*

The unit employed for measuring resistance is the resistance offered at 0° C. by a column of mercury 106.3 cm. long weighing 14.4521 gms. and being 1 square millimeter in cross section; this resistance is called an *ohm*.

The unit of electromotive force, or difference in potential, is called the *volt*. It represents the electromotive force which produces a current of one ampere in intensity through a conductor having a resistance of one ohm. If any two of the above three factors are expressed in numbers, the third can be found by the equation of Ohm's law which reads

$$\mathrm{I} = \frac{\mathrm{E}}{\mathrm{R}}, \quad \text{or} \quad \text{ampere} = \frac{\text{volt}}{\text{ohm}}.$$

Of these three factors, the current strength, or intensity, is easiest to measure. It is only necessary to insert an instrument called an *amperemeter*, or *ammeter*, in the circuit and the position of the needle on the scale shows the number of amperes. The question now arises: What is the part played in electro-analysis by the current strength?

If the deposition of an element, *e.g.*, a metal like silver, depends upon the neutralization of the positive charge of the silver ions by the negative electricity of the cathode, then the deposition of the metal must take place more rapidly, *i.e.*, in a unit of time so many more ions must be transformed into atoms, in proportion as the quantity of negative electricity offered to the positively charged silver ions at the cathode is large. While a current of one ampere will cause the deposition of 1.118 mgm. of silver from a silver salt in a second, a current of two amperes will cause the deposition of 2 × 1.118 mgm. of silver in the same time. In general, it holds for the deposition of all substances that *the quantities deposited at the electrodes in a unit of time are proportional to the current strengths.*

This law may be easily demonstrated by electrolyzing an aqueous solution of copper sulphate for ten minutes with a current of definite strength and weighing the deposited copper, then

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* The legal electrical units in the United States are defined in a Bulletin of the U. S. Coast and Geodetic Survey, Dec. 27, 1893.

repeating the experiment, using the same solution the same length of time and a current twice as strong. The weight of copper deposited in the second case will be twice that obtained in the first experiment.

What relation holds with regard to the quantities of different substances deposited in equal lengths of time by the same current? Faraday's law * answers this question. *The quantities of different substances deposited in equal lengths of time by the same current stand in the same relation to one another as do their electrochemical equivalents.*

This law may be demonstrated experimentally by taking a series of solutions containing the salts of different metals, each connected in series, and passing a current through the series of solutions for a definite length of time, and then weighing the deposited metals. It will be found that the weights obtained are in proportion to the equivalent weights of the substances in question. Thus in aqueous solutions of silver nitrate, cupric chloride, and ferric chloride decomposed by one and the same current, the weights of metal deposited will be as

$$\overset{Ag^+}{107.88} : \overset{Cu^{++}}{\frac{63.57}{2}} : \overset{Fe^{+++}}{\frac{55.84}{3}}.$$

It should be noticed particularly that the proportionality does not refer to the atomic weights but to equivalent weights, *i.e.*, to the atomic weights divided by the valence of the element in question. In a similar experiment with silver nitrate, cuprous chloride and ferrous chloride, the quantities of metal deposited would bear the relation:

$$\overset{Ag^+}{107.88} : \overset{Cu^+}{63.57} : \overset{Fe^{++}}{\frac{55.84}{2}}.$$

What holds true of the metals, which are easier to determine experimentally, holds equally true with respect to the quantities of anions discharged by the same current.

Faraday's law, in the light of the ionic theory, suggests a number of new consequences. If a current of a certain intensity will

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* The above-mentioned law expressing the proportionality between the quantities of the same substance and the current strengths was also discovered by Faraday.

deposit 107.88 mgms. of silver in the same time that 63.57 mgms. of copper are deposited from cuprous chloride, and if, as has already been stated repeatedly, the deposition is due to the neutralization of opposite charges of electricity on the electrode and ion, then the ions of 107.88 mgms. of silver must bear the same charge of positive electricity as are borne by 63.57 mgms. of copper ions; for the current of the given strength must carry to the cathode in the silver solution, in the same length of time, the same quantity of negative electricity that it carries to the cathode in the copper solution. The same quantities of electricity are carried, therefore, by $\frac{63.57}{2}$ mgms. of cupric ions, by $\frac{55.85}{3}$ mgms. of ferric ions, and by $\frac{55.85}{2}$ mgms. of ferrous ions.

In general it may be said that equivalent quantities of univalent ions (*e.g.*, 107.88 Ag and 63.57 Cu) carry the same quantities of electricity, or, in other words, all univalent ions bear equal electric charges. As regards the charges on polyvalent ions, let us imagine that a current of one ampere is passing through a solution containing cuprous ions and through another containing cupric ions. At the end of a certain period, this current will deposit 63.57 mgms. of copper from the cuprous solution and $\frac{63.57}{2}$ mgms. of copper from the cupric solution. Inasmuch as cupric ions have the same weight as cuprous ions, it follows that the number of cupric ions which by their discharge have yielded $\frac{63.57}{2}$ mgms. of copper must be half as large as the number of cuprous ions from which 63.57 mgms. of copper have been deposited. The current strength was the same in both solutions, *i.e.*, the quantities of electricity required to deposit these two different quantities of copper were the same. It follows from this, and from what was said above, that one half as many cupric ions bear the same electric charge as a given number of cuprous ions, or, that the charge borne by a cupric ion is twice that of a cuprous ion. This is designated in the symbol by two + signs: Cu^{++}. Trivalent ions bear a triple charge, *e.g.*, Fe^{+++} is the symbol of the ferric ion. The same holds for the charges on the anions; the charge is shown by the number of − signs: SO_4^{--} is the symbol of the sulphate ion and PO_4^{---} of the phosphate ion.

On page 7, it was stated that a current of one ampere would deposit 1.118 mgms. of silver from the aqueous solution of a silver salt. Using this number as a basis, it is possible to compute the strength of the current from the weight of silver deposited in a definite time.

Besides the conception of current strength, which is determined by the quantity of electricity flowing during a unit of time (one second) there is another unit for measuring the *quantity* of electricity called the *coulomb*. A coulomb is the quantity of electricity transferred by a current of 1 ampere in one second. If a current of a amperes flows for a period of t seconds, then the quantity of electricity that passes through the circuit during that period is $a \times t$ coulombs.

From these definitions it is easy to compute how many coulombs of electricity are necessary to discharge a gram-equivalent of a metal. Silver, a univalent metal, has an atomic weight of 107.88, this is the value of the gram equivalent of silver because the metal is univalent in its salts. Since, by definition, 1 coulomb of electricity deposits 0.001118 gm. of this metal, it will take $\frac{107.88}{0.001118} = 96{,}500$ coulombs to discharge a gram equivalent of silver.

This quantity of electricity, moreover, corresponds not only to the charge on a gram equivalent of silver, but it corresponds to the unit charge on a gram atom of any other element. 96,500 coulombs will discharge 63.57 gms. of copper from a solution of a *cuprous* salt, but only $\frac{63.57}{2}$ gms. of copper from a cupric salt. To reduce an atomic weight of iron from the ferric to the ferrous state requires at the cathode 96,500 coulombs of electricity; to reduce the same weight of ferric iron to metal requires $3 \times 96{,}500$ coulombs of negative electricity. The electrochemical equivalent of iron, therefore, is the atomic weight if the conditions are such at the cathode that the ferric salt is merely reduced to ferrous salt but the electrochemical equivalent is only one-third the atomic weight if the iron is deposited as such upon the cathode.

The number 96,500 represents, therefore, the electrochemical unit for the quantity of electricity; it is called the *Faraday* and is denoted by the symbol F (1 F = 96,500 coulombs = 26.82

ampere-hours). It has already been stated that an oxidation always takes place at the anode simultaneous with the reduction at the cathode and it is easy to compute how much electricity is necessary to accomplish any given oxidation. The liberation of oxygen at the anode during electrolysis corresponds to the neutralization of a double negative charge on the oxygen atom. If this is the only oxidation taking place at the anode, one *Faraday* passing through the circuit will liberate $\frac{\text{at. wt.}}{2} = 8$ gms. of oxygen gas. The oxidation of the chromium in a chromic salt to a chromate at the anode corresponds to increasing the positive charge on the chromium atom from 3 to 6 and the electrochemical equivalent of chromium is therefore $\frac{\text{at. wt.}}{3} =$ 17.33 gms.

To find how many coulombs of electricity are required to accomplish any desired reduction at the cathode or oxidation at the anode, first determine what change in valence takes place and remember that to impart a unit charge of electricity, or to neutralize a unit charge, 96,500 coulombs are required. To determine how long it will take, divide the coulombs required by the amperage of the current used. For example, how long will it take a current of 4 amperes to deposit 3 gms. of nickel from a solution, assuming this to be the only reaction that takes place at the cathode? The atomic weight of nickel is 58.68 and its valence is 2. The computation is as follows:

$$\frac{3 \times 2 \times 96{,}500}{58.68} = 4{,}934 \text{ seconds.}$$

Similarly, with the help of value F, the weights of different metals that will be deposited per second by a current of 1 ampere can be computed. Thus 1 coulomb will deposit $\frac{65.37}{2 \times 96{,}500} =$ 0.0003387 gms. of zinc because zinc is bivalent and the Faraday corresponds to the charge residing on half the atomic weight in grams of this metal. For any given time, t seconds, and any given current, a amperes, it is only necessary to multiply the above number by t and n.

For the deposition of iron from a solution of a *ferrous* salt, a corresponding computation gives the value 0.0002894 gm.

as the quantity of metal deposited by 1 coulomb of electricity. From the solution of a *ferric* salt, the iron value is 0.0001929.

It must be mentioned here, however, that the computation, with the help of Faraday's law, of the quantities of metal deposited will give the values actually obtained in an experiment only when all the current flowing through the solution is used for the discharge of the ions of the metal in question. This is not usually the case in electro-analysis, as will be shown later. In most cases some hydrogen ions are discharged while the metal is being deposited and in this way a part of the current is not utilized for precipitating the metal. The *current yield,* which is based upon the quantity of current actually used for depositing the metal itself, is in such cases smaller than the theoretical value computed with the aid of Faraday's law; on the other hand, the sum of the weights of all the ions discharged exactly corresponds to the law.

Two other units are of interest in connection with electrical measurements, the unit of *work* and the unit of *power.* The unit of work is the *joule.* It is equivalent to 10^7 ergs and is practically equivalent to the energy expended in one second by an ampere against the resistance of an ohm. If the quantity of electricity is expressed in coulombs and the electromotive force in volts, the product will be volt-coulombs (volts × amperes × time in seconds) or joules. In commercial work, the unit of power is the watt (or the kilowatt, which is 1000 times as large) which represents work done at the rate of one joule per second. *Multiplying the voltage by the amperage gives watts and multiplying this by the time in seconds gives watt-seconds or joules.*

Migration of the Ions.

If an electric current is conducted through a solution of cuprous chloride, CuCl, it is evident, from what has been said, that for each 63.57 gms. of copper deposited upon the cathode 35.46 gms. of chlorine ions will be discharged at the anode. As soon as some of the copper, or chlorine, is transformed into the electrically neutral condition at the electrode, new ions of the same kind must appear at each electrode as otherwise all the copper, or chlorine, will never be removed from the solution. The ions which are originally distributed uniformly throughout the entire solution must migrate, even from the most distant parts of the solution, toward the electrodes, the positively charged ions moving toward the cathode and the negatively charged ions moving in the opposite direction toward the anode. The discharge at the two electrodes must end at the same time, for when all the copper ions have been discharged there can remain no negatively charged chlorine ions because the solution itself at no time possesses electrical properties. The simplest assumption, therefore, would be that the cuprous ions and chlorine ions migrate with equal velocities toward the opposite electrodes. Experiment shows, however, that this is not true.

Let us imagine, using the illustration suggested by LeBlanc, that the solution of an electrolyte, such as hydrochloric acid, is divided into three compartments (Fig. 1), of which the walls *C* and *D* are easily penetrable by the ions. The solution contains 30 gram equivalents of HCl, and, assuming a homogeneous mixture, each compartment contains 10 gram equivalents of HCl. The wall *A* forms the anode and the wall *K* the cathode. If a current is passed through the solution, we know that 1 F, or 96,500 coulombs, will decompose 1 gram equivalent HCl (*cf.* p. 11) discharging at *K*, 1 gram equivalent H^+ and at *A*, 1 gram equivalent Cl^-, so that after the passage of this quantity of electricity, the entire solution will contain 29 gram equivalents of HCl.

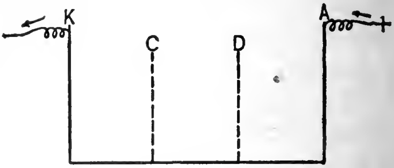

Fig. 1.

The middle compartment *CD* merely serves as a passageway between the two electrodes and no change takes place within it. At *K*, 1 gram equivalent of H^+ has left the solution; at *A*, 1 gram equivalent of Cl^-. If, now, there were no other changes in the compartments *AD* and *KC*, there would be present, besides the unchanged 9 gram equivalents of HCl, 1 gram equivalent of H^+ in *AD*, and 1 gram equivalent of Cl^- in *KC*. At the electrodes, however, it is not possible for free ions to be present, as in that case the solution in the compartments *AD* and *KC* would possess free electricity, whereas in reality it is neutral. This electrically neutral condition can be brought about only by the movement of some of the H^+ in *AD* toward *K* and of some of the Cl^- in *KC* toward *A*.

If we assume, as actually happens, that the H^+ ions migrate five times as fast as the Cl^- ions, or, in other words, that 5 H^+ enter the compartment *KC* while 1 Cl^- enters the compartment *AD*, then of the original 1 gram equivalent of H^+ in *AD*, $\frac{5}{6}$ gram equivalent will have migrated toward *K* and $\frac{1}{6}$ gram equivalent will have remained behind. Meanwhile, of the residual Cl^- in *KC*, $\frac{1}{6}$ gram equivalent has migrated toward *A* and is in equilibrium in the compartment *AD* with the $\frac{1}{6}$ gram equivalent H^+ that remained there, and forms $\frac{1}{6}$ gram equivalent HCl. In this way the electrically neutral condition of the solution in *AD* is explained; there are now present in *AD* $9\frac{1}{6}$ gram equivalents of HCl.

After the migration of the $\frac{1}{6}$ gram equivalent of Cl^- from *KC* toward *A*, there still remains $\frac{5}{6}$ gram equivalent of Cl^- in *KC*, but these ions are in equilibrium with the $\frac{5}{6}$ gram equivalent of H^+ that has migrated from *K* so that an electrically neutral condition likewise prevails in *KC*; the solution there now contains $9\frac{5}{6}$ gram equivalents of HCl.

Although no change in concentration has taken place in the middle compartment, such changes have occurred in the end compartments: *AD* now contains $9\frac{1}{6}$ gram equivalents of HCl, *KC* contains $9\frac{5}{6}$ gram equivalents of HCl and *CD* still contains, as at first, 10 gram equivalents of HCl.

Conversely, from the observed fact that the concentration of HCl in one of the end compartments is different from that of the other, the conclusion can be drawn that the ions migrate with different velocities and from the changes in concentration the ratio of the velocities of migration can be computed.

This example merely serves to impart some idea of what is meant by the different *migration velocities of the ions.* The description of the methods and apparatus used to carry out such measurements is outside the scope of this book.

In spite of the different velocities with which the ions migrate within the electrolyte, the quantities of the substances discharged at the two electrodes are always equivalent. This is due to the fact that the quantity of positive electricity which reaches the electrodes in a unit of time from the source of the current, and which we may designate as *n* coulombs, is at once neutralized at the anode by *n* coulombs of negative electricity on the anions, and, likewise, at the cathode *n* coulombs of negative electricity are neutralized by n coulombs of positive electricity on the cations. The quantities of substance discharged at the electrodes, therefore, are independent of the rates at which the ions move through the solution and are, according to Faraday's law (p. 9), directly proportional to the current strength.

The cause of the different velocities of migration lies in the different degrees of friction which the ions have to overcome in their passage through the electrolyte. This resistance must vary with the different ions, according to their nature, and when we take into consideration the extremely small masses that the ions possess we can see that it must be considerable. For sake of comparison one needs only to recall how slowly a finely powdered substance, or precipitate, settles in a liquid.

The *electrical resistance* of the electrolyte is not to be confused with this friction which the ions have to overcome.

Resistance.

If a copper wire is placed in circuit with an ammeter between the poles of a constant source of current, the instrument will show a certain current strength in amperes. If the copper wire is replaced by an iron wire of the same length and diameter, the instrument will then show a weaker current. Conductors made of different metals, but of the same dimensions, offer different resistances to the current, or, as is usually stated, different metals have a different conductance toward electricity. Resistance and conductance are reciprocal quantities. The different conductance of metallic conductors has a bearing upon electrolytic practice, for, in arranging the electrolytic circuit, good conductors should be chosen, since an increased resistance causes, in accordance with Ohm's law (p. 7), a weakening of the current and consequently a loss in energy.

The electrolytes themselves show similar differences with respect to conductance. If the current is allowed to pass through a concentrated, neutral solution of copper sulphate and again through the same solution after it has been acidified with sulphuric acid, the ammeter will show a stronger current in the latter case than in the former. Since, in utilizing the current in electrolytes, a weakening of the current results in a loss of energy, it is evident that the resistance of electrolytes must play an important part in electrolysis. In the metallic part of the circuit (the wires that carry the current) the intensity of the current can be increased, as the formula for Ohm's law shows (p. 7),

$$I = \frac{E}{R},$$

by making R smaller (*e.g.*, using shorter wires, larger wires, or wires of a metal that conducts better) or by increasing the electromotive force E. These two expedients are, to be sure, at one's disposal in electro-analysis; but in practice one is confined within narrow limits.

A lessening of the resistance by diminishing the length and cross section of the electrolyte would result from bringing the electrodes nearer together and exposing a larger electrode surface. In accomplishing such changes, the shape of the apparatus also comes into consideration.

Increasing the electromotive force is out of the question in many cases, because, as we shall find later, it is often necessary to carry out the electro-analysis under a constant potential. Even when it is necessary to maintain a certain potential, however, there remains the possibility of increasing the intensity of the current, and thereby accelerating the operation, by adding certain substances, which, as in the above example, serve to increase the conductivity of the solution. The nature of the substance added depends upon the chemical nature of the electrolyte and must be determined by experiment. Sometimes acids, sometimes alkalies and often salts may be added. A fundamental requirement, which is independent of the nature of the metal to be deposited, may be stated as follows, — a substance added to assist in the electrolysis of a solution must be, when dissolved, a good conductor of the current and must form no decomposition products which are insoluble or in any way detrimental to the analysis. Alkalies and acids, which after their decomposition are regenerated at the electrodes, as well as organic acids which form gaseous decomposition products, are frequently suitable. This last condition, together with the marked solvent effect that oxalic acid exerts, owing to the formation of double salts, has caused this acid to find widespread application in electro-analysis.

In carrying out an electrolysis, it is not usually necessary to know the resistance of the bath; in certain cases, however, it is very desirable to know the resistance or conductance of an electrolyte. For this reason, the usual method for measuring the resistance of a liquid will be outlined. It will be assumed that the reader already understands how the resistance of a metallic conductor, *e.g.*, a wire, is measured with the aid of the Wheatstone bridge. It will be recalled, on inspecting the diagram shown in Fig. 2, that in the system of resistances x, R, a and b, one of the resistances, R, can be regulated so that the current from the source S has no effect upon the galvanoscope G while flowing through the system. From the three known resistances R, a and b the unknown resistance x can be computed from the proportion

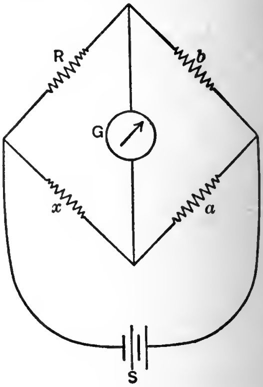

FIG. 2.

$$x : \mathrm{R} = a : b,$$

from which it follows that

$$x = \mathrm{R}\frac{a}{b}.$$

This method cannot be applied directly to the measurement of the resistance of an electrolyte, by simply inserting the liquid, with its two platinum electrodes, in place of the resistance x, for the case here is somewhat different. The current in passing through the electrolyte not only has to overcome the resistance of the liquid (Ohm's resistance) but it also has to perform chemical work, or, expressed more exactly, to transport material. This chemical work can be avoided by using an alternating current instead of a direct current. Then the anode and cathode will exchange places with each reversal of the current; the changes produced at the electrodes will thus be reversed at each reversal of the current, and, as the latter takes place very frequently during each second, it is fair to assume that practically no work is accomplished in the electrolyte. Such an alternating current has just as little effect upon the magnetic needle of a galvanoscope as it has upon the composition of the solution. It is necessary, therefore, to use, instead of the galvanoscope, an instrument which, as the resistance is varied, will show the diminution and finally the cessation of the alternating current; such an instrument is the telephone.

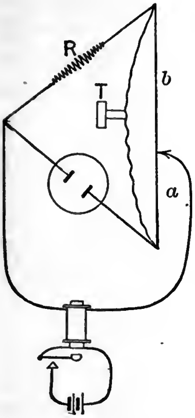

Fig. 3.

In the above diagram, which illustrates the use of the Wheatstone bridge, the source of the current is replaced by a small induction coil (Fig. 3) the secondary current of which (an alternating current) is sent through the four resistances. *T* is a telephone. In place of the resistance x, the solution of the electrolyte is inserted with its two platinum electrodes, and in place of the resistances a and b, a platinum wire is used bearing a sliding contact (the arrow in the diagram). Instead of changing the resistance R, the resistances a and b are changed by moving the point of contact along the wire. This contact is moved back and forth until the position which produces a minimum tone in the telephone is found. There then exists, between the four resistances, the equation

$$x = R\frac{a}{b}.$$

Fig. 4 illustrates the complete instrument as designed by Kohlrausch.

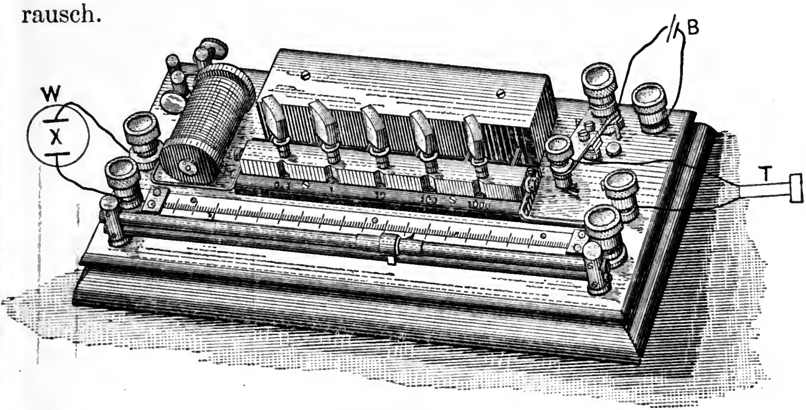

Fig. 4.

It is often desired to know the resistance of a given metallic conductor, *e.g.*, a wire; it is then merely necessary to take the wire, or a known length of it, and measure the resistance with the Wheatstone bridge. If, however, it is desired to learn the *specific resistance* of the metal, *i.e.*, the resistance of a cube having 1 cm. edges, this value must be computed from the experimental results by taking into consideration the fact that the resistance is proportional to the length and inversely proportional to the cross section of the conductor.

The resistance of an electrolyte, *or its reciprocal value known as the conductance,* is something which of itself is seldom of interest. The knowledge of the *specific conductance* is much more important.

If we imagine a liquid in the form of a cube each edge of which measures 1 cm. and two opposite faces of which form the electrodes, then its resistance, expressed in ohms, is termed the *specific resistance* of the liquid. Calling this resistance R_s expressed in ohms. then the *specific conductance* is

$$L_s = \frac{1}{R_s}$$

expressed in reciprocal ohms. If the latter unit is constructed on the same basis as that of the ohm (p. 7), then it represents the conductance of a liquid contained in a cube, with 1 cm. edges, having the resistance of 1 ohm. Then

$$L_s = \frac{1}{R_s} = 1.$$

A fifth-normal sulphuric-acid solution has a specific conductance of approximately 1 at 40° (*cf.* p. 29).

The conductance of most electrolytes increases as the temperature is raised; with metallic conductors the conductance diminishes with rise of temperature. As regards the dependence of conductance upon the dimensions of the conductor, it is true of electrolytes, as of metals, that the conductance diminishes with increasing depth (length, with metallic conductors) and increases as the cross section or distance between the electrodes increases. The conductance of electrolytes, however, also depends upon the concentration. As was mentioned on page 17, one is restricted, in working with liquids, to the dimensions of the apparatus, and, since the concentrations of the electrolytes may be very different, it is desirable to introduce, for purposes of comparison, a new

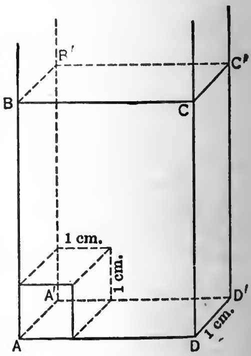

FIG. 5.

conception, namely, that of *equivalent conductance.* Let us imagine a rectangular vessel (Fig. 5) constructed so that the two opposite faces *ABCD* and *A'B'C'D'* lie 1 cm. apart and these two side faces serve as electrodes, being made, for example, of platinum. The vessel contains v cc. of a solution in which 1 gram equivalent of a substance is dissolved. The resistance of 1 cc. of this solution is its specific resistance R_s, and its specific conductivity is $\mathrm{L}_s = \frac{1}{\mathrm{R}_s}$ (*cf.* p. 20). If, now, we imagine an electric current passing through the entire solution, in such a way that it enters through the face *ABCD* and leaves through the face *A'B'C'D'*, then the resistance offered by the whole solution is v times smaller because the cross section of *ABCD* is v sq. cm.; consequently the conductivity is v times as great as that of 1 cc. of the solution. This conductance is known as the *equivalent conductance* Λ, *i.e.*, it is the conductance between electrodes 1 cm. apart of that volume, v, of the solution which contains 1 gram equivalent of the substance. Expressed in an equation,

$$\Lambda = v\mathrm{L}_s.$$

The specific conductance L_s (the reciprocal of the specific resistance R_s) is determined experimentally, and to compute the value of Λ, the equivalent conductance of the solution, the value L_s is multiplied by the number of cubic centimeters in which 1 gram equivalent of the substance would be contained at the given concentration. Thus a solution containing 100 gms. HCl in 2 liters would contain 1 gram equivalent HCl (or 36.46 gms. HCl) in 729.2 cc., for

$$\overset{\text{gm. HCl}}{100} : \overset{\text{cc.}}{2000} = 36.46 : x,$$
$$x = 729.2 \text{ cc.},$$

and the equivalent conductance of such a solution would be

$$\Lambda = 729.2\,\mathrm{L}_s.$$

Electromotive Force or Potential.*

Electro-analysis had met with remarkable success before the significance of the electromotive force or potential was recognized. After the first purely empirical methods, with galvanic cells and

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* *Potential* in electricity is analogous to temperature, and as heat tends to pass from a point at a higher to one at a lower temperature, so electricity tends to move from a higher to a lower potential. The *electromotive force* is a result

no measuring instruments, had been abandoned, the chief stress was laid upon the current strength and especially upon the *current density* at the cathode, *i.e.*, the current strength per 100 sq. cm. of cathode surface. The most favorable conditions for the deposition of a metal were determined experimentally and the directions for carrying out the analysis were given with a statement of the current density as the most important of the observed conditions. To be sure the potential of the bath as well was usually given. The directions applied to special apparatus (dishes, cones, etc.) and to a particular composition of the electrolyte. The current strength was adjusted by inserting an adjustable resistance between the source of the current and the electrolytic bath. When an electrolysis is started, under these conditions, with a definite current strength, it will be found in most cases that the current diminishes gradually in strength as the metal is being deposited. If, now, it is desired to increase the current, toward the end of the operation, so that the rate of deposition will be hastened, then with such an arrangement it is only possible to do this by increasing the electromotive force as well, for the current strength and electromotive force are mutually dependent upon one another. Often excellent results are obtained, but this is due to the fact that good deposits of metal, and sometimes good separations even, can be obtained when the two factors, current strength and electromotive force, vary throughout a considerable range. In such cases, the deposition of the last traces of metal can be accelerated by increasing the current strength without injuring the quality or purity of the deposit. In other cases, disturbances are likely to result; either, in a simple determination, the deposit becomes spongy, or, in a separation, it becomes contaminated with the metal from which the separation is to be made. Strictly speaking, every electrodeposition of a metal includes a separation, for under certain conditions hydrogen is likely to be set free at the cathode together with the metal to be determined. In fact the electric discharge of hydrogen ions together with the ions of the metal is the cause of many bad deposits, for the gas tends to form a hydride with the metal, and the subsequent breaking up of the hydride loosens up the surface of

of a difference in potential, but as both electromotive force and potential are measured in volts, and both have the same numerical value, the three terms *potential drop, electromotive force,* and *voltage* are used synonymously.

the deposit, making it spongy. In some cases the simultaneous discharge of hydrogen ions does no harm. The liberation of hydrogen while the metal is being deposited is accomplished in the same way that any two metals may be deposited simultaneously; in both cases the electromotive force is too great to permit a separation.

Kiliani (1883) was the first to point out the significance of the electromotive force in electrolysis.

It will be necessary, in order to explain the nature and significance of the electromotive force, to go into this matter a little more deeply and to consider how, according to the prevailing theory, this force originates; for, as we shall subsequently find, not only does the electromotive force, or potential, play an important part in electro-analysis but there results a second electromotive force, called *polarization,* which exerts an effect in the opposite direction (*cf.* p. 31).

If a substance soluble in water, *e.g.*, sugar, lies as a solid on the bottom of a beaker filled with water, then the molecules that lie close together in the solid substance tend to distribute themselves throughout the liquid, or, in other words, the substance dissolves. This tendency of the solid molecules to pass into the liquid may be regarded as a result of pressure and one may say that the solid substance possesses a *solution pressure.* If sufficient solid is present, then, as a result of diffusion, eventually the liquid will reach what we call the *state of saturation.* The liquid then contains an equal quantity of sugar in all its parts and at the prevailing temperature it will not take up any more sugar. There must also be some *cause* present which prevents a saturated solution from dissolving any more of the solid substance. This cause is designated as the *osmotic pressure* which the dissolved molecules exert in the solution. The dissolved molecules, like the molecules of gas over an evaporating liquid, exert a pressure which increases with their number; when the osmotic pressure produced by a sufficiently large number of molecules is equal to the solution pressure, then there is no further increase in the concentration of the solution and the solution is saturated. There is then an equilibrium established between the solution pressure and the osmotic pressure and there is just as much tendency for molecules to separate out from the solution, owing to the osmotic pressure, as there is for solid molecules to pass into solution because of the solution pressure. In the saturated solution, *i.e.*, in the solution which is in equilibrium with the solid, the solution pressure of the solid is exactly balanced by the osmotic pressure which the solution exerts. This process of dissolving sugar molecules involves no electrical effects; the same is true of the dissolving of salt because when the molecules ionize an equal number of cations and anions are formed so that the solution remains neutral.

Like the readily soluble substances, though to a lesser degree, the metals themselves have some tendency, when in contact with a liquid, to send their atoms into solution in the form of ions. This tendency is called the *electrolytic solution pressure* of the metals. On the other hand, the electrically charged ions of the metal also strive to pass over into the electrically neutral condition and the cause of this tendency is again the osmotic pressure. The electrolytic solution pressure of a metal and the osmotic pressure of its ions act mutually against one another in the same way as solution pressure and osmotic pressure.

The transformation of the atoms of a metal into the ionic condition, and conversely the transformation of an ion into the atomic condition, is closely related with the electrical phenomena which exist between the metal and the solution. The theory of solutions teaches that in a dilute solution of zinc sulphate there are present an equal number of positively charged zinc ions and negatively charged sulphate ions and the solution itself is electrically neutral. If a piece of zinc is placed in the solution, then, as a result of its electrolytic solution pressure, the metal sends some positively charged zinc ions, Zn^{++}, into solution and these ions collect around the metal and form a positively charged layer of liquid.

The electrolytic solution pressure has a definite value and the osmotic pressure which is opposed to it at any time is dependent upon the concentration of metal ions in solution. If, in Fig. 6, the arrows s.p. represent the value and direction of the electrolytic solution pressure of the metal, and if, as shown in the figure, it is greater than the osmotic pressure, ions pass into solution and the solution itself becomes positively charged while the corresponding negative charge remains upon the metal. Acting upon

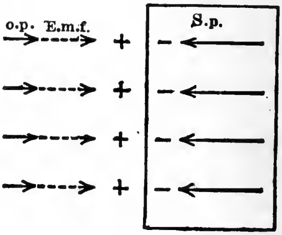

FIG. 6.

the ions in the vicinity of the metal is an electrostatic force which seeks to drive them back upon the metal. There is, therefore, an electromotive force, represented by the dotted arrows E.m.f., added to the osmotic pressure o.p. and it increases rapidly with the number of ions that pass into solution (1 gram equivalent carries a charge of 96,500 coulombs) and when the sum of the osmotic pressure plus the electromotive force is equal to the electrolytic solution pressure s.p., equilibrium results.

The conditions are somewhat analogous to the evaporation of a liquid; the liquid will evaporate until its vapor pressure is balanced by the pressure of the gas molecules. When any metal is placed in contact with a solution of its ions, more ions will enter the solution from the metal if the electrolytic solution pressure of the metal exceeds the osmotic pressure and the reverse phenomenon will take place in case the osmotic pressure exceeds the electrolytic solution pressure. In the former case, the metal becomes negative to the solution and in the latter case it becomes positive to the solution. It is customary to assume, according to Helmholtz, the existence of an *electrical double layer* at the junction of the metal and the solution. In the case of the zinc, referred to above, this consists of a negatively-charged layer on the metal and a positively-charged layer in the solution where it is in contact with the metal. The actual existence of such a double layer has been demonstrated by the work of Palmer.* It is important to bear in mind that whether ions pass from the metal into the solution depends not only upon the electrolytic solution tension of the metal but also upon the osmotic pressure already prevailing in the solution and this osmotic pressure is proportional to the concentration of the solution. The potential difference between the metal and the solution is a quantity which can be easily measured; it is called the *single potential* or the *oxidation potential* of the metal. The electrolytic solution pressure, on the other hand, cannot be measured directly. If, however, the oxidation potentials of the metals are measured against solutions of equivalent concentrations, these potentials will bear the same relation to one another as do the electrolytic solution pressures. Just as in determining the height of any object it is necessary to choose arbitrarily some zero level from which to measure, so in the same way it is desirable to choose an arbitrary

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* Z. phys. Chem., **25**, 265; **28**, 257; **36**, 364.

zero for measuring the oxidation potentials. A number of standard cells have been devised for this purpose. The usual standard for comparison is that of the hydrogen electrode. The zero potential, according to this standard, is that of an electrode consisting of a strip of platinized platinum, half in pure hydrogen gas and half in a normal solution of sulfuric acid. In accordance with this scale, the oxidation potentials of some of the more common elements and radicals against molal* concentrations of their ions are as follows:

Lithium	+3.03	Tin	+0.10
Potassium	2.93	Hydrogen	+0.00
Sodium	2.72	Copper	−0.34
Barium	2.8	Iodine	−0.52
Strontium	2.7	Silver	−0.80
Calcium	2.6	Mercury	−0.86
Magnesium	1.5	Bromine	−0.99
Manganese	1.08	Chlorine	−1.35
Zinc	0.77	Gold	−1.5
Iron	0.43	Hydroxyl, OH	−1.68
Cadmium	0.42	Sulfate, SO_4	−1.9
Cobalt	0.23	Acetate, $C_2H_3O_2$	−2.5
Nickel	0.22	Bisulfate, HSO_4	−2.6
Lead	0.12		

In the above table the positive sign has been assigned to those elements which have a greater tendency to form ions than does hydrogen.

The simple contact of a metal with a solution always results in a potential difference between the metal and solution except when the osmotic pressure exactly balances the electrolytic solution pressure. This, however, is not a permanent source of electricity because a state of equilibrium is reached quickly by either entry of ions into the solution or deposition upon the metal. If, however, two metals of different oxidation potential are placed in contact with their respective solutions, as in the Daniell cell, then electric charges of different potentials result and if the two metals are connected outside the liquids by a

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* A molal solution contains one *mole* per liter of dissolved substance. The word mole signifies a molecular weight in grams and when ionization takes place, a gram-ion is counted as a mole. Thus one mole of sodium sulfate, Na_2SO_4, when completely ionized furnishes two moles of sodium ions and one mole of sulfate ions. With respect to sodium ions, therefore, the molal concentration of the sodium sulfate solution is twice as large as it is with respect to sulfate ions. Inasmuch as the extent of the ionization of salts in solution is not positively known, it is extremely unfortunate that the values in the table should be referred to molal concentrations of the ions.

wire and within the cell the two solutions are also in contact with one another, an electric current flows from the higher potential to the lower. Since the original differences in potential are constantly re-established, a permanent current results. The positive to negative direction of the current is from zinc to copper *in the solution* and from copper to zinc *in the wire.* In the above table of oxidation potentials many physicists place negative signs to the values assigned to all the elements above hydrogen in the table and positive signs to those potentials below hydrogen. This is because the physicist thinks of the current as it flows *in the wire* from the Daniell cell and regards the copper as positive to the zinc. The chemist, on the other hand, has his attention fixed on the chemical changes involved and traces the flow of the current from the zinc to the copper *in the cell.* The chemist thinks of the elements at the top of the series as the more positive elements and, to him, it seems logical to assign positive values to the oxidation potentials of the elements which are most easily oxidized. According to this view, the potential is positive when the charge of the solution is positive to the metal.

Nernst, who suggested the above explanation of the origin of the electromotive force on the basis of osmotic relations, has worked out a formula for computing the potential difference which exists at the place of contact of a metal with a solution. If E denotes this potential difference expressed in volts, R the gas constant expressed in volts × coulombs, F the electrochemical equivalent or quantity of electricity required to deposit one equivalent weight in grams of any substance, n the valence of the metal ions, P the electrolytic solution pressure, p the osmotic pressure, and T the absolute temperature of the solution, the *Nernst formula* * reads

$$\text{E} = \frac{RT}{n\text{F}} \log_e \frac{P}{p}.$$

* This formula is derived with the aid of integral calculus. If one gram-ion of a metal is changed from the electrolytic solution tension P to the osmotic pressure p, the osmotic work done will be $\int_p^P v\,dp = RT \int_p^P \frac{dp}{p}$. Integrating this expression, we get

$$\text{Osmotic work} = RT \log_e \frac{P}{p}.$$

The corresponding electrical energy, $nF\text{E}$, using the notation as above, is equivalent to the osmotic work. Hence

$$nF\text{E} = RT \log_e \frac{P}{p}.$$

If, for R and F, we substitute their numerical values and divide by 0.4343 in order to use common logarithms instead of natural logarithms, the formula becomes

$$\text{E} = \frac{8.316 \times T}{0.4343 \times n \times 96{,}540} \log \frac{P}{p} = \frac{0.0001983\,T}{n} \log \frac{P}{p} \text{ volts,}$$

or, in round numbers,

$$\text{E} = \frac{0.0002\,T}{n} \log \frac{P}{p} \text{ volts.}$$

If we assume that the ordinary room temperature is 18° C., the value of T is $273 + 18 = 291$ and the formula becomes

$$\text{E}_{18^\circ} = \frac{0.058}{n} \log \frac{P}{p} \text{ volts.}$$

The total electromotive force of a galvanic element is equal to the difference between the single potentials and can be measured by inserting a voltmeter of high resistance between the poles of the element. In the Daniell cell, when the zinc sulphate and copper sulphate solutions are both of normal concentration, the total electromotive force of the element is the difference between the oxidation potential of zinc (+ 0.76 volt) and that of copper (− 0.34 volt) = 1.10 volts.

In the Nernst formula, the osmotic pressure, p, is determined by the concentration of the solution. If the concentration of a solution is decreased ten fold, the osmotic pressure in round numbers is also decreased ten fold and the value of the expression $\log \frac{P}{p}$ $(= \log P - \log p)$ is increased 1 unit. If the metal is univalent, the oxidation potential will be increased 0.058 volt, or 0.029 volt if the metal is bivalent. The table on page 26 shows that the oxidation potential of copper is − 0.34 volt against a normal solution bivalent copper ions. If the concentration of the cupric solution is reduced to 1×10^{-12} normal, then the oxidation of the copper will be practically 0.01. If the solution of cupric ions is more concentrated than this extremely low value, the oxidation potential of the copper will be less than that of hydrogen in the normal electrode.

Although in electro-analysis less depends upon the production of the current than upon its consumption, the above discussion will help one to understand the changes which take place in the deposition of metals; if a difference in potential is caused by the process of solution, which corresponds to the accomplishment of work, similarly, in the reverse process of depositing a metal, work must be expended in overcoming a difference in potential. It was mentioned on page 23, however, that potential differences arise in the electrolytic cell and work in opposition to these electromotive forces we have been discussing; this will be explained soon.

If two platinum electrodes are dipped into a solution of a metal salt and the electrodes are connected through a voltmeter, the instrument will not show any current. There are two reasons why no electromotive force results: first, because there is no reaction taking place at the unattacked electrodes and second, if the electrodes were attacked the reactions would be the same at each. If, however, the electrodes are connected with the poles of a source of electricity, then one will be positively charged and serve as anode while the other will be negatively charged and act as cathode. The charges on the ions will then become neutralized by the charges on the electrodes. The positive charge on the anode neutralizes the negative charge of the anions which are thereby changed to the atomic condition. Similarly, the negative charge on the cathode neutralizes the positive charge of the cations, which are likewise changed into the atomic condition and (in most cases) are deposited as such upon the cathode. This is the qualitative side of the process of electrolysis. The question now arises—What are the quantitative relations? Does an electromotive force produced at the electrodes cause in the electrolyte a current strength which corresponds to the resistance of the electrolyte? In other words, Does the process follow Ohm's law exactly as in the case of a metallic conductor? From the experiment described below one would at first sight conclude that this is not the case, but the subsequent explanation will show that Ohm's law is applicable in all cases. Imagine two platinum electrodes, each having a surface of 1 square centimeter, placed 1 centimeter apart in dilute sulphuric acid, so that the volume of liquid between the electrodes corresponds exactly to 1 cubic centimeter. With 5 per cent sulphuric acid this cube would have approximately 5 ohms resistance (*cf.* p. 20). If we send through this resistance a current of such a strength that the electromotive force is 0.5 volt between the electrodes, then, according to Ohm's law, the current strength would be $\frac{0.5}{5} = 0.1$ ampere provided the same conditions hold as in metallic conductors.

If the electromotive force is increased to 1 volt, then the current strength will be doubled and become 0.2 ampere. If these values are plotted (Fig. 7) with the abcissas representing volts and the ordinates amperes, the curve representing the ratio of volts to amperes will take the course of the straight line *OAB*. If, however, the actual values obtained by experiment are plotted on the diagram, starting with the voltage at 0, gradually strengthening it and measuring the current strength at 0.5 volt, 1 volt, etc., then the points *A′*, *B′*, *C′* will be obtained, and by connecting them the curve will show that the current strength increases much more slowly than would be expected from Ohm's law. Suddenly, at the point *C′*, which corresponds to 1.67 volts, the curve changes its direction and from this point the current strength increases more rapidly, as the line *C′D′* shows.

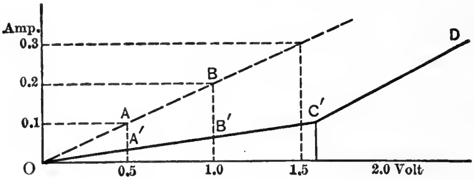

FIG. 7.

The diminution of the current-strength, and the apparent deviation from Ohm's law, $I = \frac{E}{R}$, could be accounted for by an increased resistance R, or by a diminished electromotive force E. As regards the resistance, it remains practically constant. On the other hand, it is easy to demonstrate that an electromotive force results between the electrodes which acts against that of the applied current. If, after the current has passed for a short time, the connection with the source of current is broken, and the circuit is closed again with a galvanometer or voltmeter inserted between the electrodes, a current flowing from the cathode to the anode through the acid will be detected and it will have the opposite direction to that of the original current. This current persists only a short time and the pointer of the voltmeter soon falls back to the zero reading.

Such a current is called a *polarization current* and its formation depends upon the nature of the substances set free at the electrodes. In the above case, the original current caused hydrogen to be evolved at the cathode and oxygen at the anode, *i.e.*, two gases. If the solution of a salt such as cupric chloride were electrolyzed, then copper would be deposited upon the cathode and chlorine set free at the anode, *i.e.*, a metal and a gas. This is the most common case in electro-analysis. In all cases, the original, unattacked electrodes become coated with foreign substances so that they behave like two different metals which are placed in contact with a solution and are striving to send ions into it (*cf.* p. 24); in place of the original cell Pt | $CuCl_2$ | Pt a new combination Cu | $CuCl_2$ | Cl_2 has been formed and this represents an active galvanic element. This is the opposing electromotive force in the cell which was referred to on page 23.

The potential of the polarization current, or the electromotive force of polarization, can be measured in several different ways (see below). If we designate the polarization potential as E_2, the potential of the original current as E_1, and the total resistance as R, then the equation representing Ohm's law for an electrolyte is

$$I = \frac{E_1 - E_2}{R} \quad \text{or} \quad E_1 = IR + E_2.$$

If, starting from the value zero, E_1 is made to increase slowly, measurements will show that at first E_2 is nearly equal to E_1, but as the value of E_1 increases, that of E_2 increases much more slowly, without, however, reaching a maximum.

The experiment with sulphuric acid, described on page 29 and illustrated by Fig. 7, shows that the electrolysis of the acid should not take place with a potential of less than 1.67 volts; the current strength with lower voltage currents is so slight that practically no current passes through the solution and consequently there is no appreciable decomposition of the electrolyte. All other acids behave like sulphuric acid and the same is true of solutions containing bases or salts, especially salts of the heavy metals, with which we are chiefly concerned in electro-analysis. There is for every electrolyte a certain value which must be given to the potential of the current in order to effect a permanent decomposition of the electrolyte. This value has been called the *decomposition potential* and LeBlanc has determined it for many electrolytes. The following table gives the decomposition potentials of a few salts in normal solutions: *

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* These decomposition potentials were measured by Le Blanc in 1891. The values given are those for the easiest possible decomposition. Thus, in

$ZnSO_4$ = 2.35 volts
$ZnBr_2$ = 1.80 volts
$NiSO_4$ = 2.09 volts
$NiCl_2$ = 1.85 volts
$Pb(NO_3)_2$ = 1.52 volts
$AgNO_3$ = 0.70 volt
$Cd(NO_3)_2$ = 1.98 volts
$CdSO_4$ = 2.03 volts
$CdCl_2$ = 1.88 volts
$CoSO_4$ = 1.92 volts
$CoCl_2$ = 1.78 volts

The decomposition potentials, which are to be regarded as the constant minimum of the polarization potential of a solution, vary, therefore, with different metals; the values are not far apart for the sulphates and nitrates of the same metal, as is shown in the table for the corresponding cadmium salts.

The decomposition potential E_d consists of the potential E_c required at the cathode for the deposition of the metal and of the potential E_a required at the anode to liberate oxygen or other element. Thus

$$E_d = E_c + E_a.$$

Since, however, the decomposition potential denotes the minimum potential that is required to cause an electric current to pass through an electrolyte, or, in other words, it represents the electromotive force opposed to the passage of the current that causes electrolysis, it is obvious that the main current must have a greater potential if a continuous flow or a suitable current strength is to be maintained.

The excess potential e_0 is dependent upon the Ohm's resistance R of the electrolyte and the desired current strength; according to Ohm's law

$$I = \frac{E_0}{R} \quad \text{or} \quad E_0 = IR.$$

The potential E which the voltmeter shows when placed in circuit between the electrodes during an electrolysis experiment is

$$E = E_d + E_0 = E_c + E_a + IR,$$

and from this the current strength I can be computed:

$$I = \frac{E - (E_c + E_a)}{R}.$$

This formula, therefore, expresses Ohm's law as it applies to electrolytes (*cf.* p. 29).

the case of zinc sulphate, the values are those obtained for the deposition of zinc on the cathode and liberation of oxygen (not SO_4) at the anode.

The same formula can also be used for determining the decomposition potential E_d of an electrolyte. From the equation

$$I = \frac{E - (E_c + E_a)}{R} \quad \text{or} \quad I = \frac{E - E_d}{R} \tag{I}$$

it follows that

$$E_d = E - IR.$$

In this last formula, E is the potential of the bath as shown by the voltmeter, I is the current strength shown by the ammeter, and R is the resistance of the electrolyte which can be determined as described on page 19.

The resistance value R can be eliminated from the formula by making two observations with changed current strength; for if, in a second observation, it is found that

$$I_1 = \frac{E_1 - E_d}{R}, \tag{II}$$

then from the equations (I) and (II) we find that

$$E_d = \frac{I_1E - IE_1}{I_1 - I}.$$

If in this way the value of E_d is known, then the value for R can be computed from either equation (I) or equation (II).

The decomposition potential of any given solution can be measured by placing two platinum wires in the solution to serve as electrodes and allowing the current to increase gradually in strength until a constant reading is obtained with a sensitive galvanometer placed in the circuit.

These decomposition potentials are important for two reasons; first, because they represent the minimum electromotive force that is required to effect the deposition of a metal, and second, because they show how certain metals can be separated quantitatively from one another by varying the potential. For example, if a solution contains silver nitrate and zinc sulphate, the table shows that it is possible to deposit the silver with a current at 0.7 volt while the zinc will not be deposited until the electromotive force is raised to 2.35 volts. Thus, by keeping the potential above 0.7 volt and below 2.35 volts, the silver can be deposited quantitatively and then, by raising the potential above 2.35 volts, the zinc can be deposited.

As already mentioned, Kiliani was the first to recognize the importance of the potential of the current in electrolytic separations. Profiting by the studies of LeBlanc, Freudenberg, working in Ostwald's laboratory, was able subsequently to study such relations more accurately. Use was made of these studies in methods described for determining and separating certain metals. The fact that this principle of effecting electrolytic separations by graded potentials is not applicable to all separations will be shown later.

Ordinarily, the electromotive force of the cell is measured by means of a voltmeter which shows, in volts and fractions thereof, the drop in potential that takes place in the electrolyte between the two electrodes. The voltmeter is in reality an ammeter with a large internal resistance, whereas the ammeter, which serves to measure the current strength, must have as little resistance as possible because it is placed in the circuit and must not diminish the current strength appreciably. The two wires leading to the voltmeter are each attached to one of the electrodes; the instrument is then connected as a shunt to the circuit and in parallel with the electrolyte. The resistance of the voltmeter is so great that nearly all of the current continues to pass through the cell with a practically unchanged electromotive force and only an inappreciably small fraction of the whole current passes through the voltmeter. If the resistance of the voltmeter were much less, then too large a fraction of the whole current would pass through the instrument and as a result less current would pass through the electrolyte so that the drop in potential between the electrodes would be noticeably less than when the voltmeter was disconnected.

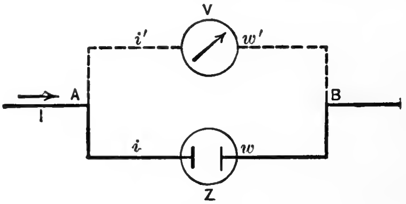

FIG. 8.

Let us assume that an electrolytic cell Z is placed between the points A and B (Fig. 8) in a circuit and that it is desired to measure the electromotive force E between A and B by means of the voltmeter V. The current strength I, which prevails in the circuit AZB before the insertion of the voltmeter, is changed, after the introduction of the voltmeter, into the two current strengths, i in *AZB* and i' in *AVB*; thus $\mathrm{I} = i + i'$.* If, now, r and r' are the respective resistances in the two branch circuits, then

$$i = \frac{\mathrm{E}}{r} \text{ and } i' = \frac{\mathrm{E}}{r'},$$

and consequently

$$i + i' = \mathrm{E}\left(\frac{1}{r} + \frac{1}{r'}\right) = \frac{\mathrm{E}}{\dfrac{rr'}{r + r'}}.$$

Since $\dfrac{rr'}{r + r'}$ is smaller than r, it is obvious that the potential E will always become smaller as a result of introducing the shunt, but it remains at approximately its original value when r' is very large. In the latter case, i' becomes very small and i retains approximately the original value I.

The voltmeter serves, as mentioned, to measure the difference in potential between any two points in the circuit, usually the electrodes of the cell. In electro-analysis, however, it is often necessary to determine a single potential and the following discussion will show how this can be done.

As stated on page 24, there result at the place of contact between metal and liquid in a cell certain differences in potential which are independent of one another and these differences are the cause of the electromotive force of the cell.

These single potentials are also called *potential drops.* In all parts of the circuit between the electrodes, outside as well as within the element, the potential falls continuously if measured between any point and the point with the lowest potential. At the place of contact of metal and liquid, however, there is a sudden change in the potential, or drop.

Such drops in potential also result at the platinum electrodes in an electrolyte when the electromotive force of the primary current has reached the decomposition value, and the electromotive force of the polarization current, just as that of the ordi-

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* Strictly speaking the current strength I is increased slightly by placing the voltmeter in the circuit because the resistance of the entire system is slightly diminished by giving the current another path to traverse; this increase in current is so slight that it need not be taken into consideration in the above explanation.

nary galvanic element, may be regarded as the difference between two independent potential drops, one at the cathode and one at the anode (p. 25). When the decomposition potential is exceeded the metal of the electrolyte appears upon the cathode so that *at the decomposition point of the solution the potential drop at the cathode must be equal to the difference in potential which the metal deposited on the cathode shows independently toward the solution* (LeBlanc).

The knowledge of the single-potential differences has become of great importance in electro-analysis. Formerly, in depositing a metal from a solution, one was content to know the total difference in potential between the two electrodes; the bath was given a somewhat greater voltage than corresponds to the decomposition value (p. 32). It was believed that two metals could be separated, if, as in the example on page 33, the voltage was kept between the decomposition potentials of the two metals and then, after one metal was deposited completely, the voltage was raised above the decomposition value of the second metal. From the studies of LeBlanc, however, a much more accurate rule to follow has been obtained; it is important that the cathode, upon which the metal is to be deposited, shall be brought to at least the potential which the metal itself shows toward the solution. Many failures attendant upon former analytical directions can be traced to the nonobservance of this rule. That it is not always sufficient to measure the total voltage and to regulate it in the deposition of a metal, or in the separation of two metals by electrolysis, is obvious when one remembers that the total voltage is the sum of the potential drops at the cathode and at the anode. Since these two drops in potential are independent of one another and since they change during the progress of the analysis, owing to the diminishing concentration of the salt in solution, and in fact these changes are independent of one another, it may happen in a simple deposition of a metal that the cathode potential may change in a manner unfavorable for the complete deposition, and at the same time the potential at the anode may change independently in such a way that the total voltage will remain about the same as at first. Thus in the deposition of a metal the point may be reached where the unfavorable evolution of hydrogen takes place before all the metal is deposited. In a separation of two metals, the cathode potential may reach a value which permits the deposition of the second metal so that a quantitative separation becomes impossible.*

It may be well, here, to explain the principles underlying the measurement of these single potentials. Since, however, the measurement of a single potential almost always depends upon the measurement of a potential difference between two single potentials, of which one is known, the first thing to describe is how a potential difference is measured. The ordinary method for doing this is Poggendorff's *compensation method.*

Just as the measurement of resistances is based upon the comparison of the resistance to be measured with a known resistance in the Wheatstone bridge (*cf.* p. 18), so, for the measurement of potential differences, or electromotive forces, a source of current is used which possesses a known and unchangeable electromotive force. Such a source of current is the so-called *normal element, e.g.*, the Weston element. One pole of this element consists of mercury in contact with mercurous sulphate and the other of cadmium in contact with cadmium sulphate. The salts of the metals are not contained, however, in solutions of varying concentrations as in ordinary elements but are present in the form of solid salts in contact with saturated solutions, whereby the action of the element becomes constant.† The chemical reactions which cause the current are metallic cadmium going into solution at the cadmium pole and mercury depositing from mercurous sulphate at the mercury pole, just as in the Daniell element zinc is dissolved and copper deposited. The current in this normal element flows within the cell from the cadmium to the mercury and outside the cell from the mercury to the cadmium. The electromotive force of the Weston element is $1.0186 - 0.00038\,(t - 20)$ volts; t is the temperature of the element when in use, and is usually the labora-

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* Similar relations prevail in ordinary analytical chemistry. If, for example, some silver nitrate solution is added gradually to a solution containing both sodium chloride and potassium chromate, at first silver chloride will be precipitated, and it is only when an excess of silver solution is present that the chromate is acted upon and silver chromate precipitates.

† The solution always remains saturated with both salts; in this way a constant concentration of the salts, upon which the electromotive force depends according to Nernst's formula, is maintained. Otherwise the utilization of the current from the cell would result in increasing the concentration of the zinc sulphate and diminishing that of the mercurous sulphate, and the electromotive force of the element would then vary.

tory temperature. The correction member of the formula shows that the electromotive force of the element is only very slightly influenced by changes in temperature.

The measurement of the electromotive force is carried out as follows: A circuit is established consisting of a storage cell, or accumulator, *A* (Fig. 9) and a wire *BC* of uniform cross section and high resistance; there then prevails in the wire between one end of it, *B*, and any other point, *D*, *D′* or *C*, a certain drop in potential which can be measured by means of the normal element. To do this, another electric circuit *BGED*, containing the normal element E and a sensitive galvanometer *G* (see p. 43), is connected at *B* in such a way that the current in this second circuit flows in the opposite direction *e* to that of the other current which has the direction *a*. Then by moving the sliding contact *D* along the wire *AC*, a point will be found for which the galvanometer *G* shows the passage of no current. Then the drop in potential between the points *B* and *D* is equal to the electromotive force of the normal element E, namely 1.0186 volts at 20°.

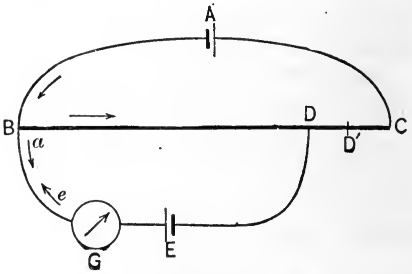

FIG. 9.

If, now, in place of the normal element E an unknown electromotive force E_x is introduced and the sliding contact is moved to a point *D′* for which the galvanometer reading is zero, then the unknown electromotive force E_x is to that of the normal element 1.0186 as the length of wire *BD* is to the length *BD′*. These lengths are known in millimeters, and

$$E_x = 1.0186\frac{BD'}{BD}$$

is the desired electromotive force.

There is, therefore, no difficulty in determining a difference of potential; *i.e.*, with any given element whose cathode potential is E_c and whose anode potential is E_a, it is easy to measure the value $E_c - E_a$ in volts. This, however, gives us no information concerning the two single potentials E_c and E_a. If, on the other hand, we are able to prepare an element in which one of the two single potentials has the value zero, then evidently the determination of the electromotive force of this element will give directly the value of the other single potential.

Such an element is obtained by placing some metallic mercury in a glass vessel, covering it with dilute sulphuric acid and introducing into the acid, from above, a capillary tube through which mercury flows in fine drops. If the mercury resting at the bottom of the vessel is connected by a wire with the mercury in the tube from which the mercury drops, a current can be detected which flows from the mercury at the bottom to the mercury in the dropping tube. The electromotive force of such an element can be measured, and since Helmholtz has concluded from theoretical considerations that the upper electrode (drop electrode) possesses the potential zero,* it is evident that the electromotive force of this element represents the potential of the mercury resting at the bottom of the vessel.

This is not the place to discuss the theory of such an element; it may be mentioned merely that we are dealing here with one of the so-called *concentration cells.* We have seen (p. 26) that different metals placed as electrodes in an electrolyte assume different potentials and that consequently a current will pass between two such electrodes if the outside ends are connected by a wire. We have also seen (p. 29) that two strips of one and the same metal placed in the same electrolyte will show no potential differences. If, however, two electrodes of the same metal are placed opposite to one another in an electrolyte in which the concentration at one pole is greater than it is at the other, then a difference in potential results; the metal in contact with the more dilute solution is ionized, or dissolved, and at the opposite electrode these ions are discharged or deposited. Thus, on closing such a circuit, a current flows inside the cell from the lower concentration to the higher concentration. Nernst has called such an arrangement a *concentration cell.*

When mercury is in contact with dilute sulphuric acid it can be assumed that slight traces of mercurous ions pass into solution; these ions result either from the presence of slight traces of mercurous oxide adhering to the metal, which dissolve in the acid, or the oxide may be formed on the mercury from dissolved oxygen that is present in the acid used. The potential of the still mercury in the element with the drop electrode is due to the

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* Nernst has questioned the correctness of this assumption.

contact of metallic mercury with the solution of its ions; and, in fact, this potential is negative, because, as was shown on page 25, the solution pressure of the noble metals is very slight, being less than the osmotic pressure of the corresponding ions.

The single potential of the mercury toward the solution of mercurous ions, measured as described above, remains the same if, as indicated on page 39, we prepare an element in which one of the electrodes consists of mercury in contact with mercurous ions while the other electrode consists of any given metal in another electrolyte. The electromotive force of such a cell can be measured by the compensation method (see p. 38), and it is only necessary to deduct from the number of volts thus found the known potential of the mercury electrode in order to obtain the potential of the other electrode.

This is a rough outline of the principles involved in the measurement of single potentials and it remains only to mention how the measurements are made in practice. It was stated above that we have to prepare a cell from the mercury electrode and the electrode whose potential we desire to measure. This must be done without disturbing the electro-analysis in the interest of which such a measurement is to be made and to accomplish this a so-called *auxiliary* or *normal electrode* is used; it is connected, as described below, with the electrode whose potential is to be measured. The glass vessel shown in Fig. 10, at one half its true size, contains at the bottom a layer of mercury and the latter is connected with a binding post by means of some platinum wire fused in the glass. The mercury is covered with a layer of mercurous sulphate *M*, and the vessel is nearly filled with 2 N-sulphuric acid, saturated with mercurous sulphate. The glass tube fused on the side carries in the middle

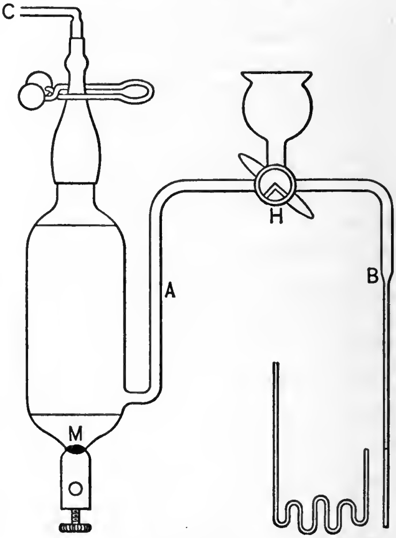

FIG. 10.

of the horizontal arm a stopcock *H* with a funnel fused to it. In the drawing the cross section of the stopcock is drawn to show the right-angled boring that it contains, by means of which the funnel can be connected either with the half *A* or the half *B*, or, when the stopcock is in the position shown in the drawing, all connections are broken. If, at the start, connection is made with *A*, then, on opening the pinchcock and blowing in air at *c*, the acid can be driven over until it reaches the stopcock *H*, when the connection is broken by turning the stopcock and thus the half of the tube marked *A* is filled once for all with the acid.

If the funnel is next connected with the half of the tube *B*, then this half of the tube can be filled with any desired solution. The tube *B* ends in a capillary which is bent up and down a number of times and finally points upward. The shape of this capillary is shown in Fig. 10 by a separate drawing; in reality the plane in which the bendings lie is perpendicular to the plane of the paper. This shape of the end of the tube is devised to prevent, as far as possible, the mixing of the electrolyte with the contents of the tube *B*. The liquid chosen is one that is indifferent toward the electrolyte and ordinarily consists of a solution of sodium sulphate.

This arrangement represents, therefore, the bottom layer of mercury, as described in the element with drop electrode, in contact with a solution containing a very few mercurous ions, as mercurous sulphate is only slightly soluble. The sodium sulphate solution serves merely as an indifferent conducting liquid, for if the end of the capillary tubing is dipped into an electrolyte, then the sodium-sulphate solution serves to make connection between the electrolyte and the sulphuric acid in *A* because the sulphuric acid and the sodium-sulphate solution are in contact with one another in the capillary space around the *ungreased* stopcock which is turned so that connection is broken on all sides.

If then the opening of the mouth of the capillary tubing is brought as close as possible to the electrode whose potential it is desired to measure, touching, for example, the gauze cathode (Fig. 24) upon which a copper deposit is forming, and the electrode is connected by means of an outside wire with the binding post of the auxiliary electrode, then this combination forms a galvanic element consisting of mercury | mercurous sulphate | electrolyte | copper.

We have prepared in this way, therefore, the desired element whose electromotive force, which is to be measured, results from the potential drop at the cathode (in this case at the coating of copper upon the gauze electrode) and the potential drop at the mercury of the auxiliary electrode; the latter value is known once for all time. Consequently it is necessary merely to measure the electromotive force of this element according to the method described on page 38 and then the potential of the metal in question against the electrolyte can be computed.

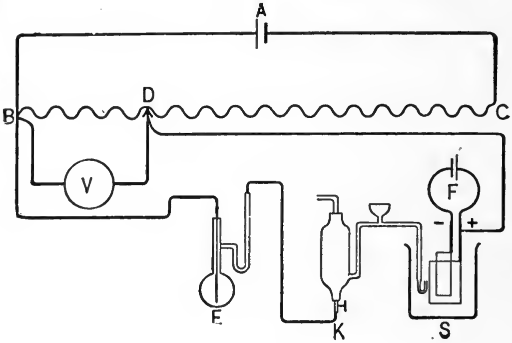

FIG. 11.

When an electrolysis is taking place, we have seen that the cathode potential tends to rise in the course of the operation and this is disadvantageous for the deposition of certain metals. It is desirable, therefore, to keep the potential constant, and since the potential of the auxiliary electrode remains constant it becomes a question merely of keeping the electromotive force of the above-described auxiliary element constant and, indeed, at a value which has been found favorable by previous investigators.

This is accomplished by means of the arrangement devised by H. J. S. Sand* to whom thanks are also due for the form of auxiliary electrode shown in Fig. 47 (see Part II).

The storage cell *A* is the source of the current in the circuit *ABCD* (Fig. 11), the most important part of which is the sliding rheostat wire *BC*. From the latter starts the branch circuit *BEKSD*, through which a part of the current flows from the storage cell and is opposed to the electromotive force of the aux-

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* The Rapid Electrical Deposition and Separation of Metals. Transactions of the Chemical Society, **91,** 380 (1907), London.

iliary element *KS*. By moving the sliding contact *D*, the potential difference *BD* in the sliding rheostat is changed until it exactly balances the electromotive force of *KS* as is shown by the zero reading of the capillary electrometer *E*, to be described below. The potential difference between the points *B* and *D* is then read directly by means of a sensitive voltmeter which is connected at *B* and *D*. The voltage thus determined is also the potential difference of the auxiliary element *KS*; this value is to be kept constant, which is accomplished by regulating the current used for the analysis in the way described under Bismuth in Part II.

The capillary electrometer referred to is that devised by Lippmann* and consists, in its most useful form, of a small glass flask (shown in Fig. 12, in natural size) with a capillary tube *A* fused to one of its sides; the capillary leads to the bottom of the tube *B* which is 6 mm. wide. The little flask is half-filled with mercury and upon the latter rests a saturated solution of mercurous sulphate in dilute sulphuric acid (1 vol. H_2SO_4 : 6 vols. H_2O). The acid is in contact with mercury at about the middle of the capillary tube and mercury is present in the arm *B* to the height shown in the figure. A platinum wire dips in the mercury of the arm *B*, and the free end of a second platinum wire, fused in narrow glass tubing to prevent contact with the acid, dips into the mercury at the bottom of the flask. The action of the instrument as electrometer can be explained as follows: Since mercury is a liquid that does not wet glass, it follows from the laws of capillarity that the surface of the mercury in the communicating tubes *A* and *B* will be lower in the capillary tube than in the wider tube. The cause of this phenomenon is the surface tension of the mercury which can be imagined to act as an elastic membrane surrounding the whole mass of mercury. The surface

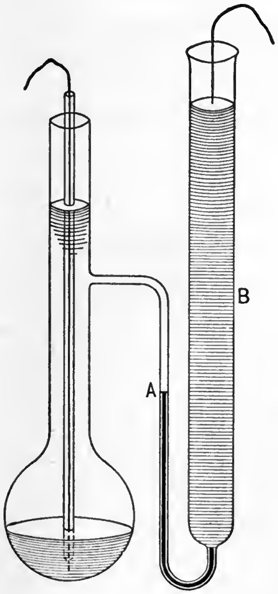

FIG. 12.

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* It is here used as a *zero instrument, i.e.*, not to measure a current but to detect the absence of a difference in potential.

tension strives to reduce the volume of the mercury to a minimum, as is evidenced by the curved surface. If, however, forces come into play that are opposed to this surface tension, then the mercury level rises in the capillary tube and the surface becomes flatter.

Without entering more into the particulars of the theory of the instrument, it may be said that differences in potential at the surface of the mercury change the surface tension, so that, for example, when a weak current passes through the mercury of the flask and the sulphuric acid to the mercury in *A*, the level falls. If, now, the current produced between *B* and *D* by the storage cell in the arrangement shown in Fig. 11, p. 42, is to be made equal to that produced by the element *KS*, it is only necessary to move the sliding contact *D* back and forth until the capillary electrometer shows the zero reading. To facilitate the accurate observation of the mercury level in the capillary *A*, a small microscope is attached to the same upright rod that holds the electrometer.

The use of the apparatus is further illustrated under the determination of bismuth.

Procedure in Electro-Analysis.*

ACTION OF THE CURRENT UPON THE ELECTROLYTE.

When it is desired to accomplish the electrolytic deposition of a metal from a solution, the first question that arises is: What is the most favorable composition of the solution to be analyzed? Even in an ordinary gravimetric analysis the nature of the solution in which the precipitation takes place is not a matter of indifference. In the case of electro-analysis no altogether general rules can be given; in practice most of the common electrolytes have been studied with regard to their qualitative and quantitative composition and in carrying out a deposition it is not safe to depart far from the directions that are given. To be sure, theory has served to clear up many points although it has not yet developed enough to act as the sole guide.

The preparation of the electrolyte is stated, therefore, in every case and only a few general points will be mentioned. In the

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* The description and pictures of the complete electrical equipment of the laboratory as given in former editions of this book is now omitted, for the most part, because the technique of this branch of science is progressing rapidly and forms of apparatus are rapidly changing. There are now a number of concerns who stand ready to supply all the necessary apparatus.

first place it would seem desirable, when possible, to use the ordinary salts of the metal in the form in which they are present in solution by the preliminary operations of analysis. The use of such solutions as the chlorides and sulphates, however, is exceptional, as will be seen from the description of the individual methods; nitrates are in most cases wholly unsuited. As regards complex salts, they will be discussed a little later.

A few examples will be given here to illustrate the reactions that take place in electrolytes through which a current is passing, whereby, in the sense of the older theory of electrolysis, "the current decomposes the solutions" (*cf.* p. 3).

Simple Electrolytes.

The passage of an electric current through a solution always accomplishes a chemical oxidation at the anode and a chemical reduction at the cathode. The passage of 96,500 coulombs of electricity (1 Faraday) causes a gram atom of some element to gain one positive charge or lose one negative charge at the anode and simultaneously a gram atom of some element loses one positive charge or gains one negative charge at the cathode. Meanwhile the cations in the solution are being attracted toward the cathode and the anions are migrating toward the anode.

The rates at which the ions migrate vary with different ions and usually the *migration* velocity of the cation is different from that of the anion. During every electrolysis, more ions are charged or discharged at each electrode in a given interval, than are brought to it by the migration of the ions. Ions in the vicinity of each electrode are acted upon irrespective of whether they have actually taken part in the transport of electricity through the solution. In many cases the reactions at the electrodes are with substances which are not ionized very much and which cannot take part to any extent in the movement of electricity through the solution.

This fact has already been mentioned (p. 6) and it is taken up again at this point because it is contrary to views which once prevailed.

The reduction that takes place at the cathode or the oxidation that takes place at the anode is always the easiest oxidation or reduction which it is possible to accomplish under the prevailing conditions. The conductivity of the solution depends upon the presence of ions in the solution, but many substances are capable of oxidation and reduction which are not ionized to any extent. The table on page 26 shows the oxidation potential of various metals in contact with solutions of their ions molal. To reduce these metals from the ionic condition to that of the free metal it is necessary to overcome the oxidation potential of the metal. In other words, the decomposition potential is reached as soon as the oxidation potential is overcome. The metals at the bottom of the series, therefore, are the ones which it is easiest to deposit upon the cathode. The Nernst formula, page 27, shows that this oxidation potential increases as the solution is more dilute; it follows, therefore, that more electromotive force is required to discharge ions from a dilute solution than from a concentrated one.

If a solution of copper sulphate is subjected to electrolysis the conductivity of the solution is due to the presence of cupric and sulphate ions; the former migrate toward the cathode and the latter toward the anode. In a 0.1–normal solution the cupric ions move about 0.6 as fast as the sulphate ions. The passage of 96,500 coulombs of electricity from pole to pole will be accompanied by a movement of the ions in proportion to their rates of migration; $96{,}500 \times 0.625$ coulombs will be carried by the anions and the balance, $96{,}500 \times 0.375$ coulombs will be carried by the cations. At the cathode a gram equivalent of copper, $\frac{\text{at. wt.}}{2} = 31.5$ grams, will be deposited by this 96,500 coulombs of electricity. Adopting the convention of representing a unit charge of positive or negative electricity by the symbols $\oplus$ and $\ominus$, the reduction at the cathode may be expressed as follows:

$$\text{Cu}^{++} + 2\ominus = \text{Cu}.$$

In the copper sulphate solution the only other conceivable reductions would be that of hydrogen from water or sulphur from the sulphate. Both of these last two reductions are harder to accomplish than that of cupric ions to the metallic state. The table on page 26 shows that copper is below hydrogen in the potential series; hydrogen, moreover, has a much higher oxidation potential against the low concentration of hydrogen cations in pure water than against a normal solution of hydrogen ions. If the copper sulphate solution contained free sulphuric acid, however, the time might come when it would be easier to discharge hydrogen ions from the acid than to discharge the cupric ions from the dilute solution.

At the anode the easiest oxidation depends somewhat upon the nature of the electrode. If a copper anode is used in the electrolysis of a copper sulphate solution, the easiest oxidation will be that of copper from the metallic to ionic condition.

$$Cu + 2 \oplus = Cu^{++}.$$

In this case, the same quantity of copper dissolves at the anode as is deposited at the cathode and the total concentration of the solution in cupric ions remains unchanged. If, on the other hand, the anode is platinum, this metal does not dissolve easily as the oxidation potential is very low. The only other possibilities are, first, the discharge of the sulphate ions, second, an oxidation of the sulphur, third, an *oxidation of oxygen.* The elements hydrogen and copper are already in their highest state of oxidation. As regards the first possibility, there is no good evidence that free SO_4 can exist by itself. It has often been assumed that $SO_4^{=}$ anion can be discharged and that it immediately reacts with water but this assumption does not seem reasonable when all the facts are considered. The second possibility is that of the formation of persulphate ions and under certain conditions this does take place:

$$2SO_4^{=} + 2 \oplus = S_2O_8^{=}.$$

Under ordinary conditions, however, this is not the easiest oxidation and there is no appreciable quantity of persulphate anions formed. In the electrolysis of a dilute aqueous solution of copper sulphate between platinum electrodes the easiest oxidation is that of oxygen from the negative condition to that of neutral oxygen gas:

$$H_2O + 2 \oplus = 2H^{+} + O_2.$$

The behavior of sodium chloride solution upon electrolysis has already been mentioned (page 5). The table of oxidation potentials (page 26) shows that sodium ions are much harder to discharge than hydrogen ions. The difference in oxidation potentials is so great that, in accordance with the Nernst formula (page 27), it is easier to discharge hydrogen from water than sodium ions from a normal solution of sodium chloride. In fact, metallic sodium decomposes water because its oxidation potential is greater than that of hydrogen toward water. In the electrolysis of sodium chloride solution, therefore, the current is carried from pole to pole by the sodium and chloride ions. At the cathode, unless it is composed of mercury, the easiest reduction is that of hydrogen:

$$2H_2O + 2 \ominus = 2OH^- + H_2.$$

If, however, a mercury cathode is used it is possible to obtain sodium amalgam. This simply means that it is easier to reduce sodium from the ionic condition in water to that of sodium dissolved in mercury than it is to reduce sodium from the ionic condition to that of the free element. It does not prove, as has been argued falsely, that sodium is always set free momentarily and then decomposes water.

At the anode, chlorine is set free during the electrolysis of sodium chloride provided the anode is not attacked.

$$2Cl^- + 2 \oplus = Cl_2.$$

As the concentration of the Cl^- anions in the solution decreases, the decomposition voltage increases and eventually it becomes easier to discharge oxygen from water than to discharge chlorine from the dilute solution. Moreover, if the conditions are favorable, the oxidation at the anode may change the chlorine into hypochlorite anions or even chlorate anions.

$$Cl^- + H_2O + 2 \oplus = ClO^- + 2H^+,$$
$$ClO^- + 3H_2O + 6 \oplus = ClO_3^- + 6\,H^+.$$

Copper is sometimes deposited electrolytically from a solution containing free nitric acid. Nitric acid itself is susceptible of cathodic reduction and, indeed, the reduction of the nitrogen may go from the quinquivalent positive condition to that of trivalent negative nitrogen in ammonia or ammonium salt (in the latter the nitrogen has four negative charges and one positive charge):

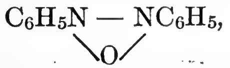
$$NO_3^- + 9H^+ + 8 \ominus = NH_3 + 3H_2O.$$
$$NO_3^- + 10H^+ + 8 \ominus = NH_4^+ + 3H_2O.$$

If the conditions are such that any considerable quantity of nitrous acid is present in the solution at any time, this compound is so easily reduced that it will not only interfere with further deposition of the copper but will cause the oxidation and solution of copper which has already been deposited. It is because of this possibility of forming nitrous acid at the cathode that nitric acid solutions are, in general, avoided for electrolytic operations.

Nitric acid at the anode is stable and the easiest oxidation in the electrolysis of nitric acid solutions is that of the oxygen from water; it is evolved as gas as in the electrolysis of sulphuric acid solutions.

It is often true that a reduction or oxidation once started will go beyond the primary stage. After two positive charges have been neutralized on the nitrogen atom in the nitrate anion, it is easier to neutralize the remaining positive charges than it was to take away the first two. An analogous condition is in the discharge of the cupric ion. The decomposition of potential of cuprous ions is so low that most cuprous compounds cannot exist in aqueous solution except in low concentrations. In other words, the stable cuprous salts are not very soluble in water. In the electrolysis of solutions containing cupric ions, therefore, cathodic reduction will cause deposition of metallic copper because it is easier to neutralize two positive charges on one cupric cation than to neutralize one positive charge on two cupric ions. In the electrolysis of a cupric chloride solution, however, this is not the case. As the cupric ion loses one charge it enters into equilibrium with the chlorine anions and insoluble cuprous chloride is formed and the concentration of the cuprous ions is so low that it is easier to reduce fresh cupric ions than to deposit metallic copper.

The presence of organic substances in solutions undergoing electrolysis often has an effect upon the products obtained at the anode and at the cathode. Some of these substances, such as the salts of organic acids, are electrolytes and take part in the conduction of the current; they are also subject to oxidation and reduction at the electrodes. At the cathode it is possible, for example, to reduce nitrobenzene, $C_6H_5NO_2$, to

C_6H_5NO, C_6H_5NHOH,  $\underset{\diagdown O \diagup}{C_6H_5N - NC_6H_5}$, $C_5H_5N{=}NC_6H_5$,

$C_6H_5NH \cdot NHC_6H_5$, $H_2NC_6H_5 \cdot C_6H_5NH_2$ and finally to $C_6H_5NH_2$.

The complete reduction of nitrobenzene to aniline may be expressed as follows:

$$C_6H_5NO_2 + 6H^+ + 6\ominus = C_6H_5NH_2 + 2H_2O.$$

Electrolysis of a solution containing acetate ions results in the formation of ethane and carbon dioxide at the anode:

$$2C_2H_3O_2^- + 2\oplus = C_2H_6 + 2CO_2.$$

Similarly, succinate ions may be oxidized to ethylene and carbon dioxide:

$$C_2H_4(CO_2)_2^= + 2\oplus = C_2H_4 + 2CO_2.$$

Lactate ions are changed to acetaldehyde and carbon dioxide:

$$C_3H_5O_3^- + OH^- + 2\oplus = CH_3CHO + CO_2 + H_2O.$$

Oxalate ions are changed to carbon dioxide:

$$C_2O_4^= + 2\oplus = 2CO_2.$$

In the decomposition of an alkali oxalate, hydrogen is set free at the cathode from water

$$H_2O + 2\ominus \rightarrow H_2 + 2OH^-,$$

and some of the CO_2 evolved at the anode may react with the hydroxyl,

$$2OH^- + CO_2 \rightarrow 2HCO_3^-.$$

Complex Electrolytes

It is sometimes desirable to electrolyze a solution containing a metal in the state of complex ions. Thus copper may be present as copper ammonia ions, $Cu(NH_3)_4^{++}$. Such a solution requires more electromotive force to reduce the copper to the metallic condition because the discharge potential of the copper is greater in proportion as the solution contains fewer cupric ions. On the other hand, it is much harder to discharge hydrogen from the ammoniacal solution than from an acid solution so that there is less danger of the nature of the deposit being influenced by the simultaneous deposition of hydrogen with the copper. In the case of nickel, it is impossible to deposit this element from an acid solution as it is easier to discharge hydrogen ions but from an ammoniacal solution containing nickel-ammonia ions all of the nickel can be deposited on the cathode.

The situation is somewhat more complicated in the electrolysis of a slightly alkaline solution of potassium cuprocyanide, $K_3Cu(CN)_4$. This salt in aqueous solution ionizes as follows:

$$K_3Cu(CN)_4 \rightleftarrows 3K^+ + Cu(CN)_4^{\equiv}.$$

The $Cu(CN)_4^{\equiv}$ ions are also in equilibrium with Cu^+ and CN^- ions, but whereas the primary ionization takes place to a very considerable extent, it has been estimated that the ratio of the concentration of the complex ion, $Cu(CN)_4^{\equiv}$, to simple cuprous ion, Cu^+, in a normal solution of potassium cyanide is as $10^{26} : 1$. The discharge potential of cuprous ions, however, is much lower than that of cupric ions of equivalent concentration.

As far as the conduction of the electric current is concerned, the $Cu(CN)_4^{\equiv}$ anions migrate toward the anode. They are, however, not discharged there if the solution contains simple cyanide ions, because the easiest oxidation is as follows:

$$2CN^- + 2 \oplus = (CN)_2.$$

At the cathode, on the other hand, it is easier to discharge cuprous ions of very low concentration than potassium ions of high concentration so that the reaction at the cathode may be expressed as follows:

$$Cu(CN)_4^{\equiv} + \ominus = Cu + 4CN^-$$

It is easy to understand that a higher potential and higher current strength will be necessary to deposit the copper from such a complex ion than from that of a simple copper salt. If, on the other hand, it is desired to separate copper from cadmium by electrolysis, it is possible to change the order of deposition. In an acid solution the copper can be deposited quantitatively and no cadmium ions will be discharged as long as the solution remains acid. In a potassium cyanide solution cadmium forms complex $Cd(CN)_4^{=}$ anions, but the ratio of the concentration of the complex ion to that of simple cadmium ions in a normal potassium cyanide solution is about $10^{17} : 1$ and it is easier to deposit cadmium from such a solution than copper. By stirring the solution it is possible to keep some of the anions in the vicinity of the cathode even although the current tends to carry them toward the anode.

Potassium cyanide solution is an excellent solvent for silver salts and such solutions are much used for silver plating. The silver exists in such solutions in the form of $Ag(CN)_2^-$ anions. If a potassium cyanide solution of a silver salt is electrolyzed with a silver anode, the easiest oxidation at this electrode will be the solution of the silver:

$$Ag + 2CN^- + \oplus = Ag(CN)_2^-.$$

By stirring, these ions can be carried to the vicinity of the cathode and then, although only very few simple silver cations are present, it is easier to discharge the silver than to accomplish the reduction of potassium or of hydrogen from an alkaline solution

$$Ag(CN)_2^- + \ominus = Ag + 2CN^-.$$

The character of the silver deposit is more satisfactory and less granular than when formed by the electrolysis of an acid solution of a simple salt.

Character of the Metal Deposit and Duration of the Electrolysis.

Two important points to be considered in electro-analysis are the nature of the deposit and the duration of the electrolysis; these two factors are closely related to one another.

As regards the nature of the deposit, it is absolutely necessary that it shall adhere firmly to the cathode in order that the solution with which it is wet may be rinsed off without loss. The most favorable form of the deposit in this respect is the finely crystalline one, with metallic luster if possible. Dull deposits are less dense, and, on account of their pulverulent nature, more likely to become spongy. If the deposit is distinctly spongy, then it adheres loosely to the cathode and this is why spongy deposits should be discarded. The principal cause of the sponginess lies in the too rapid deposition of the metal. It is conceivable that under these conditions the precipitate does not have time to assume a finely crystalline form. Formerly, attention was directed chiefly toward the current density, *i.e.*, to the number of amperes per square decimeter of cathode surface. Mention of the current density was, and is also to-day, an important factor for certain depositions. The quantity of metal deposited is, according to Faraday's law (p. 9), directly proportional to the current strength; thus a current of two amperes will deposit twice as much metal in a unit of time as will be deposited by a current of one ampere during the same time. This is one reason why too strong current densities favor the formation of spongy deposits. Currents of high intensity have the further disadvantage of favoring the evolution of hydrogen at the cathode, which also hinders the uniform deposition of the metal (*cf.* p. 22). Finally, it may happen under these conditions that metal hydrides are formed at the cathode, and these hydrides are subsequently decomposed with evolution of hydrogen leaving the metal behind in a less compact condition. It must be remembered, moreover, that the deposition of the metal can take place strictly in accordance with Faraday's law only during the first few moments of the analysis, for as soon as some of the metal has deposited, the composition of the solution becomes changed. The current then acts upon this solution somewhat differently than it did upon the solution in its original composition; this is evidenced by the evolution of hydrogen which increases in amount as the quantity of metal in the solution becomes less; the last portions of the metal, therefore, require a relatively longer time for deposition than the first portions. It is not infrequent, for this reason, to have the analysis prolonged two, four, or even six hours, according to the nature of the metal and the quantity to be deposited.

Now the shortening of the time required to effect the quantitative deposition of a metal is a factor of great importance which has received the attention of investigators for a long time. The result of the numerous investigations in this field, concerning which a historical summary will shortly be given, has placed us to-day in a position of being able to complete an electrolysis in about one fifteenth of the time formerly employed. This result has been accomplished by the use of rapidly rotating electrodes, or, what amounts to the same thing, of a rapidly moving electrolyte; the important point in all cases is the movement of the electrolyte.

Shape of the Electrodes.

A great many differently shaped electrodes have been proposed from time to time, but only a few forms have met with favor in practice. Here, a few electrodes will be described first which are employed for ordinary electrolytic methods when the work is carried out without stationary electrolytes.

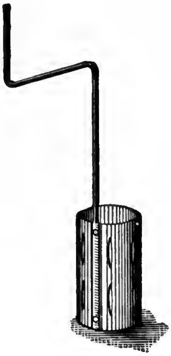


FIG. 13.

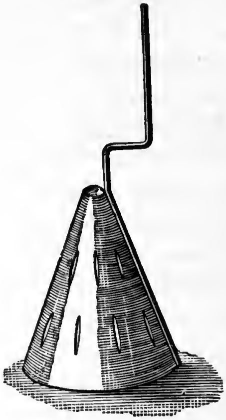


FIG. 14.

Among the oldest models are those used at the Mansfeld smelting works, chiefly for the determination of copper. The cathodes are made of platinum foil bent into the shape of a cone or cylinder, with a few slits in the foil to facilitate the circulation of the liquid. Strong platinum wires are riveted or soldered to the foil; platinum can be united to platinum without the use of a foreign solder (Figs. 13 and 14). The corresponding anodes, made of stout platinum wire, are shown in Figs. 15 and 16. Figures 17 and 18 show how these electrode pairs, attached to electrode stands, are arranged in an electrolyte contained in a beaker. Another method is to use a single stand, as shown in Fig. 19. This arrangement is a very practical one if a metal is to be deposited from a slightly acid solution; when the electrolysis is complete, the stand is quickly raised so that the attached electrodes are removed from the liquid and then they are quickly immersed, without breaking the circuit, first in a beaker filled with water, and next in one containing alcohol; it is then only necessary to dry the electrodes for a short time in an air-bath before weighing. When a single stand is used, the rod *G* (Fig. 19) must be made of glass.

Besides these types of electrodes, the use of platinum dishes, as recommended by the author, has met with much favor. Fig. 20 shows such a platinum dish in half its natural size; it weighs about 35 grams, has a diameter of about 9 cm., is 4.2 cm. deep in the center and holds about 150 cc. With 150 cc. in the dish the wet inner surface amounts to about 100 sq. cm., and with 180 cc. to

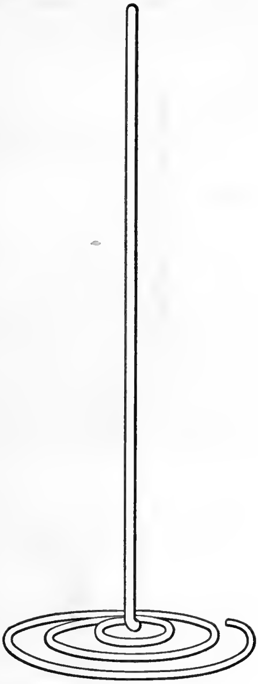


FIG. 15.

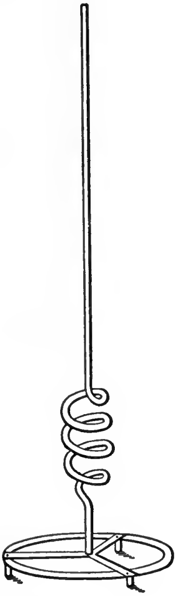


FIG. 16.

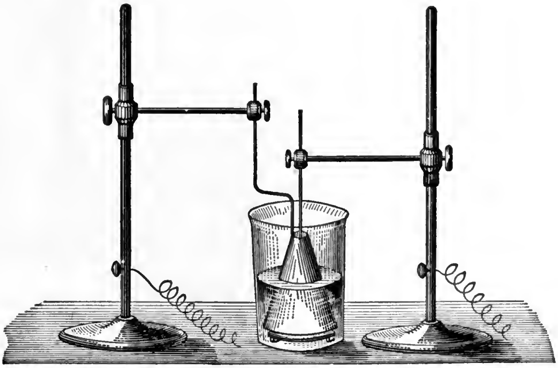


FIG. 17.

about 150 sq. cm. As it has been shown that most metals adhere better to a slightly rough surface than to a polished one, the inside of the dish is preferably roughened by means of the sand blast. In certain determinations, as in the deposition of lead peroxide, the deposit will adhere firmly only to such a dull surface.

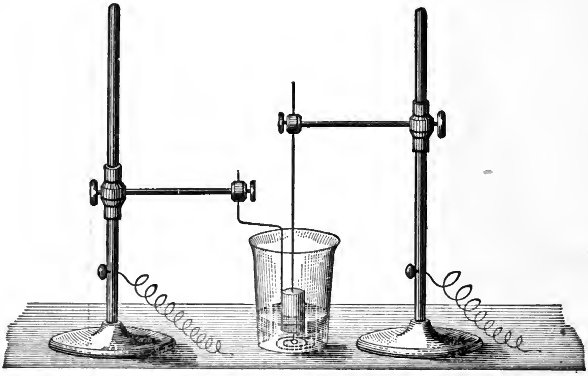


Fig. 18.

It is advisable, under all circumstances, to reserve for this purpose only the dishes used in electro-analysis and to take care that they are not dented or bent by careless handling. Dishes made of an alloy of platinum with 10 per cent iridium are not so sensitive in this respect as are those of the softer, pure platinum.

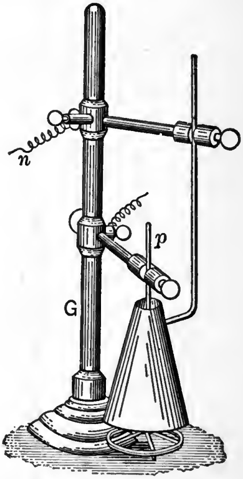


Fig. 19.

As anode (positive electrode) the author uses a disk, 4.5 cm. in diameter, made of fairly thick platinum foil which is riveted or autogenously soldered to a quite stout platinum wire (Fig. 21). For the reason already mentioned in the description of conical and cylindrical electrodes, it is well to provide the platinum disk with a number of slits. On account of the horizontal position of the disk anode in the electrolyte, if these slits are not provided the bubbles of gas that collect beneath the disk will diminish the contact surface between the solution and electrode and thereby increase the resistance of the cell. When, eventually, these tiny bubbles of gas unite to form one large bubble, this may escape from under the platinum so quickly that there is danger of losing some of the liquid by spattering.

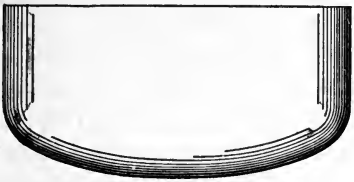


Fig. 20.

Besides the disk-shaped anode shown in Fig. 21, the author also uses an anode of the form shown in Fig. 22, which consists of a perforated platinum dish about 50 mm. in diameter and 20 mm. deep. This anode has been used by Julia Langness as a rotating anode. The use of a platinum dish as cathode has the advantage that in working with moving electrolytes the anode may be chosen of almost any form according to the special effect that it is desired to accomplish.

To hold the electrodes in position, two special stands have been designed by other investigators (Figs. 17 and 18). The author has combined these on a single stand which has proved satisfactory. The ring which serves to support the dish (Fig. 23) is provided with three short platinum contacts, and, like the arm that holds the anode, is fastened to a vertical glass rod *G*; *n* is connected with the negative and *p* with the positive pole of the source of current.

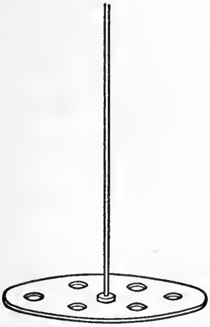


Fig. 21.

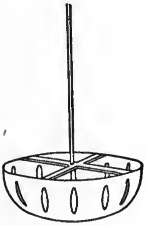


Fig. 22.

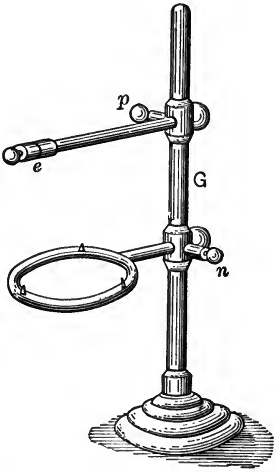


Fig. 23.

It must be admitted that the dish form of cathode has certain disadvantages. In the first place, the circulation of the liquid is likely to be unsatisfactory. At several places in this book it has been pointed out that the metal ions should be supplied to the cathode as fast as possible, not only in the interest of shortening the time of analysis but also for obtaining a satisfactory deposit. If the supply of metal ions were maintained solely by an equalization of the different densities which the liquid assumes during electrolysis, then the dish form of electrode would be advantageous because the upper layers of liquid become richer in metal and consequently denser than the lower layers, and as a result the metal ions tend to sink of their own accord to the lower levels where they are needed. A much more energetic mixing of the solution, however, is brought about by the bubbles of gas that are evolved during the electrolysis. If it be assumed that during a well-conducted electrolysis there is no evolution of hydrogen at the cathode, then it is only the oxygen bubbles evolved at the anode that can serve to stir the solution. Herein lies the fault of the dish as electrode, for with it this stirring takes place only in the upper portions of the electrolyte. Some advantage is gained, however, by warming the solution. If, however, the electrolyte is constantly stirred during the electrolysis, this objection to the use of a dish electrode disappears.

As a result of experience, it has been found that certain precipitates, which are often formed during the preparation of the electrolyte, do not influence the character of the metal deposit obtained, so that it is unnecessary to waste time by filtering, washing and evaporating. In such cases, the use of a platinum dish as cathode would have the disadvantage of having the precipitate rest upon the metal deposit, which could easily give rise to contamination of the latter. Energetic mechanical stirring would tend to obviate this difficulty.*

At the present high price of platinum, a final objection to the use of dish electrodes lies in the fact that only about one third of the total surface of the platinum is utilized in an electrolysis. Moreover, a heavier weight of platinum is not altogether desirable.

In spite of these various objections that have been raised, a

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* The results of recent experiments with respect to the determination of metals in the presence of suspensions have often conflicted with older observations, as will be discussed in the case of certain metal separations.

number of authorities, such as Hollard and Bertiaux, Riban, Exner, E. F. Smith, R. O. Smith, Langness, Ingham and others, have obtained excellent results with dishes as cathodes and various types of anodes.

With respect to the nature of the inner surface of the dishes, the author at first used highly polished dishes. After it was discovered that these polished surfaces were not suitable for holding large deposits of certain metals (*e.g.*, antimony) and still less so for holding peroxides (of manganese or lead), the author became accustomed to the use of dishes that had been dulled by sand blasting. More recently, however, careful experiments carried out in his laboratory, especially in the determination of antimony, have shown that if the surface is roughened too much there is danger of some of the salts contained in the electrolyte being included in the deposit. For this reason the author now recommends that the inner surface of the dish be only slightly dulled, as can be accomplished by warming slightly with dilute aqua regia. (See Antimony.)

This last difficulty is much more serious in the case of gauze electrodes which, according to their nature, may seriously influence the accuracy of the results by giving rise to foreign inclusions.

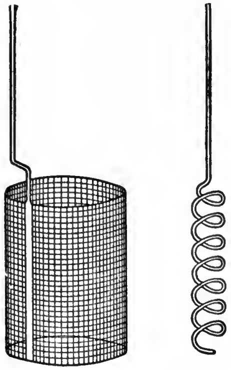
Since 1898, wire gauze electrodes, especially cathodes, have been used. H. Paweck* overcame the difficulties encountered in the electrolytic estimation of zinc, by the use of a disk-shaped cathode made of brass gauze previously amalgamated, and he was also able by means of such cathodes to obtain satisfactory zinc deposits from an alkaline tartrate solution or from a slightly acid sulphate solution. The gauze proved suitable for a good amalgamation.

Cl. Winkler used platinum gauze and made the electrode cylindrical in form (Fig. 24); as anode he used a stout platinum wire wound into a spiral (Fig. 25). The above-mentioned error occasioned by foreign inclusions is partly but not entirely avoided if the meshes of the gauze are not too fine, and if the edges of the cylinder, instead of being bent over, as was formerly customary, are soldered to a round platinum wire.

The advantage that wire gauze electrodes possess over those made from platinum foil bent into cylinders or cones consists in a uniform distribution of the current upon the inside and outside.

* Z. Elektrochem. 5, 221 (1896).

To still further aid in the uniform distribution of the current, Hollard uses an anode of the form shown in Fig. 26, a part of which is inside and a part outside the cathode.



FIGS. 24 and 25.

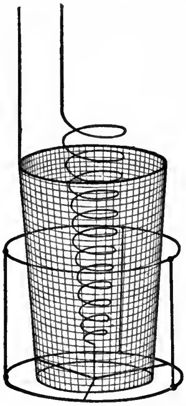
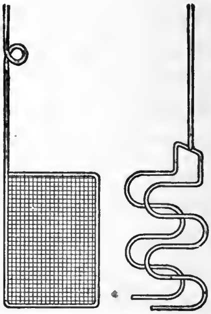


FIG. 26.



FIGS. 27 and 27a.

For the same purpose of surrounding the cathode by the anode as much as possible, F. M. Perkin uses a gauze cathode shaped like a flag (Fig. 27) and a fork-shaped anode of platinum wire bent as shown in Fig. 27a; the cathode can thus be inserted between the windings of the anode. (Oettel had previously recommended a fork-shaped anode.) The wire gauze of the cathode is soldered to a frame of platinum wire. The loop in the upper part of the cathode is for the purpose of hanging it to the balance arm.

The electrodes used for rapid electro-analysis will be described below.

Electro-Analysis with Moving Electrolytes. (Rapid Electro-Analysis.)

In analyses made with the electrodes already described, it was formerly customary to allow the electrolytes to stand quietly until the deposition was complete. The movement that naturally takes place within such a solution is caused by the ascending gas bubbles and by diffusion, the latter being caused by the fact that the solution in the neighborhood of the cathode becomes less concentrated and specifically lighter than the portions of liquid farther away. Some years ago the author pointed out the favorable effect due to heating the electrolyte. The increased rate of deposition from a hot solution is due, however, to the increased conductivity caused by heating the solution, or to a decreased resistance, and to an accelerated rate of diffusion. Subsequently, experiments were undertaken with rapidly moving electrolytes and surprising results were obtained as regards the shortening of the time required for complete deposition. After the experiments performed in the author's laboratory and elsewhere had removed all doubt concerning the value of the new method of working, the authorities at Aachen consented to provide means for fitting up the first large laboratory with the necessary apparatus for carrying out rapid electrolyses (see p. 68).

Although much remains to be explained in the theory of rapid electrolysis, still the experiments made in the past to explain the observed facts in the light of known theories are worthy of careful consideration. This is not the place to go into such matters in detail and we shall limit the discussion to the principal results that have been obtained by investigations in this direction and shall refer, in the discussion of the individual methods, to the original papers by appropriate footnotes. R. Amberg,* who, in 1903, carried out methodical determinations of palladium by rapid electrolytic methods, gives in his thesis the following table in which the second column gives the weight of deposited platinum in grams, the column headed Z_w gives the time required in each case and the last column gives the number of revolutions of the stirrer per minute.

In the column headed Z_f is found the theoretical time, in hours, required for the deposition if it took place with the best possible utilization of the current in accordance with Faraday's law (see p. 9). Column $Z_w - Z_f$ gives the difference between the actual time required, as given in column Z_w, and the computed time in column Z_f.

No.	Grams Pd deposited.	Z_w.	Z_f.	$Z_w - Z_f$.	Revolutions per minute.
1	0.77	5.50	1.55	3.95	500
2	0.6	4.45	1.20	3.25	620
3	0.95	4.5	1.91	2.49	800
4	2.3	6.0	4.62	1.38	1000

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* Z. Electrochem., **10**, 853 (1904).

If the values given in the third, fourth and fifth columns are computed to a common basis of 1 gm. of deposited metal, then the table becomes easier to comprehend and reads as follows:

No.	Grams Pd deposited.	Z_w.	Z_f.	$Z_w - Z_f$.	Revolutions per minute.
1	1	7.14	2.01	5.13	500
2	1	7.42	2.01	5.41	620
3	1	4.07	2.01	2.06	800
4	1	2.6	2.01	0.59	1000

In the third column, the shortening of the time required with increase in the number of revolutions is clearly shown.* If the deposition of the metal, from the first instant until the last traces of metal were removed from the solution, took place at a uniform velocity, then the time required would be exactly 2.01 hours.† It may be assumed that the deposition took place at first in accordance with Faraday's law and this rate continued as long as the solution remained at approximately its original concentration. Gradually, however, the solution became poorer in metal and the longer time required is due to the fact that the whole of the current, from the beginning to the end of the experiment, was not utilized for depositing the metal. By subtracting the theoretical time required from the actual time consumed, the values given in the next to the last column are obtained, and these values show that the difference between the theoretical and actual periods is smaller, the greater the velocity of revolution. The cause of this more rapid deposition, theory aside, is evidently that in the case of intense stirring the current is utilized to better advantage for the desired deposition and is not used up in other ways, as in the liberation of hydrogen, to the same extent as with a stationary electrolyte or with one but gently stirred. When the stirrer revolved at the rate of 1000 revolutions per minute (Exp. 4, p. 61) the time required for deposition (2.6 hours) was nearest to the theoretical value (2.01 hours). Thus the elimination of hydrogen was avoided throughout the entire experiment, and this,

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* Experiment 1 does not fall quite into line with the others. Eitner there is a mistake here or else the current, assumed to be 0.25 ampere, was not perfectly uniform during the whole period.

† To get this value, the atomic weight of Pd is taken as 106.5, its valence 2 and the current strength as 0.25 ampere.

as has been explained already, is a most desirable condition for obtaining a deposit of metal in compact form. If, however, the evolution of gas is prevented entirely in the rapidly stirred electrolyte, or, in other words, if the time when this evolution begins is put off as long as possible, then the cause for this behavior must be traced to the fact that a sufficient quantity of metal ions are brought in contact with the cathode, and, indeed, with such velocity that the entire electric charge of the cathode is neutralized by metal ions alone; thus the cathode, we may say, experiences no requirement for other ions until the metal is all deposited. The following explanation of the processes taking place during electrolysis must be very close to the truth. At the start, when the cathode potential becomes high enough to cause deposition of the metal, the concentration of metal ions in the vicinity of the cathode is so large that the deposition of the metal takes place according to Faraday's law. This deposition of the metal, however, often takes place faster than the positively charged metal ions migrate toward the cathode. The most desirable condition for a satisfactory electro-analysis is that the deposition may take place in accordance with Faraday's law. To this end, it is requisite that an excess of metal ions should be present all the time at the cathode and there are two ways of accomplishing this. One way consists in gradually lessening the current so that the velocity at which the metal ions are discharged is constantly less than that of the migration of these ions toward the electrode. This method of working is not only impractical but it is also very tedious.

The other method consists in artificially bringing the ions to the cathode with a velocity greater than that of the discharge of the ions. This is brought about by a rapid stirring of the liquid. The transference of the ions is supported naturally by diffusion; for as the solution in the vicinity of the cathode becomes deficient in ions of any kind, diffusion seeks to make the concentration homogeneous throughout the entire solution. In some cases this suffices to satisfy the requirement of ions at the cathode; this is the case with very complex electrolytes. Then the discharge of the metal ions takes place more slowly than from a simple electrolyte and there is thus always an excess of ions at the cathode ready to be discharged. In such cases, therefore, the duration of the electrolysis cannot be shortened materially by stirring the electrolyte.

In the other case, when the discharge of the metal ions takes place at a very high velocity, the analysis will take place more rapidly in proportion as the liquid is well stirred.

The shortening of the time required for an electro-analysis by heating the electrolyte can be explained from the same point of view. It has been mentioned on page 20 that the conductivity of the electrolyte is increased in this way. It is also true that the rate of diffusion in the liquid is likewise increased and thus the effect of rapid stirring is obtained, at least in a measure. In many cases the combined effect of heating and stirring is employed in electro-analysis. The effect of temperature upon electrolytic separations in complex electrolytes is discussed on page 94.

The important reason why the stirring of the electrolyte leads to such valuable results is because it permits the use of a much greater current strength than would otherwise be possible. This new method in fact permits one to use current densities that would be altogether out of the question with a stationary electrolyte, if it were desired to obtain deposits free from sponginess.

It has been pointed out, on page 36, how important it is for certain determinations and separations to measure the potential at the cathode. Although such a complication of the analysis is absolutely necessary in some cases, still the great advantage of being able to carry out some analyses within ten or fifteen minutes is apparent to every one (see the article on Bismuth).

A brief description of the electrolytic equipment at the Aachen Institute of Technology will be given in the following pages.* It may be mentioned at the start that experiments carried out in this laboratory have shown that it is absolutely immaterial, as regards the desired result, whether the solution is stirred by rotating the cathode, the anode, or both together, or whether an independent stirrer is used.

There are, then, three groups of electrode pairs used for rapid electro-analysis: 1. Stationary cathode, rotating anode. 2. Stationary anode, rotating cathode. 3. Both electrodes stationary, independent stirrer.

To the first group belongs the platinum dish as cathode with anodes of various types: (a) perforated, flat disk (Fig. 21); (b) perforated, corrugated disk (Fig. 28); (c) spiral (Fig. 15); (d)

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* A fuller account can be found in Z. Elektrochem., **13**, 181 (1907).

perforated dish electrode, also called a sieve electrode (Fig. 22). Sand's gauze electrode, described in the publication cited on page 42, belongs in this group. Finally, the mercury cathode used by Kollock and Smith and that used by Hildebrand deserve mention.

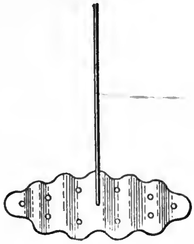
FIG. 28.

The second group is represented by (a) the rotating platinum crucible as cathode,* (b) the rotating gauze cathode devised in this laboratory by A. Fischer and which is strengthened by placing it over a hollow porcelain body (Fig. 29). The stem of the latter contains a vertical groove in which a somewhat stronger platinum wire is laid loosely. When the porcelain stem is placed in the binding post of the apparatus, this wire permits the passage of the current to the gauze with the aid of a ring of platinum foil against which the platinum wire lies, as a spring, upon the inside. The connection between the ring and the gauze is furnished by two fine platinum wires, fastened to the gauze, with the free ends placed between the porcelain stem and the platinum ring and bent over on the outside. The fixed stationary anode used with this cathode is made of platinum wire and

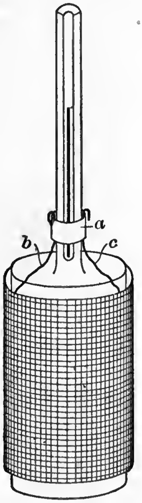

FIG. 29.

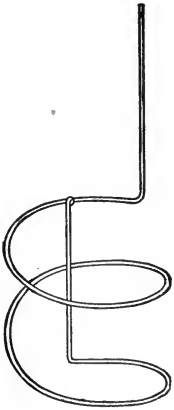
FIG. 30.

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* Gooch and Medway, Z. anorg. Chem., 35, 414 (1903).

provided with windings large enough to inclose the cathode (Fig. 30).

The third group consists of two stationary electrodes. In this laboratory A. Fischer's modification of Sand's electrode has given satisfaction. Sand's electrodes consisted essentially of two gauze coaxial cylinders of which the inner was movable and served as stirrer. To increase the stirring effect, the inner electrode was provided with a diametric partition. Sand's aim was to study the cathode potential (*i.e.*, the difference in potential between the cathode and the electrolyte), during the electro-analysis, and his electrodes were arranged with this end in view. It is necessary, for this purpose, that the auxiliary electrode, when the end of its capillary tube is placed in the neighborhood of the cathode (see Fig. 11, p. 42), should show the exact potential of the cathode. This is actually the case with Sand's electrodes; the current lines from the anode are caught so completely by the cathode that the capillary tube of the auxiliary electrode can be introduced at almost any place in the liquid outside the cathode without there being any appreciable difference in the potential values that are measured.

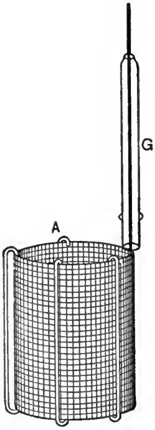

Fig. 31.

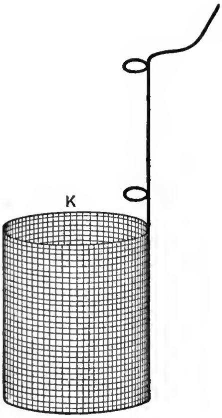

Fig. 32.

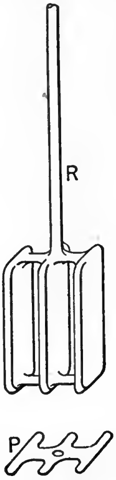

Fig. 33.

Fig. 34.

The only objection to Sand's apparatus is that the manner of connecting the stirrer to the motor was rather more complicated than necessary. A. Fischer simplified matters somewhat by making the stirrer independent of the anode; at the same time he proved experimentally that this permitted the cathode potential to be measured with the same accuracy as with Sand's arrangement.*

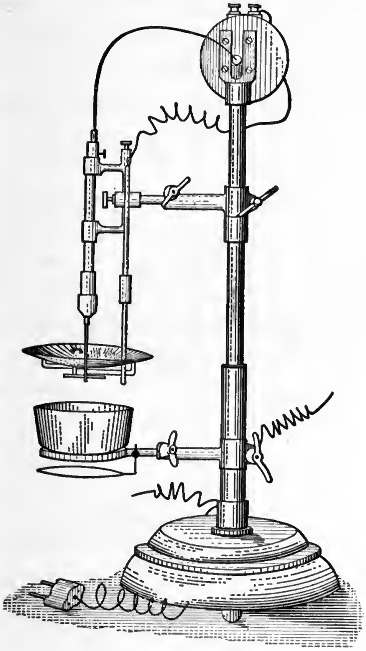

FIG. 35.

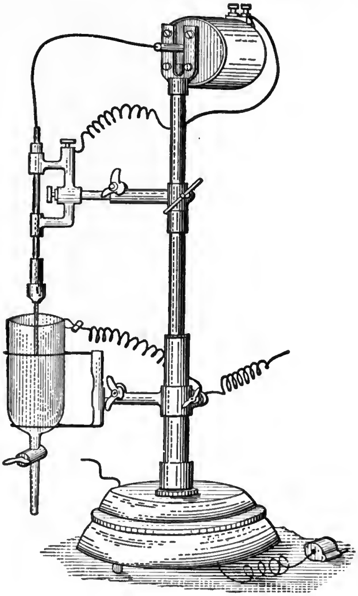

FIG. 36.

The two electrodes *A* and *K* (Figs. 31 and 32) consist of fine-meshed platinum gauze. To prevent contact between the stems of the cylinders when *K* is placed over *A*, there is placed over the stem of the latter a piece of small glass tubing *G*, over which the two loops in the stem of *K* will slip. Near the bottom of the glass tubing *G* two globules of glass are fused to it, and upon these rest the lower loop on the stem of *K*. To prevent any contact between the two cylinders, the cylinder *A* is provided with four small pieces of glass rod which are bent over at the top and bottom to hold them in place. The cylinder *K* slips over these pieces of glass with slight friction, so that all parts are joined to one another. The distance between the two electrodes is about 3 mm.

The stirrer *R* (Fig. 33) consists of three or four thin sheets of

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* Z. Elektrochem., **13**, 469 (1907).

glass, placed parallel to one another, 3 or 4 mm. apart, and fused together at the top (lattice stirrer).

The thin sheets of glass are not placed exactly tangential to the circles which they set in motion but are inclined slightly, as a glance at the horizontal projection *P* will show. The plates are fused to a glass rod of which the upper end is covered with a piece of rubber tubing to aid in connecting it with the shaft of the motor (Fig. 35). **Plate** II (back of the book), which accompanies the section on Bismuth, shows the way the stirrer is placed with reference to the electrodes shown in Figs. 31 and 32.

Sand found that his form of rotating anode was not suitable for use in the deposition of metals of which the ions in solution were likely to change in valence during the electrolysis. Thus, for example, he was unable to precipitate the last traces of copper from an ammoniacal solution. These difficulties are of the nature discussed under the deposition of copper from acid solutions (p. 121). Just as in that case the high temperature is favorable for carrying out the reversible reaction, $Cu^{++} + Cu \rightleftarrows 2\ Cu^{+}$, so in this case the violent stirring serves to effect the intimate interchange of the products of the oxidation at the anode with the products of reduction at the cathode, and this tends either to prolong the analysis or to prevent the complete deposition of the metal. To obviate this difficulty, Sand had a special anode made having a small platinum surface and small stirring face. A. Fischer accomplishes the same end by using a less effective stirrer and keeping the electrodes the same. This stirrer consists of a piece of glass rod made into the shape of a helix (Fig. 34, p. 66).

The apparatus designed by the author's assistant, A. Fischer (Figs. 35 and 36), is different from others that have been devised for the same purpose, inasmuch as the motor, which serves to drive the stirrer, is fastened to the upper end of an upright, and its motion is transferred to the electrode, or other stirrer, by means of a flexible steel shaft (a piece of steel wire wound into a helix). The motor is driven by power furnished from the lighting circuit with a potential of 110 volts and is independent of the current used for the electrolysis. During the electrolysis, the vessel is covered, to prevent loss by spattering, with a watch glass which has a small perforation in the middle, to permit the wire stem of the anode to pass through it. When the anode is raised, the watch glass is lifted with it. Through another perforation at one side of the watch glass, a thermometer, likewise attached to the upright, can be introduced. If it is desired to heat the electrolyte

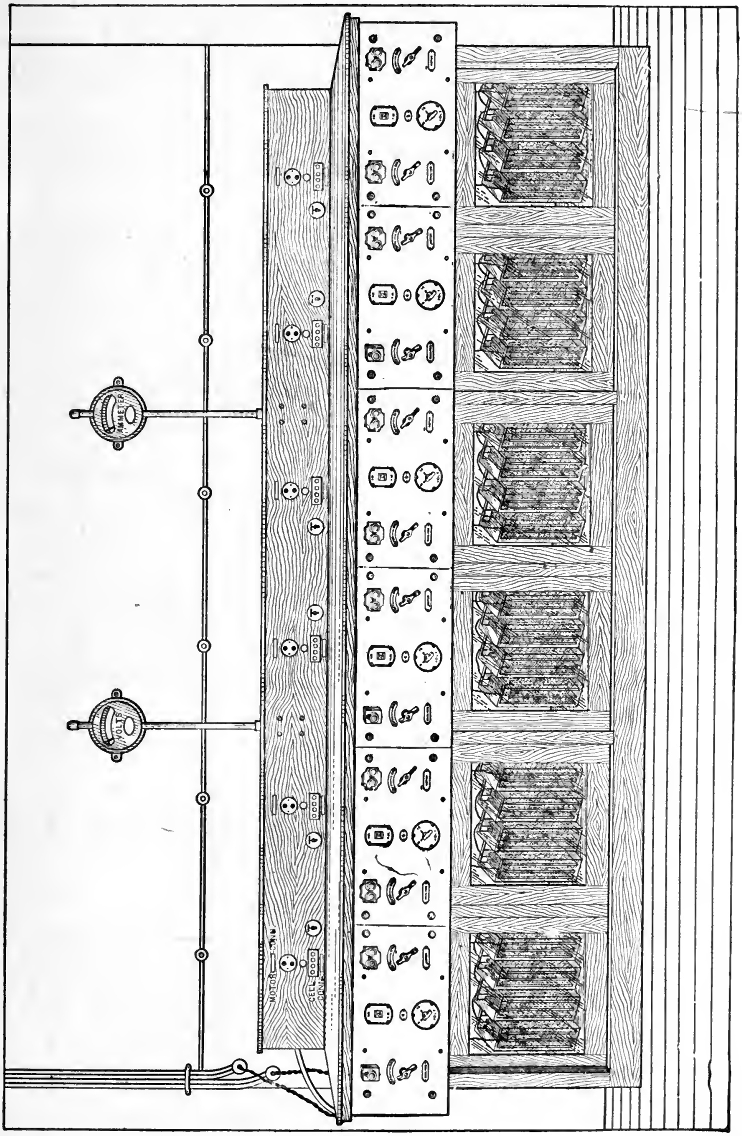


FIG. 37.

during the analysis, a piece of asbestos paper is placed on a ring a little below the dish and a small flame is placed below the asbestos, so that the dish is heated very uniformly by means of the hot air arising from the asbestos.

Figure 36 shows the apparatus fitted up for use with a rotating cathode (Fig. 29, p. 65). In this case, the glass vessel containing the electrolyte is provided with a stopcock at the bottom to facilitate the final washing of the deposit.

To permit several analyses being carried out at the same time without any interference, the working bench shown in Fig. 37 is arranged as follows:

In the closet below the bench is a battery of accumulators consisting of 24 cells. The battery rests upon a board, which is on castors so that it can be withdrawn easily in case it is necessary to make repairs.

All the cells are kept connected in series and are charged from the electric-lighting circuit, using a wire rheostat (Fig. 38 and L.R. at the lower left-hand corner of Plate I). This wire resistance is placed upon a marble slab at one end of the bench and upon the slab is a switch for turning the current on and off, also a rheostat handle for regulating the resistance and an ammeter (Fig. 38 or lower left-hand corner of Table I).

The bench is fitted up with six working places and thus four accumulator cells are furnished for each working place.

(Plate I: Group I over 1, 2, 3, 4; Group II over 5, 6, 7, 8, etc.)

To start an analysis a number of operations are necessary. At the back of the bench, next the wall, is a top piece upon which are fastened the socket for the motor connection and the binding posts for making connection with the electrolytic cell (see Fig. 39). The contact plug fastened to the end of the wires leading

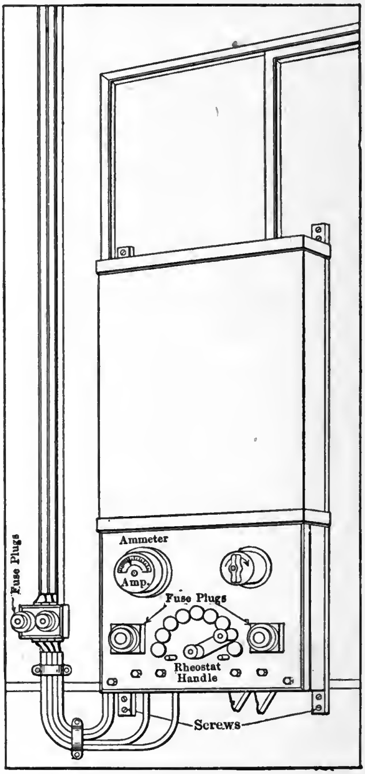


FIG. 38.

to the motor is pushed into the socket and the wires from the electrodes are inserted into the + and − posts of cell connection. Upon the front of the bench, over the closet doors, is attached a marble slab, at the right-hand side of which is the rheostat handle M.R. (Fig. 39) for turning the motor on and off as well as for regulating its velocity; this can be varied between 250 and 1600 revolutions per minute.

The line drawing in Plate I shows how the motor is connected to the middle wire and positive outside wire of the three-wire system from the electric-lighting plant.

The handle A.R., on the left-hand side of the marble slab (Fig. 39 and Plate I), is for turning the current on and off from the storage battery, from which the current used for the electrolytic cell is obtained, and this handle also serves for varying the resistance as indicated in Plate I.

For measuring the strength of the current passing through the cell, and for measuring the drop in potential of the current in passing through the cell, there is only one ammeter and one voltmeter for the six working places. These two instruments, as shown in Fig. 37, are near the wall upon uprights and fixed so that they can be revolved and read from each working place. As can be seen in Fig. 37, or more distinctly in the line drawing of Fig. 39, there is a plate in the middle of the marble slab, carrying a double-throw switch in the center. If this switch is thrown down, in the direction of the lower arrow, shown in Fig. 39, the ammeter is placed in the electrolytic circuit of this bench. If the switch

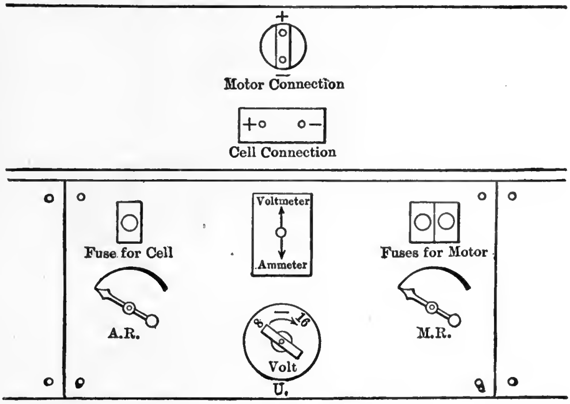


FIG. 39.

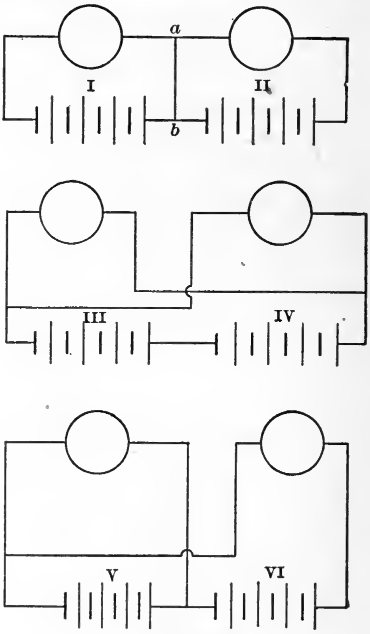
is pushed upward, in the direction of the upper arrow (Fig. 39), then the voltage of the current can be determined. After each reading, the switch must be returned to its central position, as otherwise it is impossible to make a reading from any other bench.

The electrical connections are so arranged that work can be carried out at each bench not only with the 8 volts from the four storage cells under it but, if desired, it is possible to take the current from the four neighboring storage cells and thus work can be performed with 16 volts. This adjustment of the current is effected with the key *U*, which is near the bottom of the marble slab at the middle. When the switch is turned to the point marked 8, then work at that bench is carried out with 8 volts, and when it is desired to use 16 volts, the switch is turned to the position marked 16. The connections are made so that even in the latter case there is no interference with work at the neighboring bench.

The sketches shown in Figs. 41, 42 and 43 show how the switch *U* serves in its two positions to make connections with the storage batteries for two neighboring electrolytic cells.

Figure 40 shows the connections at Places I and II when both their keys are placed at 8 volts. It is evident from this sketch that the wire *ab* plays the same part as the neutral wire in a three-wire lighting system.

If the two keys at Places III and IV are both turned to 16 volts, then the way the connections are made is shown in Fig. 41 (see also Plate I).



FIGS. 40, 41 and 42.

Figure 42 represents the connections when the work at Place V is carried out with 8 volts and at Place VI with 16 volts.

Thus, six or less students can all work independently at any time, using either 8 or 16 volts without any interference with one another.

Not only the voltage but also the strength of the current can be varied within wide limits. If, for example, the student at any one of the places is working with a battery current of 10 amperes, he can at any time get an additional 6 amperes from the lighting system, and thus carry out the work with 16 amperes, by turning the control handle *K* at the charging circuit (Fig. 38).

A cheap and practical arrangement for carrying out rapid electro-analyses has been described by A. M. Fairlee and A. J. Bone.* Their outfit is arranged especially for the determination of copper, and eight determinations can be carried out at one time with the use of only one motor.

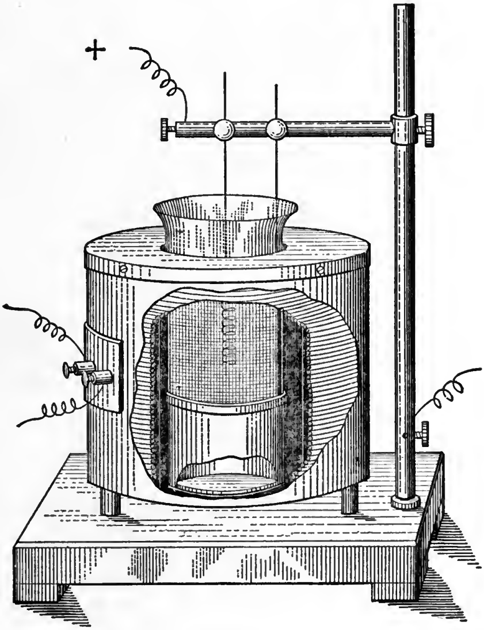


FIG. 43.

Rapid Electrolysis by Means of Magnetic Stirring.

E. A. Ashcroft,† in studying the electrolysis of fused salts, found that he was able to get a very favorable stirring of the electrolyte by surrounding the decomposition cell with a spool of wire, through which the current used for the electrolysis flowed.

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* Electrochem. Met. Ind., **6**, 19, 58 (1908).

† Ibid., **4**, 143 (1906).

F. C. Frary * applied the same principle to the electro-analysis of solutions and devised the following two forms of apparatus.

The apparatus shown in Fig. 43 consists of a spool of insulated copper wire, 1.5 mm. in diameter, having a total resistance of about 1 ohm. The wire is coiled around a cylinder of sheet copper which is made to hold the beaker in which the electrolysis is to take place. The spool is covered with a sheet-iron mantle, rests upon an iron base, and contains inside, at the bottom, a thick, hollow iron cylinder as core; the beaker rests upon this core. By this arrangement the magnetic field in which the beaker rests is strengthened and concentrated above the hollow iron cylinder. The direction of the magnetic lines of force is vertical.

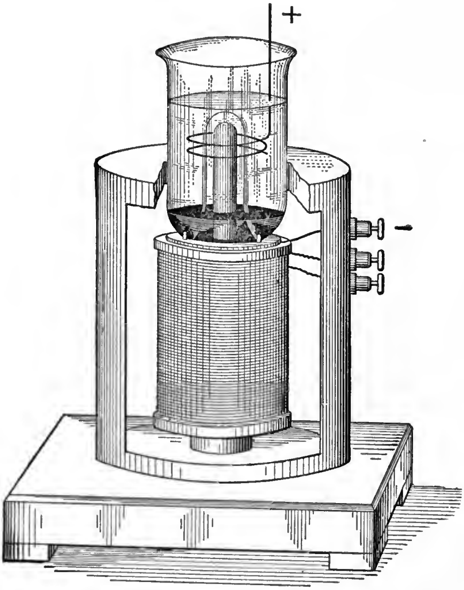

FIG. 44.

The electrodes shown in Figs. 24 and 25 on page 60 are used with this apparatus and between them the electricity flows horizontally and radially. If, now, the entire electrolyte is imagined to consist of separate radial threads, then each thread forms a conductor through which the current flows and the direction of the current is perpendicular to the magnetic lines of force passing

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* J. Am. Chem. Soc., **29**, 1592 (1907).

through the solution. Consequently, there acts upon the radial threads of liquid a horizontal force perpendicular to them and as a result the liquid is rotated about the axis of the apparatus.

The current used for the electrolysis will serve for exciting the induction current, and, in that case, the spool and the electrolytic cell are connected with one another in series, or, if more convenient, an independent current may be used in the coil (see below).

Frary was able with a current of 6 to 7 amperes during the first five minutes, and afterwards of 4 amperes, to deposit 0.85 gm. of copper quantitatively in 15 minutes. The electrolyte used was 100 cc. of copper-sulphate solution acidified with 10 drops of concentrated sulphuric acid. The potential between the electrodes was about 8 volts during the last part of the operation.

Another form of apparatus used by Frary (Fig. 44) depends upon the use of a mercury cathode. The magnetic field is produced here between the two poles of a vertically placed electromagnet; one pole is formed by the upper end of the iron core which projects from the middle of the spool, and the other pole of the electromagnet is obtained by uniting the iron core with the iron base and the iron sides of the frame in the upper annular part of the frame which surrounds the projecting core. The magnetic lines of force in this case run in a horizontal radial direction between the iron core and the annular upper part of the frame.

The bottom of the electrolyzing vessel is raised at the middle so that it looks almost as if the bottom had been pushed up at the middle by means of an inverted test tube. The hollow thus formed fits over the projecting iron core and the solution itself is contained in an annular space. Three short platinum points are fused into the bottom of the vessel and these rest upon a copper disk. In this way a connection is made between the mercury in the vessel and the copper disk and the latter is connected with the negative pole of the electrolyzing circuit by means of an insulated wire which is introduced through the frame of the apparatus. The anode consists of a platinum wire wound into a spiral; it is marked + in the picture. The current, therefore, flows vertically through the cell, and since, as mentioned above, the magnetic lines of force flow in a radial direction, the proper conditions are provided for a movement of the electrolyte. With this apparatus, the motion of the electrolyte is much more rapid than with the apparatus first described, for the simple reason that the magnetic lines of force are concentrated more by the iron core. The electromagnet, from which the copper disk is separated by another disk of insulating material, is excited by means of a separate current which is introduced at the two bottom binding posts shown at the right-hand side of Fig. 44.

Using this apparatus, Frary was able to deposit 0.1 gm. of iron in 10 minutes with a current of 4 amperes, which, in this case, also flowed through the spool of the electromagnet.

Such an apparatus has the advantage over mechanical stirring of not being as expensive and it requires less supervision. Time alone will show which method proves the better in practice.

In the author's laboratory the former of the two types of apparatus designed by Frary (Fig. 43) has been tested carefully.

When we remember that the rate at which the electrolyte is stirred depends not only upon the strength of the magnetic field but also upon the strength of the current used for the electrolysis, it is obvious that the method is limited in its application;* for, whenever the determination, or separation, of a metal takes place at a constant voltage, the current strength toward the end of the operation sinks to a very low value and that component of the stirring force which depends upon the analyzing current becomes too small to produce the desired stirring even although the magnetic field is very strong. This is just the time, on account of the very low concentration of metal ions remaining in solution, when the solution should be stirred most effectively. It is possible, to be sure, to increase the independent induction current in the spool but the size of the spool places a limit upon the extent to which this can be done. Frary gives the resistance of the spool as 1 ohm and the current as 5 amperes. Probably 6 amperes of current would be all that the coil could stand and if more were used the insulation of the wires would be likely to melt.

A current of 6 amperes would have to be used in the coil, for example, in separating copper from zinc; because, to deposit copper free from zinc, the current used for the analysis should not exceed 3.5 amperes. If the magnetizing current were less than 6 amperes, there would not be enough stirring to keep the zinc in solution.

If the strength of the current must be kept low, it will often

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* A. Fischer, Z. Elektrochem., **14**, 35 (1908).

happen that the stirring is insufficient to obtain a good deposit of metal.

Although the heating effect in the coil is favorable to the electrolysis in most cases, yet sometimes, as in the deposition of zinc from acid solutions, this proves a disadvantage. In such cases, a narrower beaker should be used in the first apparatus and the beaker should be surrounded by a coil of lead pipe through which cold water flows.

Finally, another objection that may be raised is the fact that the current consumption is considerable in those cases where the magnetizing current is made stronger than the current used for the analysis.

In electrolytic work where the deposition can be effected with high current densities, the Frary apparatus has proved very satisfactory. To show this, the following experimental results will be given.

1. Copper.

Electrolyte contained	1 cc. nitric acid (sp. gr. 1.2).
Strength of current for the analysis	3.8 to 4 amperes.
Strength of the magnetizing current	4.8 to 5 amperes.
Temperature	Boiling.
Time required	20 minutes.

Result: quantitative deposition, deposit a beautiful pink.

2. Iron.

Electrolyte contained	5 to 6 gms. ammonium oxalate to about 0.1 gm. iron.
Strength of current for the analysis	4 amperes.
Strength of the magnetizing current	4.8 amperes.
Initial temperature	50° to 60°.
Final temperature	70° to 75°.
Time required	30 minutes.

Result: quantitative deposition, deposit steel gray.

3. Nickel.

Electrolyte contained	1.5 gms. ammonium sulphate, 25 cc. ammonia (sp. gr. 0.91) to about 0.2 gm. of nickel.
Strength of current for the analysis	5 amperes.
Strength of the magnetizing current	4.8 amperes.
Initial temperature	70°.
Final temperature	80°.
Time required	20 minutes.

Result: quantitative deposition, deposit light colored and dense.

4. Tin.

Electrolyte contained	16 gms. of ammonium sulphide solution to 1 gm. of zinc-ammonium chloride.
Strength of current for the analysis	3 to 3.5 amperes.
Strength of the magnetizing current	5 amperes.
Initial temperature	50° to 60°.
Final temperature	70° to 75°.
Time required	20 minutes.

Result: quantitative deposition, deposit bright and lustrous.

5. Separation of Copper from Zinc.

The quantitative deposition of the copper was successful at the end of 20 minutes, using a current of 3.5 amperes and a magnetizing current of 6 amperes, with the other experimental conditions the same as under 1.

G. L. Heath of the Calumet and Hecla Works in Michigan has had considerable practical experience with apparatus similar to that of Frary and recommends it highly.* He uses it in two sizes; one large enough to accommodate a lipless beaker of about 6 cm. diameter and 300 cc. capacity which is suitable for the electrolysis of samples weighing 5 gms. and the other large enough to take a 500-cc. beaker and electrolyze samples weighing up to 50 gms.

The use of such large weights of metal is advocated simply in order to obtain more representative samples and to obtain solutions free from copper which will contain appreciable quantities of impurities present only to small fractions of 1 per cent.

For the smaller apparatus, a copper cylinder is made of 7-cm. diameter, using metal which is about $\frac{3}{32}$ in. thick. This is wound with 500 turns of No. 13, B. & S. gauge † magnet wire. The cylinder at the top and bottom is brazed to water-tight joints with thin plates of soft steel which complete the spool holding the coil of wire. A hole is bored in the upper steel plate of a size equal to the inner diameter of the cylinder and a 1-in. hole is bored through the bottom plate to provide ventilation or to permit the insertion of a stopper and glass tubes for water cooling.

Gauze cathodes weighing 16 to 17 gms. and having about 17 meshes to the linear centimeter are used with the apparatus.

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* J. Ind. Eng. Chem., **3**, 77 (1911).

† This is the standard gauge in the United States at this time. The initials stand for Brown and Sharpe.

At the Calumet and Hecla Works a current of 4.5 amperes is used for the electrolysis and in the coil. Five gms. of copper are deposited in about 2.5 hours.

The larger apparatus is made in the same way except that the diameter of the cylinder is larger.

As regards the directions for carrying out a rapid electro-analysis, it is impossible to make them broad enough to cover all conditions that are likely to arise. The best that can be done, at present, is to state in the form of tables some of the conditions under which good results have been obtained; it is usually possible, then, to derive from the tables the data necessary to cover any special case. Such tables are given in the section devoted to the determination of the individual metals; in each case the conditions for carrying out the analysis with the same electrolyte by the ordinary slow method are given first. The experimental conditions were either worked out in the author's laboratory or tested there, and the name of the author is given in each case.

The foregoing portions of this book contain a description of the various forms of apparatus which are used for carrying out electro-analyses and before passing on to that part of the book which treats of the directions for carrying out the work, it is necessary to discuss a few more things of a general nature.

The purpose of electro-analysis is not merely to determine the individual metals but it serves also to separate certain metals from others.

Electrolytic Determination of a Metal and Electrolytic Separations.

The only metals which, up to the present time, have been deposited satisfactorily as such by the action of the electric current upon solutions are: Zn, Cd, Tl, Sn, Bi, Sb, Fe, Co, Cu, Hg, Ag, Pd, Pt and Au. Thallium, to be sure, can be deposited as metal but cannot be weighed in this form on account of the extreme readiness with which it undergoes oxidation (see section on Thallium). The remainder of the above metals can be weighed as such upon the platinum cathode.

Manganese and lead are deposited as peroxides upon the anode and molybdenum and uranium as oxides upon the cathode. The alkali and alkaline-earth metals may be deposited as amalgams on a mercury cathode and weighed in this form.

The fact that the most suitable solution from which an electroanalysis can be made is not the same with different metals, so that general directions can be given which will apply in all cases, has already been mentioned on page 44. Similarly, there are no general rules governing the deposition of a second metal after the first has been quantitatively deposited.

The underlying principle upon which methods of separation rest is to remove one metal at a low potential and then, when all of this metal has been deposited, to deposit the second metal by raising the potential. Sometimes simple acid solutions are suitable but at other times it is necessary to provide the requisite differences in decomposition potential by transforming the metals into complex salts of such a type that one of the metals enters into a stronger complex, or one decomposed with greater difficulty than the other. In many instances it is necessary to change the original acid or complex solution into some other kind of solution before the second metal can be deposited.

According to the decomposition potentials of the metals given on page 31 *et seq.*, it might be imagined that it is merely necessary to increase the voltage of the bath above these values to effect the deposition of the various metals. In practice, however, one of the chief considerations is the nature of the deposit formed; the metal must not only be deposited pure but it must adhere firmly to the electrode. That the evolution of hydrogen acts as a disturbing factor has already been mentioned on page 53 and elsewhere. Now, as is well known, practically all solutions contain more or less hydrogen ions. Thus water itself is slightly dissociated into hydrogen and hydroxyl ions. In many cases, however, the concentration of hydrogen ions is kept fairly high by adding acid to the electrolyte. If the decomposition potential of the metal ion lies close to that of the hydrogen ion, even though it is lower, there is considerable danger of hydrogen ions being discharged and this danger increases as the solution becomes poorer in metal ions, during the progress of the electrolysis. It is a matter of common observation that at the beginning of an electrolysis there is absolutely no evolution of hydrogen, but after a little while the hydrogen gas begins to appear and the evolution increases constantly as the work proceeds. It is necessary, therefore, in order to obtain good deposits, to carry out the operation so that the evolution of hydrogen, if not altogether prevented, is put off as long as possible until a fairly strong deposit has been formed which is less affected by the gas. To understand better the conditions under which a simultaneous discharge of two different ions takes place, let us leave hydrogen out of consideration for the time being and assume that we have a solution of two metals, such as zinc and cadmium, present in approximately equal concentration at the start of an electrolysis. If the potential between the electrodes is increased gradually, the time soon comes when one of the metals begins to deposit and this is when the decomposition potential of that metal has been reached; or, since the decomposition potential is an electromotive force composed of cathode potential and anode potential, it is more accurate to say that the deposition of one of the metals starts when the requisite cathode potential is reached. Since cadmium has a lower decomposition potential than zinc, at first only cadmium is deposited and as a result the solution gradually becomes poorer in cadmium ions. Now it has already been explained that the current strength is proportional to the quantity of ions neutralized at the electrode and consequently the current must necessarily weaken unless sufficient cadmium ions are present in the vicinity of the cathode. If the current strength is kept the same, then the voltage of the current gradually increases and, as a result of this, the decomposition potential of zinc ions is reached before all the cadmium is deposited and then both zinc and cadmium are precipitated together.

The above representation holds equally true if we substitute hydrogen ions for the zinc ions. The simultaneous discharge of metal ions and of hydrogen ions is not the only part that the latter play in electro-analysis.

As was shown on page 32 and as is apparent from the above example with cadmium and zinc, the cathode potentials of different metals are unlike and when two or more kinds of metal ions are present in a solution, the deposit first obtained will be of the metal having the lowest decomposition potential. Hydrogen, in respect to the more important metals, occupies an intermediate position in the potential series. The order is as follows: Mg, Al, Mn, Zn, Fe, Cd, Co, Ni, Pb, Sn, H, As, Bi, Cu, Sb, Hg, Ag, Pd, Pt, Au. Since those metals to the left of hydrogen have a higher potential than hydrogen while those at the right have a lower potential, it is plain, from what has been said, that the metals on the right are precipitated more readily and those on the left less readily than hydrogen. The further conclusion that zinc and cadmium are deposited only after all the hydrogen ions are discharged (*i.e.*, practically not at all) is not quite true. This fact is due to the so-called *overvoltage* of hydrogen toward different metals. If, namely, hydrogen requires a certain low voltage in order to be set free when in contact with so-called *platinized* * platinum, it requires a higher voltage to discharge hydrogen ions when in contact with polished platinum, or with cadmium, zinc and other metals. This excess voltage, which not only varies with different metals but also depends upon whether the surface of the metal is rough or smooth, upon the temperature, and upon whether the current density is high or low, is called the *overvoltage of hydrogen toward the metal in question.* In other words, it is harder for hydrogen ions to be set free when in contact with some metals than when in contact with others and this is the reason why zinc and cadmium can be deposited by the electric current from a solution containing very dilute acid (see following section). A number of theories have been advanced to account for overvoltage. Nernst has assumed that when ionic hydrogen is discharged it is in the form of monatomic hydrogen which at a slower rate is converted into diatomic hydrogen molecules. Newbury has regarded hydrogen overvoltage as due chiefly to the formation of metallic hydrides with higher solution tensions than that of hydrogen. More recently, however, MacInnes and Adler † have argued convincingly that this overvoltage is due, primarily, to a layer of supersaturated, dissolved hydrogen in the electrolyte surrounding the cathode. If the electrode can adsorb large hydrogen gas nuclei to start the formation of bubbles, the supersaturation cannot rise to high values and the electrode will have a low overvoltage. Metals with small adsorptive powers hold small nuclei and have high overvoltages. MacInnes and Adler have obtained experimental evidence of the presence of such nuclei, and have tested their theory in several ways.

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* Platinized platinum, *i.e.* platinum coated with platinum black, is obtained by electrolyzing a three per cent solution of chloroplatinic acid, to which one-fortieth of a per cent of lead acetate has been added. By using a current such that there is only a slight evolution of gas, the platinum cathode becomes sufficiently coated within a few minutes.

† J. Am. Chem. Soc. **41,** 194 (1919).

The Deposition of Metals from Simple and from Complex Electrolytes.

H. Danneel* raised the following questions in 1903: "What can we accomplish by an electrolysis and what do we know about electrolysis?" It is quite proper to raise such questions now and then and to look back over the path which investigation has followed in the field of electro-analysis. It was not long ago when our knowledge of electro-analysis was practically limited to the manner in which certain metals could be deposited quantitatively from their pure solutions and to means of separating metals from solutions containing more than one metal. The most favorable experimental conditions were, for the most part, discovered empirically, as is always the case during the first stages in the development of a new branch of science. It is worthy of mention that the development of the theory of solutions and the improvement of practical electro-analysis took place almost simultaneously.

The fact that this theory of solutions soon bore fruit in the field of electro-analysis is not to be wondered at, when one remembers that the theory of electrolytic dissociation is one of the main supports of electrolytic reactions. The revolution which took place in electro-analytical investigation as a result of the modern theoretical conception can be best illustrated by the fact that formerly, in searching for the best experimental conditions, chief stress was laid upon the significance of the quantities of electricity, as determined by the strength of the current and the current density, but gradually the significance of the other factor, the voltage, began to be realized.

However undeniable are the advantages which have resulted from the theory in practical electro-analysis, it must not be forgotten, on the other hand, that a powerful impulse toward the development of the theory was furnished by the success which characterized analyses made in this way. The neatness of electro-analytical methods, the accuracy of the results, and the rapidity of the reactions soon won the respect of both scientific and industrial laboratories and it acted as a particular stimulus upon theoretical investigation to realize that the results ob-

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* Z. Elektrochem., 9, 760 (1903).

tained were duly appreciated by practical men. The formula on page 27,

$$E_{18^\circ} = \frac{0.058}{n} \log \frac{P}{p},$$

proposed by Nernst in 1889, which permits one to compute the potential difference E between a metal and a solution containing its ions, from the electrolytic solution tension P and the osmotic pressure p, has proved of great practical importance for the problems of galvanic polarization as well as for the problems connected with the galvanic production of the current. The latter, to be sure, plays a subordinate rôle since dynamos have become the common source of the electric current. On the other hand, most of the problems with regard to the rational deposition of metals are closely related to this Nernst formula and its significance for electro-analysis will be clear after reading the following discussion.

When a metal is deposited from a solution by means of an electric current, the first question that arises, as Danneel correctly remarked, is this: Under what conditions is the metal deposited? In other words, what application of energy is required to transform the metal from its ionic into its atomic condition, so that it will deposit upon the cathode? As regards the quantity of electricity, we need not pay any attention to this for the present. A perfectly analogous question to the above would be this: What temperature is requisite for the coagulation of albumin? We know that a temperature of at least 70° is necessary to coagulate an albumin solution and that there is no coagulation, no matter how much water is present, provided the temperature is kept below 70°. Just as in this case it does not make any difference how much heat energy is present, provided the temperature is not high enough for coagulation, so, in the same way, no matter how much electricity is conducted through the solution, there will be no deposition of metal unless the current has a certain voltage. The Nernst formula tells us about this potential. One way to read the formula is as follows: If the electrolytic solution tension is equal to P and the osmotic pressure equal to p then the metal on being dipped in the solution will have the voltage E. When read this way, we consider E as a function of the two other values and it is equally accurate to read the formula as follows: In order to deposit a metal from a solution in which it has the electrolytic solution tension P and the osmotic pressure p, an electromotive force of at least E volts is requisite.

Thus, in order to compute E, we must know the values P and p. There are well-known methods for determining the osmotic pressure p. The only way of determining the electrolytic solution tension is to measure the potential E experimentally and from this, together with a knowledge of p, compute the value P. This roundabout method is necessary because, as we must not forget, what we term electrolytic solution pressure is not a sensible pressure which can be measured. The conception of electrolytic solution tension is merely a postulate of the theory, and we can only say that metals in contact with a solution act as if they were sending out ions with a certain force. In other words, we ascribe to the metals the power to send ions into the solution and this tendency is unchangeable for each metal at a constant temperature but varies with different metals and at different temperatures. Thus the value P may be regarded as a constant, dependent upon the nature of the metal.

The aim should be, as Danneel stated, to ascertain the solution tensions of all metals; this knowledge will place us in a position to compute the various voltages required, at a given concentration of the ions, and we shall then have a proper scientific basis for separating metals from one another.

Enough has been said to indicate the importance of the voltage measurements described on page 36 *et seq.*, and it should be emphasized that modern investigation makes use of these means most thoroughly.

Besides the question concerning the requisite conditions for the deposition of a metal, Danneel enunciated the no less important questions: "In what condition do the metals deposit? What are the properties of the deposits?"

The importance of these questions has been pointed out on page 52. For analytical purposes, it is a general rule that the deposit, aside from being chemically pure, must be dense and have a smooth surface, because it is only when the metal is in such a condition that it can be washed and weighed without loss and without undergoing change by oxidation. The conditions which may cause an uneven deposition were studied by Danneel, who took as an example the deposition of silver from potassium-cyanide solution, which requires the decomposition of the complex salt $K[Ag(CN)_2]$.

If an uneven deposit is formed, the most apparent cause is that more metal had been deposited at the same time on some parts of the electrode than on others. What is the explanation of this behavior? If we attempt to draw a picture of the transport of the ions through the electrolyte until they are discharged at the cathode, we find that the current lines, *i.e.*, the paths along which the ions are carried, are not always the shortest distances between the electrodes. Thus we find when a conical platinum electrode is used, with no openings on the sides (see p. 54), that copper is deposited on the outside of the cone as well as on the inside. On the other hand, we must assume that the current will always seek the most convenient path; thus in many cases a scattering of the current lines is observed. If we take a corrugated cathode, then at the beginning of the electrolysis, when the ion concentration is the same at all parts of the cathode surface, the most convenient path for the current to take is that leading to the ridges on the electrode, and the current lines will be directed toward these high places and there the first deposit of metal will be noticed. In this way the solution in the vicinity of the ridges becomes robbed of its metal ions and the result of this is, as the Nernst formula indicates, that the decomposition potential is increased; this is because a lessening of the ionic concentration causes a diminution in the osmotic pressure p and if this value is diminished the formula shows that E becomes larger (p. 84). This increase in the decomposition potential at the ridges of the electrode causes the current lines to be directed no longer toward them and these lines now find the path toward the indentations of the electrode the most convenient one. Soon, however, the latter portions of the electrode are robbed of metal ions sufficiently so that the current lines are turned away from them and are again directed toward the projections on the surface of the electrodes.

Now, if we follow the course of electro-analysis still farther, we may next ask: What tends to prevent the impoverishment of the metal ions at the cathode? In the first place, the supply of metal ions is favored by the migration of the ions, which is a result of the action of the current (see p. 13); in this migration the positively charged metal ions are repelled from the anode and attracted by the cathode. There is here a marked difference noticed according to whether the electrolyte contains a simple or a complex metal salt. In the solution of a simple metal salt, such as silver nitrate, the metal ions can move in only one direction and that is toward the cathode. In the solution of a complex salt, on the other hand, the electrolytic dissociation takes place in such a way that the positively charged potassium ions are attracted toward the cathode while the negatively charged $[Ag(CN)_2]^-$ ions move toward the anode. The latter ions are, to a very slight extent, dissociated into Ag^+ and CN^- ions, so that a limited supply of silver ions is present at the cathode. The metal ions, therefore, will be supplied much more slowly in complex electrolytes than in a simple electrolyte.

Although the metal present in a complex anion migrates away from the cathode it is clear that if the metal is present in a complex cation, as in the ammoniacal solution of a silver salt, it then will migrate in the opposite direction. Thus, the silver-ammonia cation $[Ag(NH_3)_2]^+$ migrates toward the cathode.

In solutions of simple, as well as of complex, salts the supply of metal ions is also supported by diffusion, *i.e.*, by the equalization of the metal concentrations in the impoverished and in the richer parts of the solution. Diffusion will be chiefly toward those parts of the solution where the impoverishment of metal ions has been the greatest, *i.e.*, toward the ridges, the edges and corners of the cathode.

It was pointed out on page 63 how this diffusion could be hastened by violent stirring. Attention was called to the fact that there would be a difference in the effectiveness of the stirring according to whether the natural tendency of an electrolyte is to furnish metal ions slowly or quickly.

It is easy to realize that the rate at which the solution is impoverished is dependent, to a high degree, upon the current density. Danneel sought out all the conditions which lead to an impoverishment of the solution and all those which had the opposite effect, and, after contrasting these, he attempted to determine the effect that a preponderance of one or the other of these causes would have upon the nature of the deposit. He came to the following conclusions: If the current density is so low that diffusion has time to prevent any serious impoverishment of the solution wherever it is in contact with the electrode, throughout its entire surface, then the most convenient path for the current lines to follow is to the elevated portions of the electrode, and the metal deposit develops long, well-formed crystals, such as are observed in a silver coulomb-meter when very low current densities are employed. With moderate current densities, the behavior of the solution is that outlined on page 86, and the deposit takes place alternately upon the elevations and upon the depressions of the electrode surface; as a result the metal is uniformly deposited over the entire electrode. If, however, the current density is high and the solution is impoverished so rapidly that diffusion has no chance to keep up the supply of metal ions, then the behavior mentioned on page 86 is encountered; the discharge potential of the metal increases, because of the diminution in the osmotic pressure of its ions, until it becomes equal to the discharge potential of hydrogen and, as mentioned on page 53, because of the simultaneous discharge of hydrogen ions the metal is deposited loosely and in a spongy condition.

The foregoing explanation is in perfect accord with the fact mentioned on page 63, that, by energetic stirring, the evolution of hydrogen can be prevented even with high current densities. H. J. S. Sand* pointed this out in 1900. This explanation also accounts for the fact, known for a long time, that certain metals are deposited much more uniformly from the solution of a complex salt than from one of a simple salt, although we have not yet explained why the complex salts are better suited for certain metals than for others. It was mentioned above that silver is usually deposited in coarse crystals from the solution of a simple silver salt; from a solution of the complex salt $K[Ag(CN)_2]$, on the contrary, the silver deposits more uniformly and we can explain this by the slow breaking down of the $[Ag(CN)_2]^-$ anion; the few silver ions present in the solution at the start are sent toward the elevations on the surface of the platinum electrode, then the current is directed toward the lower portions of the surface where there are still some silver ions, and during this time the anion $[Ag(CN)_2]^-$ is decomposed enough to restore the disturbed equilibrium, and the process is repeated over and over again.

The conditions mentioned above, under which the metal deposit is loosened by or accompanied by the evolution of hydrogen, will be brought out more clearly by the following logical conclusions drawn from the Nernst formula. They show, in connection with

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* Z. phys. Chem., **35**, 648 (1900).

the theory of overvoltage outlined on page 82: 1. Why it is possible to precipitate quantitatively a metal from a solution by electrolysis, *i.e.*, until the last weighable traces are removed, in spite of the increasing impoverishment of the metal ions and the resulting decrease in the osmotic pressure, which causes the decomposition potential to rise. 2. Why certain metals, although the discharge potential of their ions is greater than that of hydrogen, can be deposited before hydrogen is liberated.

Let us first examine what information the Nernst formula shows concerning the diminution of the concentration of the solution, as this is something which must take place in every electrolysis. Choosing a bivalent metal, for simplicity, then, since $n = 2$, the Nernst formula reads:

$$\mathrm{E} = 0.029 \log \frac{P}{p}.$$

The electromotive force E has, therefore, a definite value for a given osmotic pressure p, *i.e.*, for a definite concentration of metal ions.

As the concentration diminishes during the progress of the electrolysis eventually the value of p sinks, for example, to one tenth its original value. Then the formula becomes

$$\mathrm{E}_1 = 0.029 \log \frac{P}{p/10} = 0.029 \log 10 \frac{P}{p} = 0.029 \left(\log 10 + \log \frac{P}{p}\right),$$

or

$$\mathrm{E}_1 = 0.029 + 0.029 \log \frac{P}{p},$$

Thus, when the dilution is increased tenfold, the electromotive force E is only increased 0.029 volt.

Similarly, when the concentration of the solution has been reduced until p is only $\frac{1}{100}$ of its original value, then

$$\mathrm{E}_2 = 0.029 \left(\log 100 + \log \frac{P}{p}\right),$$

or

$$\mathrm{E}_2 = 2 \times 0.029 + 0.029 \log \frac{P}{p}.$$

This computation shows, therefore, that for every time the solution is diluted tenfold, the value of E is increased 0.029 volt,*

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* If the metal in consideration is univalent, this value becomes 0.058 volt, if trivalent 0.019 volt, and if quadrivalent 0.015 volt. In other words,

and thus if the concentration were diminished until the osmotic pressure of the solution became $\frac{p}{10^6}$, the value of E would be increased only 6 × 0.029 = 0.174 volt, or not quite 0.2 volt.

When the concentration has been reduced to one-millionth of its original value, the quantity of metal remaining cannot be detected, in most cases, by the ordinary reagents and the deposition may be regarded as complete. Mathematically, it will be impossible ever to reach the true zero concentration. The significance of the increase in potential of nearly 0.2 volt will be shown at once.

If we examine the Nernst formula to determine under what conditions a metal can be deposited, we shall find that it shows us the conditions under which the potential of the metal remains smaller than that of hydrogen, *i.e.*, when

$$0.029 \log \frac{P}{p} < 0.058 \log \frac{P_H}{p_H}.$$

P and p refer to the metal, P_H and p_H to hydrogen.

In the course of the analysis the above inequality, which must persist for the desired purpose, changes; the expression on the left becomes larger, because p grows smaller, and the expression on the right becomes smaller, because p, which is proportional to the concentration of the hydrogen ions, is usually increased by the formation of acid.

There is, therefore, a tendency for the two sides of the above inequality to become equal to one another, or, in the most unfavorable case, for the potential of the hydrogen to become greater than that of the metal.

The following table gives the discharge potentials in volts for six metals from normal solutions as determined for moderate current densities at the cathode.*

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where the change in valence is one, changing the concentration tenfold changes the electromotive force required to discharge it 0.058 volt at 18°; if the valence change is n a corresponding change of concentration changes the electromotive force $\frac{0.58}{n}$ volt.

* Coffetti and Foerster, Ber., **38,** 2934, and Z. angew. Chem., **19,** 1842 (1906). The values here given are in round numbers and those for Cd have been obtained to some extent by interpolation. For the details of making the measurements, the original paper should be consulted.

Current density in amperes per sq. cm.	Zn.	Fe.	Ni.	Co.	Cd.	Cu.
0	+0.79	+0.66	+0.60	+0.52	+0.44	−0.31
0.0023	+0.84	+0.71	+0.63	+0.56	+0.49	−0.27
0.0046	+0.85	+0.73	+0.65	+0.58	+0.50	−0.26
0.0091	+0.88	+0.75	+0.66	+0.59	......	−0.24

The values in the above table represent the difference between the discharge potentials of the metals and that of hydrogen from a normal solution of hydrogen ions. Thus, if the last value given for copper is inserted in the above inequality, it becomes

$$-0.24 < 0$$

and the expression shows that it is possible to deposit copper from an acid solution. The inequality remains in the same sense if we assume the maximum value applicable to the extremely dilute copper solution, at which the discharge potential of the copper will be not more than 0.2 amperes in addition to its previous value, for

$$-0.24 + 0.2 < 0$$

In other words, copper can be deposited completely, or at least to within the limits that can be detected qualitatively, from an acid solution of a simple salt.

The more noble metals, mercury, silver, etc., behave like copper in this respect, because their position in the potential table is to the right of copper.

Other metals, like cadmium, have discharge potentials which are more positive than that of hydrogen and they should not, in accordance with this view, be deposited before hydrogen is liberated, for the reversed inequality expression becomes

$$0.029 \log \frac{P}{p} > 0.058 \log \frac{P_H}{p_H}.$$

As a matter of fact, cadmium can be deposited from fairly acid solutions and the reason for this is to be sought in the overvoltage, mentioned on page 82, which hydrogen shows to these metals. The inequality expression which expresses the condition for the possibility of the deposition of these metals, takes the following form:

$$0.029 \log \frac{P}{p} < 0.058 \log \frac{P_H}{p_H} + \eta,$$

in which η represents the overpotential in volts for hydrogen toward the metal in question.

Foerster* took values determined by J. Tafel† and arranged them in the following table:

Current density in amperes per sq. cm.	Overpotential of hydrogen in volts, on				
	Hg.*	Sn.	Cu.	Ni.	Pt, platinized.
0.01	1.18	0.98	0.57	0.56	0.05
0.05	1.26	1.11	0.70	0.68	0.06
0.10	1.30	1.16	0.79	0.74	0.08

If these values are placed on the right-hand side of the above inequality expression, the possibility of the metal being deposited before hydrogen will be shown.

All the above explanation has been with reference to solutions of simple salts, and especially the sulphates.

It has been pointed out that the deposition from complex salts takes place less readily than from simple salts. With reference to this fact, Foerster § has collected the following values, which show that the deposition potentials of zinc, copper and cadmium in alkali-cyanide solution lie much higher than the corresponding values in sulphate solutions. The figures given in the last three columns of the table hold true for solutions containing $\frac{1}{10}$ mole of the metal cyanide in question, and this is designated by the general symbol $M(CN)_z$, in the presence of $\frac{2}{10}$ or $\frac{1}{10}$ and $\frac{10}{10}$ moles of potassium cyanide. The first column gives, for comparison, the values in a normal solution of the sulphate.

M.	$\frac{1}{2}$ mole MSO_4 in 1 liter.	$\frac{1}{10}$ mole $M(CN)_z$ $+\frac{2}{10}$ mole KCN in 1 liter.	$\frac{1}{10}$ mole $M(CN)_z$ $+\frac{4}{10}$ mole KCN in 1 liter.	$\frac{1}{10}$ mole $M(CN)_z$ +1 mole KCN in 1 liter.
	volt	volt	volt	volt
Zn..................	+0.79	+1.03	+1.18	+1.23
Cd..................	+0.44	+0.71	+0.87	+0.90
Cu..................	−0.31	+0.61	+0.96	+1.17

From this table it is clear, (1) that the potential in a potassium-cyanide solution is considerably higher than in a sulphate solution;

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* Z. angew. Chem., **19**, 1843 (1906). † Z. physikal. Chem., **50**, 641 (1905).

‡ The values for lead, cadmium and zinc are close to those for mercury.

§ Z. angew. Chem., **19**, 1846 (1906).

(2) that the potential increases as the potassium-cyanide content is raised; (3) that the potential of copper increases relatively faster than that of the other two metals and, under the experimental conditions of the fourth column, it is even greater than that of cadmium. Consequently, in a solution containing considerable potassium cyanide, cadmium will be deposited before copper, whereas in a dilute sulphuric-acid solution the reverse is true. From the closeness of the values given for copper and zinc in the fourth column, it is clear why these metals can be deposited simultaneously in the form of brass from a potassium-cyanide solution, which is altogether impossible in a sulphuric-acid solution owing to the difference between the discharge potentials of these metals in acid solution.

The influence of heat upon the deposition and separation of metals in simple and complex electrolytes will next be shown, the data being taken from an article by F. Foerster.*

Influence of Temperature on the Separation of Metals in Complex Electrolytes.

If, during the electrolytic deposition of a metal, the potential at the cathode is measured by means of an auxiliary electrode

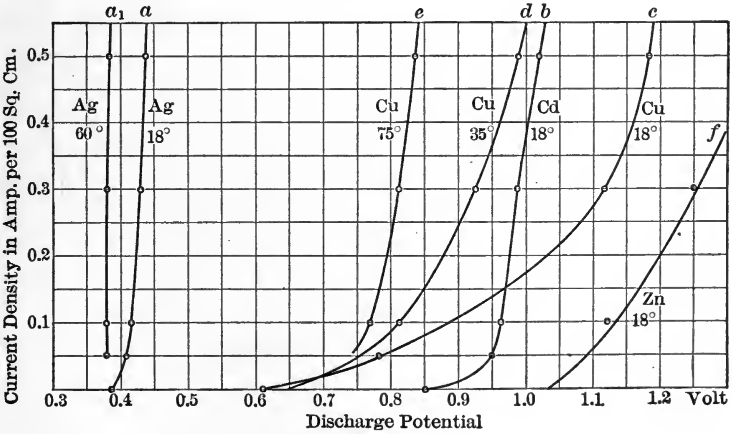

FIG. 45.

(*cf.* p. 40), or, in other words, if the discharge potential is measured at varying current densities but at a uniform temperature of

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* Z. Elektrochem., **13,** 561 (1907).

the electrolyte, *e.g.*, at 18°, and if the corresponding values for current density and potential are plotted, with the former as ordinates and the latter as abscissas, it will be shown by the rapid rise of the curve that the cathode potential is increased but slightly as the current density is raised. A curve obtained in this way is similar to that of *a* in Fig. 45. This is generally true, however, only for simple electrolytes, such as, for example, the sulphate solutions of copper, cadmium and zinc.

If the same measurements are carried out for a given metal at a higher temperature, *e.g.*, 50°, the curve shows a steep ascent as before, but there is the difference that the new curve lies to the left of the one plotted for the lower temperature because the discharge potentials at high temperatures are lower than those at low temperatures. This diminution of the potential value depends upon the decrease of the resistance of the electrolyte caused by heating it. Aside from this lessening of the resistance, which naturally corresponds to a better current yield, the raising of the temperature, as the author was the first to point out, also results in an improvement in the nature of the deposit obtained; it is denser and adheres more firmly to the cathode.

If corresponding measurements are made in complex electrolytes, *e.g.*, in a potassium-cyanide solution, the current density vs. potential curves will show that the metals behave differently with respect to the increase of discharge potential with rise of current density.

In Fig. 45, the curve *a* represents the deposition of silver from a potassium-cyanide solution at 18°; it shows that, similar to the deposition from a solution of a simple salt, the discharge potential increases but slightly with increased current density. The curve a_1, lying to the left of *a*, represents the deposition of silver from a potassium-cyanide solution at 60°. These two curves show that the behavior of silver in potassium-cyanide solution is similar, in this respect, to the behavior of silver in a simple electrolyte.

The same is true of cadmium, of which only the curve *b* at 18° is drawn.

Copper, on the other hand, behaves quite differently in an alkali-cyanide solution. The curve *c*, which represents copper in a potassium-cyanide solution at 18°, shows that the discharge potential increases considerably at this temperature with increasing current density. The curves *d* and *e*, for 35° and 75° respectively, show that the behavior of copper at higher temperatures corresponds more nearly to its behavior in the solution of a simple electrolyte. Thus the curve *e*, being so nearly a vertical line, makes it clear that the discharge potential varies but slightly with increasing current density.

Zinc, for which only the curve *f* at 18° is drawn, behaves like copper.

Now, if we study the curve *c* more closely, we shall find that, in the deposition of copper from a potassium-cyanide solution at ordinary temperature, the discharge potential for copper increases considerably as the current density is raised, or, conversely, if it is desired to deposit copper with high current densities, and thus more rapidly, it requires a much higher voltage. A comparison of the curve *c* with the curve *a*, for silver at 18°, and with a_1, for silver at 60°, shows that the relations are much more favorable for silver inasmuch as the potential for this metal in cyanide solutions whether at 18° or at 60°, increases very slightly with increasing current density; in other words, a slight increase in the voltage of the current results in a marked increase in the current density and a much more rapid deposition of the metal. Foerster* explains the behavior of copper and zinc by assuming that there is a "reaction resistance" to overcome in the case of the cyanide solutions of these metals. This resistance, of which the nature is still unknown, is lessened by raising the temperature, as the curve *e* for copper at 75° clearly shows. The fact that such a reaction resistance is not shown in the solution of silver in alkali cyanide is an argument against the assumption that such a resistance is, in general, found in complex electrolytes and that the resistance can be explained by the difficulty in decomposing the complex that contains the metal. However, it must be remembered that there are gradations in the complexity of such solutions, and this is true not only in the complexes of different metals, as, for example, between the copper-cyanide ion and the silver-cyanide ion, but also in the complex of one and the same metal at different temperatures and concentrations of the solution. If the degree of complexity is judged by the anomalous reactions which the solutions show, then the argenticyanide ion $[Ag(CN)_2]^-$ must be regarded as less complex than the cuprocyanide ion $[Cu_2(CN)]_8^{\equiv\equiv}$; the solution of silver cyanide in potassium cyanide gives a precipitate when treated with hydrogen sulphide while this is not

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* Z. Elektrochem., **13**, 561 (1907).

the case with a potassium-cyanide solution containing dissolved copper. Moreover, the complexity of the potassium-cuprocyanide solution becomes increased as the potassium-cyanide content is raised; thus F. P. Treadwell and v. Girsewald[*] have found that complete complexity, *i.e.*, the failure of the usual reactions for detecting copper, especially the hydrogen-sulphide test, is only brought about when the solution contains more than enough potassium cyanide to form the salt $K_6[Cu_2(CN)_8]$ (*cf.* p. 48). The two facts discovered by A. Brunner[†] are in accord with this. Brunner found that by increasing the amount of potassium cyanide added to the solution he could prevent the electrolytic deposition of copper and that at a higher temperature, as the curve *e* shows, the deposition took place normally. In the case of copper, therefore, the influence attributed to reaction resistance, which influences the velocity of the metal deposition with high potassium-cyanide content and low temperatures, can be explained by the highly complex nature of the solution.

Whatever the truth of the matter may be, the experiments of Foerster and his co-workers have served to explain a number of important facts already known concerning electrolytic deposition. Thus, for example, cadmium can be deposited before the copper in a potassium-cyanide solution with a current of 2.6 volts, provided sufficient potassium cyanide is present. The possibility of this separation cannot be traced to the difference in potential between the two metals, for it is only about 0.2 volt in such a potassium-cyanide solution and this is not sufficient for a satisfactory separation. The separation is based rather upon the different reaction velocities with which the metals are deposited under the given conditions.

The curve *e* shows that this reaction velocity is much greater for copper at 75° and it then is very near to the reaction velocity of cadmium, and since the discharge potentials of the two metals are near one another at this temperature, it is clear that it is impossible to effect a satisfactory separation at high temperatures.

The opposite case, where a separation can take place at a high temperature although impossible at the ordinary temperature, will be discussed in the separation of nickel from zinc.

[†] Z. anorg. Chem., **38,** 92 (1904).

[‡] Z. Elektrochem., **13,** 562 (1907).

Non-electrolytic Methods of Electrochemical Analysis.

This book, according to its title, embraces methods of electrolytic analysis in which the metal is, as a rule, deposited upon the cathode and weighed in the metallic condition. There are, however, three other methods of quantitative analysis which are associated with the electrochemistry of aqueous solutions. These are (1) potential measurements which serve to determine the concentration of ions in very dilute solutions; (2) conductivity measurements which are often convenient for determining the concentration of solutions; and (3) electrometric titrations in which the end-point of a reaction is determined by a sudden change in the decomposition potential at the cathode. The theory of these processes is so closely related to that of ordinary electrolytic work that it seems desirable to discuss the principles briefly at this point and to include a few such methods in the following sections of the book.

We have seen (page 28), that the electromotive force developed at 18° by contact of a metal with its ions may be expressed mathematically by the Nernst formula:

$$E_{18^\circ} = \frac{0.058}{n} \log \frac{P}{p} \text{ volts.}$$

Since the osmotic pressure is proportional to the concentration of the dissolved ions, it is mathematically correct to substitute the ionic concentration of the solution, c, for the osmotic pressure, p, and to replace the solution pressure, P, by the ionic concentration, C, which prevails in the solution when $E = O$. The Nernst formula then becomes

$$E_{18^\circ} = \frac{0.058}{n} \log \frac{C}{c} \text{ volts.}$$

Since the logarithm of 10 is 1 and of 0.1 is -1, the value of $\log \frac{C}{c}$ $(= \log C - \log c)$ is decreased one unit if the ionic concentration, c, is increased tenfold and the value is increased one unit if c is decreased to one-tenth its former value. The value of E, therefore, is decreased $\frac{0.58}{n}$ volt if the concentration of the solution is increased tenfold and increased by the same value if the solution is diluted tenfold.

If a silver electrode, for example, is placed in a 0.1 normal solution of silver nitrate, and another silver electrode is placed in a 0.01 normal solution of silver nitrate, then on joining the electrodes by means of a wire and placing the two solutions in contact with one another, a current will flow through the wire from the concentrated solution to the dilute one and its electromotive force will be 0.058 volt; the silver will dissolve in the dilute solution and will be deposited from the concentrated solution.

This principle may be applied to the determination of the solubility of difficultly soluble substances. A convenient way of doing this is to determine the decomposition potential at the cathode, with the aid of a hydrogen electrode, or a normal calomel electrode, using a solution of known ionic composition at one electrode and a saturated solution of the difficultly soluble substance at the other. Applying the Nernst formula to the two solutions of concentrations c_1 and c_2, and subtracting one from the other to get the difference in potential, we have

$$E_{18^\circ} = \frac{0.058}{n} \log \frac{C}{c_2} - \frac{0.058}{n} \log \frac{C}{c_1}$$

$$= \frac{.058}{n} (\log C - \log c_2 - \log C + \log c_1) = \frac{0.058}{n} \log \frac{c_1}{c_2}.$$

To illustrate, if the measured value of E is 0.216 in a cell of which the cathode is silver against a tenth-normal solution of silver ions and the anode is silver against a saturated solution of a slightly soluble silver salt, then

$$\log \frac{0.1}{c_2} = \frac{0.216}{0.058} = 3.73;$$

$$\frac{0.1}{c_2} = 5.37 \times 10^{+3};$$

$$c_2 = 1.86 \times 10^{-5}.$$

The solubility of the silver halides may be determined in this way.

The application of the conductivity principle to the concentration of solutions involves the same principle as when any other physical property, such as specific gravity, is used for the purpose. The specific gravity of all mixtures of water and alcohol is known; by determining the specific gravity of a mixture of alcohol and water, therefore, it is easy to find out the percentage of alcohol present by consulting tables that have been prepared. In the same way, if the conductivity of solutions of any electrolyte is known for various dilutions it is possible to tell what the concentration of a solution is by measuring the conductivity. Thus the small quantity of mineral salt present as impurity in a sugar solution or in a mineral water can be determined fairly well by measuring the conductivity.

The principle involved in electrometric titrations is similar to that of determining solubility by measuring the cathode potential. The quantitative methods of acidimetry and alkalimetry consist in measuring the concentration of the hydrogen ion. Ordinarily an indicator, such as methyl orange, methyl red, or phenolphthalein, is used which changes color at a certain definite concentration of hydrogen ions.

Kohlrausch and Heydweiller* have determined the conductivity of very pure water. Assuming that its conductivity is due to the presence of an equal number of hydrogen and hydroxyl ions, the concentration of each was found to be 10^{-7} in moles per liter. If we designate the concentration of hydrogen ions by $[H^+]$, that of hydroxyl by $[OH^-]$ then the mass action law applied to the ionization of water reads

$$\frac{[H^+] \times [OH^-]}{[H_2O]} = \text{a constant.}$$

Since the total volume of the water is not influenced appreciably by the ionization, and its value is very large in comparison to the concentration of the hydrogen and hydroxyl ions, we may say that the equilibrium between H^+ and OH^- ions can be expressed in all cases by the equation:

$$[H^+] \times [OH^-] = 10^{-14}.$$

In a 0.001-normal acid solution the concentration of the hydrogen ions is 10^{-3} but in a 0.001-normal caustic alkali solution the concentration of the hydrogen ions comes entirely from the water and since the hydroxyl concentration is 0.001, it follows that the hydrogen ion concentration is 10^{-11}. In other words,

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* Wied. Ann., **53**, 209 (1894).

as the solution changes from the acid side to the alkaline side during the addition of alkali, a sudden change takes place in the concentration of the hydrogen ion. If the cathode potential is compared with that of the hydrogen electrode, or of the normal calomel electrode, and a galvanometer is placed in the circuit, the needle of the galvanometer will be deflected suddenly when the acid is just neutralized. Bottger * has applied this principle to the titration of a number of acids and bases. J. H. Hildebrand † has shown how the experimental technique can be simplified.

We have seen that all chemical changes that take place at the cathode are reductions and when we measure the cathode decomposition potential in a solution of hydrochloric acid we are really measuring the electromotive force necessary to reduce the hydrogen from the positively charged to electrically neutral condition. Any other reaction of oxidation and reduction may be studied in the same way. Thus Crotogino ‡ has determined the end-point in oxidation and reduction reactions with the use of a platinum electrode and galvanometer. Ostwald, Luther and Drucker,§ Hildebrand ¶ and Forbes and Bartler ** have discussed in particular the titration of ferrous salts with potassium dichromate. These electrometric titrations are particularly useful in solutions which are highly colored so that ordinary indicators are not helpful.

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* Z. phys. Chem., **24,** 253 (1897). See also van Suchtelen and Itano, J. Am. Chem. Soc., **37,** 1793 (1915).

† J. Am. Chem. Soc., **35,** 845 (1913).

‡ Z. anorg. Chem., **24,** 225 (1900).

§ Physikal-chemische Messungen, p. 454.

¶ J. Am. Chem. Soc., **35,** 869 (1913).

** J. Am. Chem. Soc., **35,** 1527 (1913).

HISTORICAL.

Like every new branch of science, the development of electrochemical analysis was at first almost wholly empirical. The most suitable conditions for the quantitative separation of metals by electricity were determined from a great number of experiments, conducted with diligence and perseverance, while the nature of the reactions involved was not always clearly understood. The relatively recent development of electrochemistry has served to throw much light on the theory of quantitative electrolysis, and the importance and significance of the electrical factors and other conditions are now much more clearly understood.

The first attempts at the electrolytic determination of the metals were entirely qualitative in character. Shortly after the discovery, by Nicholson and Carlisle (1800), of the decomposition of water by the electric current, Cruikshank (1801), having observed the separation of metallic copper, suggested that the galvanic current might be used for the qualitative determination of other metals. This suggestion awakened but little interest. In 1812 Fischer employed an electrolytic method for identifying arsenic in animal fluids, and later, in 1840, Cozzi used a similar method for the detection of metals in general in such solutions.

The discovery of galvanoplasty, a most important technical process closely allied to electrochemical analysis, dates from 1839 and was made by Jacobi.

Gaultier de Claubry, in 1850, recommended the use of the electric current for detecting poisonous metals in mixtures containing organic substances, and in 1860 Charles L. Bloxam continued this work and devised numerous methods by which he attempted to make the identification of arsenic and antimony possible in the presence of other metals. In this work he was assisted somewhat by the directions for the separation of metals from mixtures published by Morton in 1851.

Becquerel observed, as early as 1830, that lead and manganese often separated in the form of oxides on the anode, a property which permitted these metals to be readily separated from others which deposit on the cathode. Investigations chiefly on the qualitative decomposition of inorganic salts of the metals were also carried out by Despretz (1857), Nicklès (1862), and Wöhler (1868). The work of A. C. and E. Becquerel (1862) on the electrolytic reduction of the metals was likewise of an entirely qualitative character.

It can be readily understood that with such abundant data at hand the development of quantitative electrolysis could now take place quite rapidly.

The field of quantitative investigation was first opened by W. Gibbs (1864), who carried out an investigation on the electrolytic determination of copper and nickel, which included a description of the methods for the determination of silver and bismuth in the form of metals, as well as of lead and manganese in the form of peroxides. He also published studies on the separation of zinc, nickel and cobalt. The possibility of the quantitative determination of copper was confirmed by Luckow (1865), who had worked at it for a number of years. The quantitative electrolytic determination of metals was entitled by him "electro-metal-analysis." This author published at the same time a series of directions for the method of using the current for analytical work, and by these precise instructions laid the foundation for many later researches.

The attention of investigators was first turned chiefly toward the chemical reactions taking place in the electrolytic cell and less weight was placed upon the source of the current and the physical condition of the experiment. The metal salts most suitable for electrolysis, the best solvents and the proper substances to be added to the solutions were investigated and determined. Thus Wrightson (1876) called attention to the fact that the accuracy of copper determinations was influenced by the presence of other metals and ascertained the limits under which copper could be accurately determined in the presence of antimony. The results obtained in the electrolytic determination of cadmium, zinc and other metals were not yet satisfactory.

Simultaneously with the announcement of the electrolytic determination of gallium in alkaline solutions by Lecoq de Boisbaudran (1877) came the announcement by Parodi and Mascazzini that zinc could be determined in a solution of its sulphate to which an excess of ammonium acetate had been added, and that metallic lead could be quantitatively precipitated from an alkaline tartrate solution containing an alkali acetate.

We are indebted to Riche (1878) for the first accurate directions for the determination of manganese. He observed that this element may be completely separated at the positive pole in the form of an oxide from solutions of the nitrate. This property permits the electrolytic separation of manganese from other metals, *e.g.*, copper, cobalt, nickel, zinc, etc.

Other papers which were published at that time by Luckow, F. W. Clarke, and J. B. Haunay described the electrolytic determination of mercury, which was found to separate readily from solutions of the chloride and sulphate.

A method for the electrolytic determination of cadmium was found by F. W. Clarke (1878), who succeeded in precipitating this metal from solutions of its acetate, and Yver (1880) employed a similar solution for separating cadmium from zinc.

Cadmium is not deposited in the presence of nitric acid and the attempt was made by Yver to separate this metal from copper, although the results were not entirely satisfactory.

The determination of zinc from solutions of the double cyanides was carried out by Beilstein and Jawein (1879), and Fresenius and Bergmann (1880) successfully precipitated metallic nickel and cobalt from solutions containing an excess of free ammonia and ammonium sulphate.

Edgar F. Smith showed (1880) that if uranium-acetate solutions were electrolyzed the uranium was completely precipitated as uranyl hydroxide; and, further, that molybdenum could be deposited as hydrated sesquioxide from warm solutions of ammonium molybdate in the presence of free ammonia.* We are indebted to the same author and his students for a large number of valuable contributions to the literature of electrochemical analysis.

Luckow (1880) rendered a special service in the publication of his observations on the reactions which take place during electrolysis. He pointed out the reduction from higher to lower states of oxidation in the case of chromic acid, iron and uranium salts, and demonstrated, on the other hand, that sulphites and thiosulphates are oxidized to sulphates. He summed up the results of his observations in a law, that in general the electric current

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* M. Heidenreich could not obtain good results by this method. Ber., **29**, 1587 (1896).

exerts a reducing action on acid, and an oxidizing action on alkaline, solutions. Recent investigations have shown, however, that other factors are of importance in these reactions.

In the year 1881, Alexander Classen and his students began a series of investigations on quantitative analysis by electrolysis which ultimately included nearly all of the metals. It was he who first pointed out the value of oxalic acid and the double oxalates. A large number of electrolytic methods originated by him will be described in this book.

At about the same time Reinhardt and Ihle proposed the double oxalates for the electrolytic determination of zinc.

An attempt was made (1880) by Gibbs, who used a mercury cathode, to determine metals by observing the increase in weight of the mercury due to the formation of an amalgam, and a similar method was employed by Luckow (1886) and later by Paweck for the determination of zinc.

The mercury cathode has been recently used extensively for determinations and separations by Kolloch and Smith and by Hildebrand.

Since the year 1886, a great number of publications on electrochemical analysis have appeared, and it is unnecessary to enumerate them all. Especially worthy of mention at this point, however, are the experiments conducted by Vortmann (1894) on the electrolytic determination of the halogens with silver anodes and by Specketer (1899) on the separation of the halogens in a similar way.

The investigations of Kiliani (1883), on the significance of the electromotive force in electrolytic determinations, served to draw attention to this important factor, and the later work of Le Blanc (1889) on the electromotive forces necessary for the decomposition of solutions of the salts of various metals added greatly to the available theoretical data. In 1891 Freudenberg successfully separated a number of metals from solutions containing several metals by carefully regulating the electromotive force of the current which he employed.

Hand in hand with the working out of electrolytic methods, improvements were made in the apparatus. The laboratory at Aachen played an important part in the introduction of electrolytic appliances and devices. As source of current, dynamos and storage cells were used here at a comparatively early date.

The application of electro-analysis has recently experienced a revolution through the introduction of rapid electrolytic methods. The first step in this direction was evidently based upon the suggestion of v. Klobukow, in 1886, to stir the electrolyte in order to hasten the deposition of the metal.

In 1897, A. Classen recommended, in the fourth German edition of this book, the stirring of the electrolyte in order to hasten the deposition of copper. In 1903, Dr. Amberg attempted to determine the atomic weight of palladium by electrolytic measurements, but as he was unsuccessful with stationary electrolytes, A. Classen suggested rotating one of the electrodes and this led to the desired end.

Since 1903, a great deal of similar work has been done independently by American, English and German investigators: Acree, Ashbrook, Cutcheon, Dennis, Exner, A. Fisher, Flanigen, Frary, Gooch and Medway, Hildebrand, Ingham, Langness, Lukens, Pawek, Perkin, Price and Judge, Sand, Shepherd, E. F. Smith, R. O. Smith and others. Their results will be mentioned in connection with the individual methods described.

In 1907 A. Classen described an outfit for carrying out rapid electrolytic determinations,* which permitted the simultaneous carrying out of a number of electro-analyses of various types.

Such is, in brief, the history of the development of methods used in quantitative analysis by electrolysis.† A short account will now be given of the progress of chemical theory concerning electrolysis.‡

Grotthus, in 1805, explained electrolysis on the basis of a successive decomposition and recombination of the molecules of the electrolyte. Thus, when water was subjected to electrolysis, a molecule of water was decomposed at the cathode and hydrogen was evolved as a gas. The oxygen then robbed a neighboring water molecule of its hydrogen and this process continued over and over again until finally at the anode the last molecule of water decomposed was unable to find hydrogen from any other molecule of water and free oxygen was evolved.

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* Z. Elektrochem., **13**, 181.

† A detailed account of all typical reactions which have been developed with the aid of electrolysis can be found in F. Foerster's very valuable book, Elektrochemie wässeriger Lösungen, 2nd Edition, Leipsic (1915).

‡ In preparing this outline, much of the information has been obtained from F. J. Moore's History of Chemistry, New York, 1918.

Sir Humphrey Davy (1778–1829) was of the opinion that chemical affinity could be explained on the basis of electrical attraction. Previously chemists had compared chemical affinity to gravitation. Davy believed that when two atoms capable of combining with one another are brought near one another they assume opposite electrical charges which are neutralized when the chemical compound is formed. Electrolysis, according to this idea, served to give back to parts of the original molecule the charges possessed before combination took place.

Michael Faraday (1791–1867) also believed that chemical affinity is of electrical nature. He understood clearly the relations that exist between the quantity of electricity required to deposit a given weight of metal and considered the weights deposited as the best criterion for the determination of atomic weights. He believed that only salts consisting of a positive and a negative atom are electrolytes. Faraday introduced the terms anode, cathode, anion and cation. He believed, however, that molecules were decomposed into anions and cations by the action of the electric current. Faraday believed that the voltage required to effect electrolysis was a measure of chemical affinity.

Berzelius (1779–1848) placed special weight upon oxygen and electricity in the development of his chemical theory. He assigned to every atom two poles like those of a magnet. For any given atom the positive charge at one pole was usually unequal to the negative charge at the other pole, so that, with the exception of hydrogen, which was regarded as practically neutral, each element was more or less positive or negative in nature. Berzelius arranged the elements in a series, much as we do to-day, placing potassium at the positive end, oxygen at the negative end, and hydrogen in the middle. Oxygen, according to Berzelius, was absolutely negative. Every compound substance was believed capable of being resolved into two parts, one electro-positive in nature and the other electro-negative. Salts were composed of an oxide of a metal and an oxide of a non-metal; in the former the positive charge of the metal predominated and the oxide was positive in nature, but in the latter the negative character of the oxygen was not overcome. According to this *dualistic theory*, the electric current resolves a salt into positive and negative oxides which appear as primary products at the cathode and anode respectively. According to Berzelius, an acid is not decomposed by the current but merely serves to increase the conductance of water which is itself decomposed into hydrogen and oxygen. Potassium sulphate, according to the dualistic theory, would be written, $K_2O \cdot SO_3$. During the electrolysis of a solution of this salt, K_2O would be the primary product at the cathode and SO_3 the primary product at the anode. Both of these are hydrated by the water and potassium hydrate, $K_2O \cdot H_2O$ remains in solution at the cathode and $SO_3 \cdot H_2O$ remains dissolved at the anode as final products of the electrolysis. Zinc sulphate, $ZnO \cdot SO_3$, on being subjected to electrolysis in aqueous solution is decomposed into zinc at the cathode and oxygen at the anode; this Berzelius explained by assuming that the ZnO was decomposed instead of the entire salt.

In 1851 Williamson advanced the idea that atoms and molecules in compounds exist in a state of dynamic equilibrium. A molecule instead of being a rigid structure was always exchanging material with neighboring molecules. Clausius in 1857 applied this idea to the theory of electrolysis. According to his view the electric current could either favor or hinder such an exchange of material between adjacent molecules. If the decomposed molecules can follow the electric force in their movement then the decomposition will be favored.

Hittorf in 1853 conducted a remarkable series of experiments on the rates at which the ions moved toward the poles during electrolysis. He found that the velocity at which the cation moves toward the cathode is usually different than the rate at which the anion moves toward the anode. The ratio of the velocity of one ion to the sum of the velocities of both ions he termed the *transference number.* Hittorf concluded that *electrolytes are salts* and that the electrolyte, not the solvent, carries the current.

Kohlrausch in 1876 confirmed the work of Hittorf and showed that the conductance could be calculated additively from the mobilities of the ions. Arrhenius in 1887 drew the conclusion that in any conducting solution only a certain part of the dissolved substance is responsible for the conductivity. He explained various abnormalities which had been noticed in the physical properties of solutions by assuming that ions were formed as soon as the electrolyte was dissolved in water. Previous investigators had thought that the current split the molecule into ions.

The views of Arrhenius concerning electrolytic dissociation, or ionization, are now accepted by most chemists.

Since 1887 important progress has been made in the physical conception of the ultimate composition of matter. In 1879 Sir William Crookes had noticed that when an electric current of high potential was passed through evacuated tubes containing gases at very low pressures, rays are emitted from the cathode of remarkable nature. These *cathode rays* proceed in straight lines but their path can be deflected by means of a magnet. Röntgen, in 1895, found that when cathode rays impinge against a solid a new ray is generated which can penetrate material that is opaque to ordinary light rays. These rays were called *x-rays.* In 1896, Becquerel discovered that similar rays could be obtained from uranium salts and in working over pitchblende, the well-known uranium ore, Madame Curie, aided by her husband, P. Curie, and G. Bémont, discovered the element radium in 1898. Radium was given its name because of the intensity of the radio-active emanation which it yields. Radium spontaneously emits rays of three different types: (1) α-rays which have proved to be positively charged helium atoms, (2) β-rays, which are identical with the cathode rays noticed by Crookes, and (3) γ-rays which resemble the so-called x-rays and have a very high penetrative force.

In addition an inert gaseous element, niton, is evolved. Thus radium, a chemical element of high atomic weight (226) is continually losing matter and energy and as a result of this decomposition more stable elements of lower atomic weight are formed.

Since 1900 Rutherford and Soddy have studied such phenomena and advanced a theory of atomic disintegration. Likewise J. J. Thompson has worked out the so-called *electron theory* to account for the ultimate composition of all matter. This theory is applicable to all branches of chemistry and serves to explain in simple terms the changes that take place during electrolysis.

The cathode rays detected by Crookes apparently consist of minute electro-negatively charged particles. They have the smallest mass of any particles yet known and have been called *corpuscles* or *electrons.* The atom of an element, according to Thomson, instead of being a simple, indivisible mass as we were taught, is really quite complex in nature and consists of an assemblage of negative electrons held together by a positively charged nucleus. The positive charge balances the total charge on all the electrons so that the atom itself is neutral. The approximate number of electrons present is proportional to the atomic weight of the element, the hydrogen atom containing either one or a very small number of electrons. The electrons are regarded as moving with high velocities in orbits within the atoms and they occupy a very small part of the atom as a whole.

According to Rutherford, the atom has a small central core of positive electricity surrounded by electrons, *i.e.*, negative charges of electricity. The atom also contains an outer system of electrons which are held together much less firmly than those of the inner system. The ability to lose one or more electrons from the outer system gives to the elements its chemical valence and accounts for its general chemical and physical behavior. If the element loses one or more electrons from the inner system it becomes changed into another element of lower order.

According to the electron theory, electric conduction in a solid conductor is due to a movement of the electrons of the outer system. This means that the current flows in exactly the opposite direction than that which has been assumed arbitrarily. Instead of the current moving in what we are accustomed to call the positive to negative direction, in reality only negative electricity moves and that in the direction which we arbitrarily call from a lower to a higher potential. In other words, chemists formerly fastened their attention upon the positive electricity. We now know a great deal more about negative electricity than we do about positive electricity, and in fact, the actual existence of positive electricity has been questioned.

The electron theory easily accounts for chemical combination. An element can lose one or more of its electrons from the outer system, provided it can find some other element to accept it. Thus the element sodium can give up one of its electrons to another element, such as chlorine. The sodium atom then possesses a unit positive charge simply because it has lost negative electricity. The chlorine, originally neutral, has become negatively charged in virtue of its having accepted an electron from the sodium atom. The chemical attraction that holds the sodium and chlorine together in the molecule of sodium chloride is merely the attraction of the positively charged sodium for the negatively charged chlorine.

The tenacity with which an element holds on to the electrons in the outer system varies with different elements. The unit charge or quantity of electricity lost by all univalent elements is the same but all kinds of energy may be resolved into two factors, the intensity factor and the capacity factor. Variations in the intensity factor of chemical energy account for the different degrees of chemical affinity.

The valence of an element is determined by the number of electrons it can lose or can accept in the outer system. An element which ordinarily has a positive valence of two has the power of losing two electrons; an element which ordinarily has a negative valence of two has the power of holding quite firmly in the outer system two negative electrons more than that corresponding to the neutral condition.

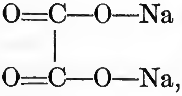
When acids, bases and salts are dissolved in water they break down to a certain extent into positively charged cations and negatively charged anions. The electron theory makes it possible to understand where these charges originate. The ionization of the neutral molecule also takes place in melted salts and can be detected in solids at temperatures below the melting-point.

Oxidation and reduction processes are easily explained by the electron theory. An element is said to be oxidized whenever the atom is made to lose one or more electrons, an element is said to be reduced whenever the atom accepts one or more electrons. Thus when the atom of iron is made to lose two electrons, the iron is oxidized to ferrous salt and when it is made to lose three electrons it is oxidized to ferric salt. The permanganate anion, MnO_4^-, is composed of four atoms of oxygen, each bearing a double electro-negative charge and one atom of manganese which has lost seven electrons. In contact with ferrous ions the atom of manganese is able to take away one electron from each of five atoms of iron whereby the iron is oxidized to the ferric condition and the manganese is reduced (because it has accepted negative electrons) to manganous salt:

$$MnO_4^- + 5Fe^{++} + 8H^+ = Mn^{++} + 5Fe^{+++} + 4H_2O.$$

In the cases thus far considered the polyvalent elements lost or gained electrons to correspond to their valence numbers. In many compounds, however, the atom is positive toward certain constitutents in the molecule and negative toward others. In the ammonia molecule, for example, the nitrogen has accepted an electron from each of three hydrogen atoms. When ammonia combines with hydrochloric acid to form ammonium chloride, NH_4Cl, the nitrogen has combined with an additional atom of hydrogen, and thereby gained an electron, and also combined with a negative chlorine atom, thereby losing an electron. The nitrogen in ammonium chloride, therefore, has gained electrons from four hydrogen atoms and lost an electron to the chlorine atom. The valence of the nitrogen in ammonium chloride is five, but of these five charges four are negative and one is positive. Ammonium chloride, therefore, belongs to the same state of oxidation as ammonia. This is sometimes expressed by saying that the *polarity* of the nitrogen remains -3 in ammonium chloride.

The polarity of any ion containing more than one atom is the algebraic sum of the valences of the atoms it contains. Thus as oxygen in nearly all of its compounds has a negative valence of two, it is apparent that the valence of manganese in MnO_4^- is $+7$, of nitrogen in NO_3^- is $+5$ and of chlorine in ClO_3^- is $+5$. The application of this rule to ions containing more than one atom of a given element may lead to confusion. Thus it would seem that the valence of the carbon in the oxalate ion, $C_2O_4^=$ is $+3$. The graphic symbol for sodium oxalate, however, is



$$\begin{array}{l} O{=}C{-}O{-}Na \\ \quad\;\; | \\ O{=}C{-}O{-}Na, \end{array}$$

and it is clear that each carbon has a valence of four. On the other hand, it is reasonable to assume that the valence of the carbon atom is positive toward the atoms of oxygen but obviously one carbon is positive to the other carbon atom if it is assumed that one end of each valence bond is positive and the other end negative. Hence one atom of carbon in oxalic acid has a positive valence of four, but the other atom of carbon has a positive valence of three and a negative valence of one. The polarity of the two atoms of carbon = is $+4+3-1=+6$.

We may say that in oxalic acid the average polarity of the carbon atom is $+3$. When oxalic acid is heated, it decomposes into water, carbon monoxide, and carbon dioxide. Evidently the atom of carbon in the carbon monoxide is the atom which was negative to the other carbon atom in the oxalate molecule.

The electron theory offers a very simple explanation of the decompositions that take place during electrolysis. At the cathode negative electrons enter the solution and serve to accomplish a chemical reduction there. At the anode, electrons leave the solution and pass to the electrode whereby an oxidation is accomplished in the solution. We may express the unit charge of an electron by a small Greek letter ϵ enclosed in a circle, $\textcircled{\epsilon}$. When the electric current is passed through a solution of sodium sulphate, the sodium ions migrate toward the cathode and the sulphate ions toward the anode. In this way the electric current passes from pole to pole. At each electrode, however, it is easier to decompose water than to discharge either sodium or sulphate ions. The reaction that takes place at the cathode, therefore, may be expressed as follows:

$$2H_2O + 2\ \textcircled{\epsilon} = 2OH^- + H_2.$$

The reaction that takes place at the anode is

$$2H_2O + 4\ \textcircled{\epsilon} = 4H^+ + O_2.$$

Two molecules of hydrogen are set free at the same time one molecule of oxygen is liberated.

In 1895 Ostwald published a paper on "The Overthrow of Scientific Materialism." He pointed out that all we know in the universe concerns changes in energy. According to Ostwald, energy is the only reality and matter is merely hypothetical. Most of us, however, cannot conceive of energy except associated with matter and cannot think of matter except associated with energy. Ostwald, however, did a distinct service to chemical science in pointing out that we really know more about energy than we do about matter and in emphasizing the fact that every chemical change is associated with a transference of energy. The electron theory does not tell us much about positive electricity, but it explains the possibility of an atom losing its identity merely as a result of losing energy from its inner system and it explains how an element, such as manganese, may show entirely different properties as a result of gaining or losing electrons.

PART II.

ELECTRO-ANALYTICAL DETERMINATIONS.

It is customary and convenient in the study of methods of analytical chemistry to divide the elements into groups. Thus in qualitative analysis the metals are divided into groups on the basis of the solubilities of their chlorides, sulphides, hydroxides and carbonates; likewise the acids have been classified on the basis of their volatility and the solubility of their silver and barium salts. Practically the same classification may be followed to advantage in the study of ordinary gravimetric analysis. Titration methods, on the other hand, are usually divided into reactions of acidimetry and alkalimetry, reactions of oxidation and reduction, and reactions of precipitation.

The reactions of electrolysis always involve a chemical reduction at the cathode and a chemical oxidation at the anode. Most of the methods discussed in this book depend upon cathodic reduction. Most of them involve the quantitative determination of a metal.

Any satisfactory classification of electro-analytical methods, must take into consideration the relative ease with which the metals are reduced at the cathode or, in other words, their position in the electromotive series (page 26). To deposit a metal upon the cathode it is necessary to overcome the oxidation potential of the metal. Other things being equal, the lower a metal stands in the potential series, the easier it is to deposit the metal upon the cathode.

It has been pointed out repeatedly, however, that the relative position of the elements in the electromotive series is not always the same. Many elements can exist in aqueous solutions in more than one state of oxidation. The oxidation potential of iron against a solution of a ferrous salt is greater than that of iron against a solution of a ferric salt of the same concentration. Moreover, if the metal exists in solution in the form of a complex ion this has a very marked effect upon the oxidation potential of the element against the solution. Thus the oxidation potential of iron against a solution of potassium ferrocyanide is much greater than that of iron against a solution of ferrous sulphate containing the same quantity of iron. For these reasons a rigid classification of electrolytic methods of analysis in accordance with the electromotive series does not work out perfectly. It also has the disadvantage of placing certain of the rarer elements among those to be considered first. The order in which the methods will be discussed in this book will be based partly upon theoretical considerations and partly upon practical grounds. The elements will be classified into the following groups: *

Group I. Metals which are electro-negative to hydrogen and can be deposited quantitatively on the cathode from acid solutions. The elements in this group are copper, silver, mercury, gold, palladium, rhodium, platinum, (iridium), bismuth, antimony, tin, (arsenic),† tellurium, (selenium). Copper will be considered first because this element has been determined electrolytically more than any other element and methods of great accuracy have been perfected for its determination to which it will be convenient to refer in considering the determination of other elements.

Group II. The metals indium, cadmium and zinc. The exact position of indium in the series is not known. Cadmium and zinc are above hydrogen in the electromotive series, but these elements can be deposited upon the cathode from dilute acid solution owing to the overvoltage which hydrogen shows toward them.

Group III. The metals iron, nickel, and cobalt. It is practically impossible to deposit these metals quantitatively unless the concentration of the hydrogen ions in solution is kept very low, as in the case of a little oxalic acid in the presence of a large excess of alkali oxalate. As a rule these metals are precipitated from an alkaline solution.

Group IV. Metals which are deposited as oxide upon one of the electrodes. These elements are lead, thallium, manganese, chromium, molybdenum, uranium (tungsten, vanadium, niobium, and tantalum).

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* *Cf.* A. Fischer, Electroanalytische Schnellmethoden, Stuttgart, 1908.

† An element in parentheses signifies that the element belongs in this group, but no satisfactory electrolytic method for its determination will be discussed.

Group V. Strongly electro-positive metals which cannot be deposited even from alkaline solutions except in the form of amalgams. This group includes (aluminium, glucinum, and rare earths), calcium, strontium, barium, potassium, sodium and (ammonium).

Group VI. Metalloids and anions which undergo anodic oxidation. Fluorine, chlorine, bromine, iodine, sulphur, carbonate, ferrocyanide, phosphate and nitrate anions, etc.

First the electrolytic methods will be discussed on the assumption that no other metal likely to interfere is present in the solution. Then, after all the groups have been considered, some separations will be described with special reference to electrolytic methods that have been found useful in commercial practice.

Electrolytic work is capable of yielding very accurate results, but often a slight change in the conditions, such as size and shape of the electrodes, volume of the solution, the acidity or the temperature will cause trouble so that it is advisable to follow directions very closely. Many of the methods have been worked out before the theory of electrolysis was well understood and emphasis was placed upon relatively unimportant conditions. For this reason, in describing the methods of various investigators there will be some duplication of data and in some cases apparent contradiction.

Important general data concerning each element will be given. This will include the atomic weight (At. Wt.), the electro-chemical equivalent (Elec. Equiv.), or weight deposited by one ampere in one second, the electrolytic or oxidation potential (Elec. Potential), of the element referred to the normal hydrogen electrode as of zero potential, and the overvoltage which hydrogen shows against a cathode of the metal in question. In giving the values of the oxidation potential, a positive sign will indicate that the element is above hydrogen in the potential series.

GROUP I.

METALS ELECTRO-NEGATIVE TO HYDROGEN.

Copper.

At. Wt. = 63.6. Elec. Equiv. = 0.328 mg. Elec. Potential = -0.34 volt for Cu^{++} ions. Overvoltage of H_2 = 0.03–0.23 volt.

AT least six distinct methods have been proposed for the electrolytic determination of copper. (1) The analysis is carried out in a sulphuric-acid solution; (2) in a nitric-acid solution; (3) in an ammoniacal solution; (4) in an alkalicyanide solution; (5) in an acid-oxalate solution; (6) in a phosphate solution.

Only the first three of these methods will be discussed in detail. The deposition of copper from an alkalicyanide solution is useful in the separation of this metal from iron, molybdenum, platinum, palladium and selenium. The use of a complex copper oxalate as electrolyte offers no special advantages for the quantitative determination. Such an electrolyte is excellent, however, when it is desired to obtain quickly a dense, glistening deposit of copper, for the purpose of subsequently determining zinc. The experiments of M. Heidenreich carried out in the author's laboratory have shown that the deposition of copper from a phosphate solution is not to be recommended.

1. *Deposition of Copper from Sulphuric-acid Solution.*

According to the older methods for carrying out the electrolysis in a sulphuric-acid solution, it was necessary to add certain substances to the electrolyte. When a solution of copper sulphate in dilute sulphuric acid is subjected to electrolysis with a current having a certain strength at the start, the current gradually diminishes in strength as the copper is deposited and thus it requires a very long time for the removal of the last traces of the metal. It used to be customary, therefore, to turn on more current toward the end of the operation, and thus the work was carried out with a current of practically constant strength. In such cases, however, the cathode potential in the solution impoverished of copper ions becomes greater than the discharge potential of hydrogen ions and this is the reason why the last traces of copper are deposited in a spongy condition (*cf.* p. 22). It was found possible to prevent the formation of a spongy deposit by adding one of a number of different substances, such as urea, hydroxylamine, nitric acid, or ammonium nitrate. The reason why nitric acid or a nitrate has a favorable effect is because the reduction potential of the nitrate anion is lower than the discharge potential of hydrogen; the anion can be reduced to ammonium cations or to free ammonia without evolution of hydrogen.

The reduction of the nitrogen from its positive valence of five in the nitrate anion to a negative polarity of three (or negative valence of four and positive valence of one) can be expressed by the equation:

$$NO_3^- + 10\,H^+ + 8\,\textcircled{e} = NH_4^+ + 3H_2O.$$

This reaction shows that the acidity of the solution decreases rapidly during the progress of the electrolytic reduction of the nitrate anion. When the hydrogen ions are all neutralized, free ammonia is formed:

$$NO_3^- + 8\,\textcircled{e} + 7H_2O \rightarrow NH_4^+ + 10\,OH^- \rightleftarrows NH_3 + 9\,OH^- + H_2O.$$

The neutralization of the acid may cause metals to precipitate as hydroxides or to deposit upon the cathode with the copper.

Ammonium ions and free ammonia, however, are not the only possible products from the electrolytic reduction of nitrate ions. Under certain conditions considerable hydroxylamine is formed and often an appreciable quantity of nitrous acid. Usually very little nitrous acid is present in the solution at any one time, because it is reduced farther very easily. The presence of any considerable quantity of nitrous acid will cause a copper deposit to dissolve off the electrode even while the current is still passing and it is chiefly due to the presence of a little nitrous acid that special precautions are often necessary in removing the electrode from the solution at the end of the electrolysis when all the copper has been deposited.

Careful experiments indicate that metallic copper is not appreciably soluble in cold, dilute nitric acid which contains no nitrous acid. If nitrous acid is present copper dissolves very rapidly and fresh nitrous acid is constantly formed during the progress of the reaction.

$$Cu + 2NO_2^- + 4H^+ \rightarrow Cu^{++} + 2NO + 2H_2O,$$

$$HNO_3 + 2NO + H_2O \rightarrow 3HNO_2.$$

It is possible to remove nitrous acid by adding urea

$$CO(NH_2)_2 + 2HNO_3 = CO_2 + 2N_2 + 3H_2O.$$

Foerster's method of carrying out the electrolysis makes the addition of nitric acid superfluous because the electrolysis is not carried out with a current of constant amperage but rather with one of constant voltage. When the potential of the current is kept at two volts, as when a single accumulator cell is used which has this potential when not too far exhausted, a voltage is provided which is enough higher than the decomposition potential of copper sulphate to effect the complete deposition of the copper, while, on the other hand, the overpotential of hydrogen ions toward the copper plated on the electrode is so large that there is scarcely any evolution of hydrogen (*cf.* p. 82). There is, therefore, nothing to cause the copper to be deposited in a spongy condition. There is no reason why several electrolytic cells should not be connected together in parallel and be simultaneously fed with the current of two volts.

As regards the accelerating effect obtained by heating the solution, this is partly explained by the fact that the diffusion velocity is greater in the hot solution than in the cold, and, therefore, the copper ions are carried toward the cathode with greater rapidity. The higher temperature of the liquid also lessens the overpotential of the oxygen at the anode. For, just as the hydrogen experiences an overvoltage toward the metal at the cathode, so, in the same way, the oxygen experiences a similar effect at the anode. This increase of anodic potential serves to lessen the current strength and thus the opposite effect is obtained by heating the solution (see also p. 92).

The duration of the electrolysis cannot be shortened indefinitely by raising the temperature above 80°. It is a well-known fact that metallic copper tends to form a small quantity of dissolved cuprous sulphate in accordance with the equation,

$$CuSO_4 + Cu = Cu_2SO_4,$$

or

$$Cu^{++} + Cu = 2\,Cu^+.$$

This reduction of the cupric sulphate may take place at the cathode even while the current is passing through the solution and the higher the temperature the greater the tendency for the reduction to take place. The reaction is thus a reversible one,

$$Cu^{++} + Cu \rightleftarrows 2\,Cu^{+},$$

because the cuprous sulphate is constantly being oxidized back to cupric sulphate by the oxygen of the atmosphere as well as that of the anode, so that the above equilibrium expression represents the true condition. Thus, while a part of the current is being used for depositing the copper at the cathode, another part is lost, in consequence of the reversible process just mentioned, for the wasted current serves only to effect the reduction of the cupric ions to cuprous ions. There would be no loss of current if the cuprous sulphate were, in its turn, reduced directly to metallic copper. Since, however, there is a tendency to form cupric ions again, there must be a certain amount of current wasted and this waste of electricity becomes greater as the temperature is raised. It is, therefore, advisable to keep the hot solution between 70° and 80° rather than to heat it to a higher temperature.

Precise directions will now be given for carrying out the electrolytic determination of copper in sulphuric acid solution by two well-tested methods.

Procedure. **Method A.*** Weigh out about 0.3 gm.† of the metal into a beaker of about 150-cc. capacity. Cover the beaker with a watch-glass, to prevent loss by spattering, and dissolve the metal in 10 cc. of 6-normal nitric acid with gentle heating. When the metal is all dissolved, wash down the sides of the beaker and the bottom of the cover glass with a little water, add 5 cc. of 6-normal sulphuric acid and evaporate, without boiling, until all the nitric acid is expelled and heavy fumes of sulphuric acid are evolved. Cool, dilute to 100 cc., and electrolyze, preferably with a gauze electrode (page 67), keeping the e.m.f. of the current at 2 volts. If a lead accumulator is used, connect

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* F. Foerster, Z. angew. Chem., **19,** 1890 (1906); Ber., **39,** 3029 (1906).

† For practice, about 1 gm. of blue vitriol ($CuSO_4 \cdot 5H_2O$) may be used. Dissolve 1 gm. in 10 cc. of double-normal sulphuric acid and 90 cc. of water. The solution is then ready for electrolysis. Double-normal sulphuric acid contains 98 gms. of H_2SO_4 per liter, or about 55 cc. of concentrated H_2SO_4 per liter.

the cathode with the negative pole (lead plate) and the anode with the positive pole (peroxide plate).

The complete deposition of the copper requires, under these conditions, about eight hours, and it is convenient, therefore, to let the current pass through the solution overnight. The end of the reaction can be told fairly closely by the marked lessening of the oxygen evolution at the anode. A few drops of solution are then removed, with the aid of a short piece of glass tubing, transferred to a porcelain tile and mixed with a drop of potassium-ferrocyanide solution. There should be no evidence of red cupric ferrocyanide.*

The time required for the analysis can be shortened considerably by heating the electrolyte to 70 or 80° (keeping a small flame under the beaker until the analysis is finished); in this way from 0.15 to 0.25 gm. of copper is deposited in from 60 to 80 minutes.†

If the deposition took place at the room temperature, it is simply necessary, at the end of the operation, to disconnect the current, quickly remove the cathode, rinse off the adhering solution with a stream of water from the wash bottle, dip the electrode in a beaker of distilled water that is ready at hand, then in alcohol, and dry it in the air bath at from 80 to 90° before weighing. The total weight of the electrode with the copper upon it minus the original weight of the electrode gives the quantity of copper that was present in the solution electrolyzed.

If, however, the deposition of the copper took place from a hot solution, the current must not be disconnected until after the washing of the cathode has been completed, because otherwise the hot, dilute sulphuric acid, with the aid of atmospheric oxygen, will dissolve considerable copper from the electrode.

From the hot solution, withdraw the electrode slowly and wash it with a stream of water from the wash bottle while withdrawing it. Do not disconnect the current until the electrode has been withdrawn from the solution.

Finally, wash the electrode with alcohol, heat in the drying oven just long enough to evaporate off the alcohol, cool in a large desiccator, and weigh.

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* In every electrolysis, the solution should be tested at the end to see if all metal has been deposited within the limits to which it is possible to detect it qualitatively. The time stated in the above directions can be influenced by a number of factors and should not be regarded as absolutely accurate.

† Under these conditions (temperature, voltage and degree of acidity) copper can be separated from large quantities of nickel, cadmium and zinc.

In case there is doubt whether all the copper has been deposited, clean the electrode by means of hot dilute nitric acid and electrolyze a little longer to see if any further deposit is formed. If this is the case, its weight should be added to that previously obtained.

Procedure. **Method B.** Dissolve about 0.5 gm. of metal in nitric acid and evaporate with sulphuric acid as in Method A. Cool, dilute to 100 cc., add 1 gm. of solid ammonium nitrate and electrolyze for twenty hours with a current of 0.1 ampere. At the end of this time, add 0.25 gm. of urea and a little water. If, after stirring the solution and allowing the current to pass for half an hour longer, there is no evidence of further deposition of copper, carefully remove the cathode, as directed in Method A when working with a hot solution, wash well with water, rinse in alcohol and dry at 105° for a few minutes. Cool and weigh. Clean the electrodes with nitric acid and see if any further deposit of copper can be obtained; or, test the solution for copper to see if a blue color is obtained with excess of ammonium hydroxide.* In case a blue color is obtained, make the solution slightly acid and electrolyze again.

Rapid Deposition of Copper from Sulphuric-Acid Solutions.†

No fault can be found with the accuracy of the electrolytic determination of copper with a stationary electrolyte during a period of from 12 to 24 hours. It is, however, often desirable to obtain results in a much shorter time. Moreover, if a large number of analyses are to be made in a given time with platinum electrodes, the expense of equipment increases as the time re-

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* Nickel also gives a blue color with an excess of ammonium hydroxide. The color in each case is due to complex ions; *e.g.*, $[Cu(NH_3)_4]^{++}$.

† General references to the literature concerning the rapid electrolytic determination and separation of copper from various solutions: Gooch and Medway, Am. J. Sci. [4], **15**, 320 (1903); Z. angew Chem., **35**, 414 (1903). Exner, J. Am. Chem. Soc., **25**, 896 (1903). E. F. Smith, *ibid.*, p. 884. A. Fischer and Boddaert, Z. Elecktrochem., **10**, 945 (1904). D. S. Ashbrook, J. Am. Chem. Soc., **26**, 1283 (1904). E. F. Smith and Kollock, *ibid.*, **27**, 1255 (1905). Flanigen, Thesis, 1906, U. Pa., Philadelphia. Langness, Thesis, 1906, U. Pa., Philadelphia. Perkin, Chem. News, **93**, 283 (1906); Z. Elektrochem., **13**, 143 (1906). H. J. S. Sand, J. Chem. Soc., London, **91**, 373 (1907); Z. Elektrochem., **13**, 326 (1907). A. Fischer, Z. angew. Chem., **20**, 134 (1907); Z. Elektrochem., **13**, 469 (1907). Frary, Z. Elektrochem., **13**, 308 (1907); Z. angew. Chem., **20**, 1897 (1907).

quired for electrolysis is lengthened. For these reasons a great many experiments have been made since 1900 in the study of methods requiring less time than those described above.

Since a current of 1 ampere will deposit 0.328 gm. of copper in one second, or 1.181 gm. in an hour, it is clear that the problem of the rapid determination of copper by electrolysis resolves itself into the determination of conditions under which current strengths of 1 or more amperes may be used without detriment to the character of the deposit and of conditions under which practically all of the current will be utilized, as long as copper ions remain in solution, for the deposition of metal.

As already pointed out, high current densities are likely to give spongy deposits because the natural migration of the ions does not take place fast enough to keep copper ions in the vicinity of the cathode; a time soon comes when it is easier to discharge hydrogen ions than to deposit copper from the solution which has become impoverished with respect to copper ions.

In general, more current can be used in proportion as the solution is concentrated and the electrode surface large. Increasing the electrode surface by diluting the solution is undesirable.

A platinum gauze electrode (*cf.* p. 67) is useful because a large electrode surface is obtained in proportion to the weight of the electrode and because the meshes of the gauze permit the ready passage of the electrolyte when it is stirred by convection currents or otherwise. Heating the solution helps by accelerating the rate of diffusion but when a strong current is used enough electrical energy is transformed into heat energy to raise the temperature of the solution, sometimes even to the boiling-point. By using a gauze cathode and a current of 6 amperes, J. L. Stoddard was able in ten minutes to get a good deposit and complete deposition of the metal from a solution containing 0.5 gm. of copper in 50 cc.

Stirring the solution, by means of an independent stirrer, by causing either the anode or the cathode to rotate, or by means of a magnetic effect (*cf.* p. 73) has also proved very helpful. The following table gives a summary of conditions under which good results have been obtained by various analysts with stirred electrolytes.

The abbreviation ND_{100} used in this table and elsewhere signifies the amperage per 100 sq. cm. of electrode surface in the electrolyte. This is the way in which the current density is usually expressed.

	Experiments performed by			
	A. Fischer at Aachen.	Gooch and Medway.	Exner.	H. J. S. Sand.
Kind of electrode.....	Platinum dish and rotating disk	Rotating platinum crucible as anode	Platinum dish and rotating spiral	Sand's electrode, p. 62
Electrolyte contained.	12 cc. conc. H_2SO_4	6 or 7 drops H_2SO_4 (1: 4)	1 cc. H_2SO_4 (1: 10)	0.75 cc. to 1 cc. conc. H_2SO_4
Volume..............	125 cc.	50 cc.	125 cc.	85 cc.
Quantity of metal.....	0.3 gm. as sulphate	0.25 gm. as sulphate	0.5 gm. as sulphate	0.5 gm. as sulphate
Temperature..........	55°–65°	Begun in the cold	Boiling	Luke warm or boiling
Voltage..............	2.8–2.6 volts	About 8 volts	14–9 volts	2.8–3 volts
Current density, ND_{100}	....	....	5 amperes	10 amperes
Number of revolutions per minute of the stirrer.	800	600–800	600	300–600
Duration............	33 minutes	10–15 minutes	3–5 minutes	5–7 minutes

Solenoid Method. G. L. Heath recommends the following method for the examination of samples of commercial copper.* The use of a large sample is advocated in order that the results may be more representative. It is claimed that the use of a mixture of nitric and sulphuric acids of the specified concentrations has been found empirically to give good results even when 0.5 per cent of arsenic is present.

Procedure. Dissolve 5 gm. of metal in a mixture of exactly 7 cc. of nitric acid, sp. gr. 1.42, 10 cc. of concentrated sulphuric acid and 25 cc. of water. Use a lipless beaker of 300-cc. capacity which is about 12 cm. tall and of 0.5 cm. diameter. Cover the beaker with a watch glass and heat just below the boiling-point

* J. Ind. Eng. Chem., **3**, 77 (1911).

until the copper is all dissolved. Rinse off the moisture that has condensed on the watch glass and wash down the sides of the beaker with a stream of water from the wash bottle, finally diluting to about 100 cc. Place the beaker in the solenoid apparatus (*cf.* p. 73 and p. 74) and electrolyze with a gauze cathode, using a current of 4.5 amperes through the solution and through the coil. Cover the beaker with a pair of split watch glasses to prevent loss. In about two hours and a half the solution will become colorless and the copper all deposited. It is important not to continue the analysis much longer than necessary (*cf.* p. 117). When the solution has become colorless, wash the bottom of the watch glasses and the sides of the beaker with a little water and continue the electrolysis for about half an hour longer. Then withdraw about 1 cc. with a medicine dropper and test it for copper with freshly-prepared hydrogen sulphide water. If a negative test is obtained, quickly transfer the cathode to a beaker of cold water. Then turn off the current, wash the electrode well with water and finally rinse with alcohol. Dry at 110 to 120° just long enough to evaporate off the alcohol; weigh when cool.

Deposition of Copper from Nitric-acid Solution.

The deposition of copper from a solution containing free nitric acid was first accomplished successfully by Luckow who determined in this way small amount of copper in the Mansfeld slates.

Procedure. For the analysis of a copper salt, dissolve about 1 gm. in 120 to 150 cc. of water. Of copper wire, dissolve 0.25 gm. in 4 or 5 cc. of nitric acid, sp. gr. 1.2. Dilute the solution to 120 cc. and boil very gently, with the beaker covered, to expel all nitrous fumes. Then rinse off the cover glass and wash down the sides of the beaker. To the solution prepared in either of these ways, add 2 or 3 cc. of nitric acid, sp. gr. 1.2, and about 0.1 gm. of urea to react with nitrous acid, in case any is present. Electrolyze with a current of 0.5 to 1 ampere per 100 sq. cm. of exposed electrode surface, using either a platinum dish, platinum cylinder, platinum cone, or platinum gauze * electrode. Toward

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* A fairly satisfactory gauze electrode can be made from copper gauze such as used in the determination of nitrogen in organic substances by the Dumas method. It is necessary to make sure that any lacquer or oxide is removed before using such an electrode, which may be accomplished by

the end of the analysis add a little more urea. The temperature of the solution may be from 18 to 30°.

As regards the termination of the electrolysis, the manipulation varies a little with the nature of the cathode. When the platinum cone or gauze electrode is used, the cathode should not be entirely covered by electrolyte, although it must reach to near the bottom of the beaker. To determine whether all the copper has been removed from the solution, raise the level of the liquid a few millimeters by mixing a little water with the solution and after some time has elapsed note whether there is any deposit formed on the freshly exposed surface of the electrode. If this is the case, the electrolysis must be continued. If, on the other hand, there is no further deposit of copper formed after ten or fifteen minutes, remove a little of the solution and test with potassium-ferrocyanide solution (see p. 120). If a platinum dish is used as cathode, it should be only about two thirds full at the start; there is then enough space left to expose a fresh platinum surface by diluting.

On account of the solubility of copper in nitric acid it is not advisable, when most accurate results are desired, to remove the cathode in the simple manner described on page 120, or, in case a platinum dish is used, to simply pour out the electrolyte and rinse it with water; when nitric acid is present the washing should be effected before the circuit is broken. To accomplish this, allow distilled water to run slowly into the cell through rubber tubing from a bottle placed above it. Cause the water to flow against the sides of the beaker or dish, and, while the water is being added, draw off the original contents of the cell through a siphon leading from the bottom of the vessel. By means of a pinchcock on the rubber tubing, it is easy to regulate the flow of water into the vessel and by joining some rubber tubing to the siphon, it is also possible to

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heating and then plunging the electrode into a large test tube containing a little methyl alcohol at the bottom. Care should be taken not to melt the wire during the heating and to get complete reduction. If there is no lacquer on the wire, the electrode may be cleaned by heating with dilute nitric acid for a short time. It should be washed and dried in exactly the same way as in the copper analysis.

Caution! This treatment of the electrode should never be given to platinum gauze. The copper will alloy with the platinum when heated in the flame.

regulate in the same way the rate at which the liquid runs through the siphon.

As soon as the solution shows but faint reaction with blue litmus paper, or when lights in the circuit grow dim, it is safe to break the current and to wash the cathode with water and alcohol as described on page 120.

This method of removing the solution at the end of the electrolysis is open to the objection that when other determinations are to be made after the removal of the copper it is often necessary to evaporate and concentrate the solution and this causes a tedious delay. If there is no further use for the liquid from which the copper has been removed, or if the presence of acetate and acetic acid does no harm to further work, the nitric acid may be rendered harmless, after the electrolysis is over, by adding a sufficient quantity of sodium acetate. This salt reacts with the nitric acid and forms free acetic acid which does not exert an appreciable solvent effect upon the deposited copper (Rüdorff).

The vessel shown in Fig. 46 is very convenient to use when it is desired to wash a deposit before breaking the circuit. On filling the vessel with solution, the latter comes to about the line *a* in the siphon tube but during the electrolysis the bubbles of oxygen from the foot of the anode cause enough diffusion to prevent this part of the solution from escaping the action of the electric current. Similar vessels in which a straight tube with stopcock is fused into the middle of the bottom of the beaker are not so satisfactory; the solution flows down to the stopcock and retains its original density for a long time while the solution above it becomes specifically lighter owing to the removal of the copper; thus the diffusion takes place very slowly.

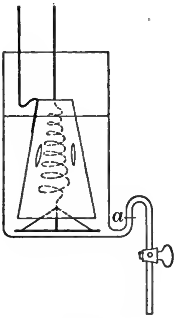

FIG. 46.

The deposition of copper from a pure nitric-acid solution is advantageous if it is necessary to use nitric acid for the solution of the original substance (copper, its alloys, ores, etc.), and if there is no reason to evaporate the solution with concentrated sulphuric acid as when it is desired to remove the lead as sulphate. If such an operation is necessary, it is better to carry out the analysis from a pure sulphuric-acid solution, as described on page 116, without the addition of any nitric acid. The deposition from a nitric-acid solution is to be recommended especially when considerable iron is present as in the analysis of pyrites.

There are two sources of error to guard against in the electrolysis by the nitric-acid method. It was stated on p. 117 that nitric acid can be reduced to ammonia by the action of the electric current during electrolysis. If, therefore, too little nitric acid is used there is danger of the solution becoming ammoniacal and the metal will deposit in a spongy condition. The formation of ammonia is disadvantageous when it is desired to separate the copper from other metals which are not deposited while the solution contains free nitric acid. It is always necessary, therefore, to make sure that the nitric acid in the solution never disappears entirely. In this case the deposition of the metal can take place at a constant potential (see p. 119). On the other hand it is not advisable to use too much nitric acid as this will prevent the deposition of the copper until the excess of nitric acid has been reduced to ammonia and thus the electrolysis will require a long time. Especially in hot solutions the retarding effect of an excess of nitric acid is very pronounced.

If considerable iron is present in the solution the ferric nitrate exerts a solvent effect upon the deposited copper and there are thus two causes which tend to retard the deposition of the copper when too much nitric acid is used. If much iron is present it is necessary to limit the amount of nitric acid added very carefully. For the details of the procedure see page 293, where the electrolysis of solutions rich in iron is described.

The conditions under which good results have been obtained in the rapid electrolytic determination of copper are given in the following table (p. 128). As regards the results obtained when the electrolyte is subjected to magnetic stirring, see page 77.

RAPID DEPOSITION OF COPPER IN NITRIC-ACID SOLUTIONS.

	Experiments performed by A. Fischer in the Aachen Laboratory.				H. J. S. Sand.*	Exner.
Kind of electrode.	Platinum dish and rotating disk electrode.			Gauze electrode and lattice stirrer (Fig. 33)	Sand's electrode	Platinum dish and rotating spiral
Electrolyte contained.	12 to 20 cc. HNO_3 (1.2)	2 cc. HNO_3 (1.2)	1 cc. HNO_3 (1.2)	1 cc. HNO_3 (1.4)	1 cc. HNO_3 (1.4)	1 cc. HNO_3 (1.4) + 5 cc. NH_4OH (0.96) after 10 minutes
Volume........	125 cc.	125 cc.	125 cc.	110 cc.	85 cc.	125 cc.
Quantity of metal.	0.3 gm. as sulphate	0.3 gm. as sulphate	0.3 gm. as sulphate	0.3 gm. as sulphate	0.24 gm. as sulphate	0.24–0.29 gm.
Temperature...	20°–30°	95°	90°	Hot	Hot	90°
Voltage of the bath.	2.5 to 3 volts	3 to 3.5 volts	8.5 volts	2.8 to 3 volts	2.8 volts	8–10 volts
Current strength.	....	....	....	....	10 amp.	....
Number of revolutions.	800 to 1000	800	800	1000 to 1200	800	800
Duration in minutes.	52 to 62	40	20	10	6	15 to 20

* J. Chem. Soc., London, **91,** 391 (1907).

Rapid Electrolysis with Stationary Electrolyte. With the aid of a gauze cathode it is possible to use enough current to get 0.5 gm. of copper deposited in less than fifteen minutes, even without stirring the electrolyte. There is, however, much more danger of getting spongy deposits than when the electrolyte is stirred. The size of the electrode, volume, and acid-content of the solution are factors which must be kept within narrow limits. The following procedure, if followed closely, has been found to give good results in the analysis of brass.

Procedure. Dissolve 0.5 gm. of the metal in 10 cc. of 6-normal nitric acid. Dilute to 50 cc. in a tall, slender, lipless beaker of about 80 to 102-cc. capacity. Cover the beaker and boil very gently for about one minute to remove nitrous fumes. Add 6-normal ammonium hydroxide slowly until a slight permanent precipitate is formed and then add enough 6-normal sulphuric acid (about 0.5 cc.) to cause this precipitate to dissolve. Electrolyze this solution with a current of about 1 ampere until all the copper is deposited. As cathode use a platinum gauze cylinder 3 cm. or more long and about 3 cm. in diameter with approximately 20 meshes to the linear centimeter. As anode a platinum spiral may be used and it should be placed in the center of the cylinder. Cover the beaker with split watch glasses, to prevent loss, and keep the solution heated to about 70° during the electrolysis. When the solution has become colorless, add about 0.2 gm. of urea, wash down the sides of the beaker and bottom of the cover glass, and continue the electrolysis a little longer. It is important not to continue the electrolysis much longer than necessary to remove all the copper. At the most, one hour should be sufficient. Test the solution for copper, as directed on page 120, and finish the work as there described.

Deposition of Copper from Ammoniacal Solutions.

When either of the above methods is used for the electrolytic determination of copper, the solution should not contain any chloride as the latter usually gives rise to a spongy deposit of copper and, moreover, there is danger of the platinum anode being attacked; the dissolved platinum will then deposit upon the cathode. If a solution of a copper salt contains chloride, and it is desired to avoid evaporation with sulphuric acid, the electrolytic determination may be carried out in an ammoniacal solution.

This method also possesses certain advantages over other methods when it is desired to effect the separation from a metal such as antimony. Rüdorff obtained a compact deposit of copper from an ammoniacal solution to which ammonium nitrate was added.

In the laboratory of the Munich Polytechnic Institute, the following directions have been worked out for the electrolysis in ammoniacal solution. Add ammonia to the copper solution (chloride, nitrate or sulphate) in slight excess, or until the precipitate formed redissolves. Then, if not more than 0.5 gm. of copper is present, add 20 to 25 cc. more of ammonia, sp. gr. 0.96. If as much as 1 gm. of copper is present, increase the quantity of ammonia added to 30 or 35 cc. Dissolve 2 or 3 gms. of ammonium nitrate in this solution and electrolyze with a current $ND_{100} = 2$ amperes. Wash the deposit before breaking the circuit.

The presence of chlorine, zinc, arsenic and small amounts of antimony do no harm when this method is followed; in the presence of lead, bismuth, mercury, cadmium and nickel, the results are too high.

In sulphuric- or nitric-acid solutions the copper is present largely in the form of simple, bivalent copper ions, Cu^{++}, and when the concentration of the ions is diminished as a result of their discharge at the cathode, then the undissociated molecules of $CuSO_4$ or $Cu(NO_3)_2$ quickly dissociate to form new cupric ions. In ammoniacal solutions, of the sulphate for example, the complex salt $[Cu(NH_3)_4]SO_4$ is formed, which dissociates first into the complex cupric ammonia cation $[Cu(NH_3)_4]^{++}$ and $SO_4^{=}$ anions. The cupric ammonia ions are not very stable and break down to an appreciable degree as illustrated by the equilibrium expression,

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

and the concentration of cupric ions resulting from such dissociation is sufficient to permit the deposition of copper when the potential of the current is less than 2 volts. For, according to the formula on page 26, the cathode potential depends upon the osmotic pressure and thus upon the concentration of the metal ions, and as long as this potential is less than the potential between the electrodes of the cell, there will be deposition of metal.

According to Foerster's experiments, it is possible to effect the electrolytic deposition of copper from ammoniacal solutions by the use of a single lead accumulator cell, as in the electrolysis of sulphuric-acid solutions of copper. Foerster takes the solution containing 0.2 to 0.3 gm. copper in 100 cc., adds 2 gms. ammonium sulphate and 10 cc. ammonia (sp. gr. 0.96) and obtains a quantitative deposition in 4 hours with one accumulator cell. Under these conditions the copper is separated from arsenic if the quantity of the latter present in 100 cc. of the solution is not more than 0.2 gm.; but it is absolutely necessary that all the arsenic be present as arsenate (see page 233).

Silver.

At. Wt. = 107.88. Elec. Equiv. = 1.118 mg. Elec. Potential = −0.771 volt for Ag^+ ions. Overvoltage of H_2 = between 0.05–0.15 volt.

Of the various methods for the electrolytic determination of silver only those using nitric acid, potassium cyanide and ammonium hydroxide solutions as electrolytes will be considered.

Deposition of Silver from Nitric-acid Solution.

According to the studies of F. W. Küster and H. von Steinwehr,* the electrolytic determination of silver succeeds best if the solution, which may contain from 0.3 to 2 gms. of silver in 150 cc., is heated to 55° or 60°, treated with 1 or 2 cc. of nitric acid † (sp. gr. 1.4) and 5 cc. of alcohol, and electrolyzed with the potential of the bath kept constant between 1.35 and 1.38 volts. The deposited metal must be washed without breaking the current and dried at about 100°. As cathode, a platinum dish with dull inner surface and as anode a disk or spiral may be used.

The addition of the alcohol serves to reduce immediately any silver peroxide that may be formed during the process.

According to the above-mentioned authors, the most important condition for a successful electrolysis is keeping the voltage constant within the stated limits. If the voltage rises above 1.38 volts a spongy deposit is obtained. The unreliability of most other methods for the electrolysis of a nitric-acid solution of silver salt can be traced to the use of too high voltages. In the older methods, chief stress was laid upon the current density, so that although the potential was right at the start of the analysis, during the progress of the electrolysis it rose above the critical value as the solution became deprived of metal ions (*cf.* p. 89).

It is, therefore, very important in the electrolytic determination of silver to use a source of current such that the voltage cannot rise above 1.38 volts. For this purpose a Gülcher's thermopile may be used which has a maximum voltage of about 4 volts. If a wire resistance of suitable length is inserted between

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* Z. Elektrochem., 4, 451 (1898).

† If from 0.3 to 2 gms. of a silver alloy is dissolved in 2 to 4 cc. of nitric acid (sp. gr. 1.4) the further addition of acid is unnecessary.

the binding posts of the thermopile, the current can be adjusted so that the electromotive force of the current from the pile is reduced to 1.36 volts and it is then only necessary to connect the electrolytic cell directly with these binding posts. Instead of short circuiting the terminals with a resistance wire, another way of getting the proper voltage is to connect one electrode of the cell with the binding post and the other electrode with one of the metal wings of the thermopile. It is possible, however, to get a finer adjustment of the voltage by the use of resistance wire.

In accordance with what was said on page 118 concerning work carried out at a constant voltage, the strength of the current will necessarily diminish constantly during the progress of the electrolysis and thus a determination will require from six to eight hours. The quantity of metal present in the solution has but little influence upon the duration of the analysis because the strength of the current is greater in proportion to the concentration of the silver solution. Thus it is the deposition of the last traces of metal which requires the most time and this is about the same in all cases.

Rapid Deposition of Silver from Nitric-acid Solution.

Two difficulties often encountered in the rapid electrolysis of silver solutions are the formation of large crystals on the cathode and the deposition of a little silver peroxide on the anode. By stirring the electrolyte, keeping the solution hot, and controlling the cathode potential, these objectionable features can be avoided.*

Procedure. To about 85 cc. of the neutral solution containing up to 0.5 gm. of silver as nitrate, add 2 to 5 cc. of 5-normal nitric acid and electrolyze at 100° with a platinum gauze cathode and a rotating spiral anode. Begin with a current of about 3.5 amperes with 1.5 volts e.m.f. between the terminals and cause the anode to revolve at the rate of 800 to 1000 r.p.m. With the aid of the apparatus described on page 148, keep the cathode potential to 0.1 volt or less, so that at the end of fifteen minutes, when the electrolysis should be finished, the current will be reduced to 0.2 ampere. Wash, dry and weigh the deposit as described under Copper.

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* *Cf.* Fischer, Elektroanalytische Schnellmethoden, Stuttgart, 1908.

Deposition of Silver from Ammoniacal Solution.

Silver when deposited from ammoniacal solutions with a stationary electrolyte is likely to be in the form of a spongy deposit, not suitable for accurate weighing. According to Sand * dense deposits can be obtained which cannot be rubbed off if the following procedure is followed:

Procedure. To the neutral solution containing about 0.5 gm. of silver as nitrate, add 10 cc. of 15-normal nitric acid and 25 cc. of 15-normal ammonium hydroxide. With a total volume of 85 cc., and using a gauze cathode and a platinum spiral anode revolving 800 r.p.m., start the electrolysis with a current of 4 amperes and 1 to 1.3 volts between the terminals. During the progress of the electrolysis do not let the voltage rise higher than this value, so that at the end of about ten minutes, when all the metal should be deposited, the current will be reduced to about 0.2 ampere.

The use of the ammoniacal electrolyte is particularly suitable when silver is to be deposited in the presence of arsenic and antimony.

Deposition of Silver from Potassium-cyanide Solution.

Luckow first suggested the determination of silver by the electrolysis of the complex silver-potassium cyanide (*cf.* p. 51). If a neutral silver solution is at hand, add potassium cyanide solution until the silver cyanide precipitate redissolves and then add as much more of the cyanide solution. Dilute the solution to a volume of 100 to 120 cc. and carry out the electrolysis with a current of ND_{100} = 0.2 to 0.5 ampere. The potential of the bath under these conditions lies between 3.7 and 4.8 volts. With the same quantity of silver, the electrolysis requires from 5 to 1.5 hours, according to whether 0.2 or 0.5 ampere of current is used. The temperature of the solution should be between 20° and 30°. To determine whether the deposition of metal is complete, add nitric acid to a little of the solution, boil off the hydrogen cyanide under a good hood and test for silver with ammonia and ammonium sulphide. If a black precipitate of silver sulphide is obtained; it should be filtered off, dissolved in

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* Proc. Chem. Soc., **22,** 43 (1906).

nitric acid, the solution treated with potassium hydroxide solution till alkaline, then with potassium cyanide and the resulting solution added to the original electrolyte for further electrolysis.

If insoluble silver compounds, such as the chloride, bromide, iodide or oxalate, are to be analyzed, they are dissolved in potassium-cyanide solution.

This was the only reliable method for determining silver electrolytically until the method of Küster and v. Steinwehr was published. It is important to use pure potassium cyanide in the analysis as the presence of small quantities of cyanate or other impurity prevents the adherence of the silver to the cathode.

Rapid Deposition of Silver from Cyanide Solution.

In spite of the tendency to get a little silver peroxide formed on the anode, Gooch and Medway [*] and E. F. Smith [†] have obtained good results in the rapid electrolysis of silver in alkali cyanide solutions. Gooch and Medway used as cathode a platinum crucible which, with the aid of a rubber stopper, was fastened to the end of a rotating metal shaft and was connected also with the negative pole of the electrolytic circuit. Smith, on the other hand, rotated the anode, and kept the solution near the boiling point.

Procedure. To the neutral solution of silver nitrate containing as much as 0.5 gm. of silver, add 2 gms. of potassium cyanide. Dilute to about 125 cc., heat nearly to boiling and electrolyze the hot solution with a current of $ND_{100} = 2$ to 2.8 amperes and rotating the anode 700 r.p.m. A platinum gauze electrode may serve as cathode. All of the silver will be deposited in about ten minutes.

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[*] Am. J. Sci., 4, 15, 320.

[†] Electro-analysis, 1918, p. 117.

Mercury.

At. Wt. = 200.6. Elec. Equiv. = 2.078 for Hg^{++} ions. Overvoltage of H_2 = 0.42–0.78 volt. Elec. Potential = − 0.750 volt.

Deposition from Nitric-acid Solution.

The solution containing the metal as nitrate, chloride or sulphate is treated with 1 or 2 per cent by volume of nitric acid (sp. gr. 1.36) and electrolyzed at room temperature with a current of ND_{100} = 1.0 ampere.

The solution may contain small quantities of hydrochloric acid, or chloride, but large quantities are harmful. If other metals are present which require acid to prevent their precipitation, 5 per cent by volume of nitric acid should be added and the current density reduced to 0.5 ampere.

A roughened platinum dish or a gauze electrode must be used as cathode. The mercury deposits upon these electrodes as a uniform coating, whereas if a polished electrode is used it is obtained in the form of small globules. To test whether the deposition is complete, a little of the solution may be treated with ammonia and ammonium sulphide, or a bright copper or gold wire may be suspended in the solution over the cathode and watched to see whether it becomes amalgamated. In all cases, the deposit must be washed without interrupting the current and only water should be used, because alcohol tends to loosen the film of mercury from the cathode. On account of the volatility of this metal, the electrode must be dried at the room temperature in a desiccator. To avoid slight losses which may result even then, Borelli * recommends that a dish of mercury be placed in the bottom of the desiccator so that the air there is kept saturated with mercury vapors.

Again, owing to the volatility of mercury, it is not advisable to carry out the analysis from a heated electrolyte, for, if the electrolysis is carried out for a long time, some of the liquid will evaporate and, unless the cell is closely watched, this will leave an exposed mercury surface from which, if hot, appreciable volatilization of mercury may take place. The dish, or beaker, should be kept covered with a watch glass during the analysis.

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* Z. Elektrochem., **12,** 889 (1906).

The following table gives the conditions under which the rapid electrodeposition of mercury has been obtained successfully.*

RAPID DEPOSITION OF MERCURY FROM NITRIC-ACID SOLUTION.

	Experiments performed by			
	A. Fischer and Boddaert at Aachen.	Exner.	R. O. Smith.	H. J. S. Sand.
Electrode	Dish and rotating disk	Dish and rotating spiral	Dish and rotating spiral	Sand's electrodes
Electrolyte contained	1 cc. HNO_3 (sp. gr. 1.4)	1 cc. HNO_3 (sp. gr. 1.4)	1 cc. HNO_3 (sp. gr. 1.4)	1.5 cc. HNO_3
Volume	125 cc.	125 cc.	115 cc.	85 cc.
Quantity of metal	0.23 gm. as chloride	0.3 to 0.6 gm. as nitrate	0.25 to 0.5 gm. as nitrate	0.58 gm. as nitrate
Temperature †	22° to 45°	Hot	Hot	Warm

Deposition of Mercury from Potassium-cyanide Solution.

This method, proposed by Edgar F. Smith, gives good results when carried out as follows: To the solution, containing not more than 0.5 gm. of mercuric chloride, add 3 gms. of potassium cyanide, whereby a clear solution of complex potassium-mercuric cyanide, $K_2Hg(CN)_4$, is obtained in which the mercury is present as the bivalent mercuric-cyanide anion. After diluting the solution to 150 cc., carry out the electrolysis at room temperature with a current of from 0.5 to 1 ampere; the analysis is finished in about 15 hours. To determine whether the deposition is complete, take out a little of the solution with a pipette, add nitric acid, boil off the hydrogen cyanide, and test for mercury with ammonia and ammonium sulphide. If a negative test for mercury is obtained finish the electrolysis as in the previous method.

Higher current densities are to be avoided because these will heat the solution which is likely to cause volatilization of some

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* General reference to the literature on the rapid electrolytic deposition and separation of mercury in different solutions: Exner, J. Am. Chem. Soc., **25**, 896 (1903); A. Fischer and Boddaert, Z. Elektrochem, **10**, 945 (1904); R. O. Smith, Thesis U. of P., 1905; A. Fischer, Chem.-Ztg., **31**, 25 (1907); E. F. Smith, and Kollock, J. Am. Chem. Soc., **27**, 1527 (1905).

† Regarding the effect of temperature, see the above text.

of the mercury. Moreover, the platinum electrode is attacked by a hot solution of potassium cyanide. There are thus two sources of error if the electrolysis is carried out in a hot solution.

The rapid electrodeposition of mercury from a cyanide solution is inexpedient for the same reason, as such methods involve higher current densities or hot solutions.

Insoluble mercury compounds, as mercuric sulphide or mercurous chloride, are suspended in a solution of common salt, or in very dilute hydrochloric acid, and electrolyzed under current conditions described for the electrolysis of nitric-acid solutions. (See also the article on Cinnabar.)

Deposition of Mercury from Sodium Sulphide Solution.

E. F. Smith * has found that an alkaline sulphide solution of mercuric salt can be electrolyzed without difficulty.

Procedure. Add 20 cc. of sodium sulphide solution, sp. gr. 1.19, to the neutral solution of the mercuric salt and dilute with water to a volume of 125 cc. Electrolyze in a platinum dish, which also serves as cathode, with a platinum spiral as anode. Use a current of $ND_{100} = 0.11$ ampere at 70° for five hours. Keep the dish covered during the electrolysis to prevent evaporation, to avoid mechanical loss, and to prevent mercuric sulphide being formed at the top of the deposit where the solution has evaporated away.

When the electrolysis is finished, siphon off the solution, and wash the deposit with cold water. Dry on a moderately warm plate or in a desiccator over sulphuric acid.

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* Electro-analysis, 1918, p. 101.

Gold.

At. Wt. = 197.2. Elec. Equiv. = 0.328 mg. for Au^{+++} ions. Elec. Potential = $< -$ 1.083 volt. Overvoltage of H_2 = 0.02–0.06 volt.

When deposited from acid or alkaline solutions, brown, non-adherent, amorphous gold is often formed and, in many cases, the electrolyte itself is of a greenish or purplish hue, due to gold remaining in colloidal solution. Satisfactory deposits, however, may be obtained: (1) from a solution in potassium cyanide, (2) from a solution in sodium sulphide, and (3) from a solution in ammonium thiocyanate.

Deposition from Potassium-cyanide Solution.

If a slightly acid solution of auric chloride is treated with a solution of potassium cyanide, a yellow precipitate of auric cyanide is obtained which dissolves in an excess of potassium cyanide forming colorless potassium auricyanide:

$$AuCl_3 + 3\,KCN = Au(CN)_3 + 3\,KCl$$
$$Au(CN)_3 + KCN = KAu(CN)_4.$$

This salt dissociates into K^+ and $Au(CN)_4^-$ ions; the gold, therefore is a constituent of the anion, which is itself dissociated to a slight extent:

$$Au(CN)_4^- \rightleftarrows Au^{++++} + 4\,CN^-;$$

and as the gold ions are discharged at the cathode more of them are formed by the progressive dissociation of the complex anion.

To prepare a suitable electrolyte, the gold solution, which should not contain too much free acid,* is treated with 2 or 3 gms. of pure potassium cyanide, and diluted to 120 cc. The electrolysis is conducted in the solution heated to 60° in a roughened platinum dish, using a current of ND_{100} = 2.7 to 4 volts. The deposition of 0.05 gm. of gold requires 2 or 3 hours. If the electrolysis is carried out at ordinary temperatures, the complete deposition of the same quantity of gold requires 12 to 14 hours.

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* If much acid is present, it is removed either by evaporation at a temperature too low to cause decomposition of the auric chloride, or by neutralization with caustic potash solution. For a practice experiment, crystallized sodium chloraurate, $NaAuCl_4 \cdot 2H_2O$, may be used or pure gold may be dissolved in aqua regia and the excess of acid removed by evaporation.

The end of the electrolysis is determined, as described on page 125, by raising the level of the solution.

The following table shows the conditions under which gold has been determined rapidly from well-stirred solutions.

RAPID DEPOSITION OF GOLD FROM POTASSIUM-CYANIDE SOLUTION.*

	Experiments performed by		
	Withrow; Exner.	A. Fischer.	H. E. Medway.
Electrode	Dish and rotating spiral	Dish and rotating disk	Rotating crucible cathode
Electrolyte contained	1 to 2 gms. KCN	1 to 2 gms. KCN	Excess of KCN, 40.1 cc. conc. NH_4OH
Volume	80 to 125 cc.	100 cc.	25 cc.
Quantity of metal	0.14 to 0.2 gm. as $AuCl_3$	0.1 to 0.15 gm. as $AuCl_3$	0.065 gm. as $AuCl_3$
Temperature	Boiling	Boiling	Ordinary
Voltage	11 to 10.5 volts	8 to 10 volts	†
Revolutions	800 to 500	800	650 to 700
Duration in minutes	6 to 10	10	25 to 30

Deposition of Gold from Sodium-sulphide Solution.‡

Gold solutions behave toward alkali-sulphide solutions similar to those of antimony. If a gold-chloride solution is treated with sodium-sulphide solution, a brownish precipitate of gold sulphide is formed which dissolves upon the addition of a considerable excess of the reagent forming sodium thioaurate. The decomposition of this salt by the electric current takes place as in the electrolysis of the corresponding antimony solution (p. 154), and the deposition of the gold is a result of a purely secondary reaction.

The gold solution is treated with a sufficient amount of sodium-

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[*] General references on the rapid deposition and separation of gold from various solutions: Medway, Am. J. Sci. [4], **18,** 56 (1904), Z. anorg. Chem., **42,** 114 (1904). Exner, J. Am. Chem. Soc., **25,** 896 (1903). Withrow, Thesis, U. of P., 1905. E. F. Smith and Kollock, J. Am. Chem. Soc., **27,** 1527 (1905).

[†] The voltage is not given but the current density was ND_{100} = 1.8 to 3.3 amperes.

[‡] Smith and Wallace, Ber., **25,** 779 (1892).

sulphide solution, saturated at room temperature, to cause the complete solution of the gold precipitate that is first formed, and the resulting solution is electrolyzed with a current of ND_{100} = 0.1 to 0.25 ampere for 5 or 6 hours.

Deposition of Gold from the Solution in Ammonium Thiocyanate.

F. M. Perkin and W. C. Preble * have found that gold can be deposited equally well from a solution in ammonium thiocyanate. The gold solution is poured, with constant stirring, into a warm solution (50° to 60°) of 70 or 80 gms. NH_4CNS in 70 or 80 cc. of water. After diluting with water to a volume of 120 cc., the solution, which is reddish at first but later becomes colorless, is electrolyzed with a current of ND_{100} = 0.2 to 0.4 ampere either at the laboratory temperature or at a temperature of 40° to 50°. In the former case the time required is 4 to 6 hours; in the latter, 1.5 to 2 hours.

Although in the other two methods the gold deposit has a pure yellow color, by this method a darker deposit is obtained sometimes with equally accurate results.† If, however, potassium thiocyanate is used as solvent instead of the ammonium salt, a discolored deposit is obtained.

To determine whether all the gold has been deposited, the solution is tested as described on page 125, or a little of it is boiled with a few drops of concentrated sulphuric acid and a little stannous-chloride solution is added; if gold is present the purple-of-Cassius test is obtained.

Various suggestions have been made with regard to the removal of the gold from the platinum electrode but the simplest method, according to Perkin and Preble, is the treatment with a potassium-cyanide solution to which 3 or 4 cc. of hydrogen peroxide or a little ammonium persulphate is added. The gold will dissolve in a few seconds.

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* Electrochemist and Metallurgist, **3**, 490 (1904).

† A yellow precipitate is often noticed in the solution; this is "Kanarin," a dyestuff formed by the anodic oxidation of the thiocyanate.

Platinum.

At. Wt. = 195.2. Elec. Equiv. = 0.505 mg. for Pt^{++++} ions. Elec. Potential = < -0.863 volt. Overvoltage for $H_2 = 0.07$–0.09 volt.

Although it is difficult to get a gold deposit that will adhere to the electrode in an acid solution, in the case of an acid platinum solution it is easy to obtain a deposit which will adhere to either a polished or a roughened platinum surface.

If the platinum, as is usually the case, is present as chloroplatinic acid, H_2PtCl_6, the solution is acidified with 2 per cent by volume of dilute sulphuric acid (1 : 5) heated to 60° or 65° and electrolyzed with a current of $ND_{100} = 0.01$ to 0.05 ampere. The potential, which is about 1.2 volts at the start, rises later to 1.7 volts and as much as 0.4 gm. of the metal is deposited quantitatively in 5 hours. The determination is so accurate that W. Halberstadt has used it for the determination of the atomic weight of platinum. When all the platinum has been deposited, a little of the solution, on being heated with hydrogen-sulphide water, will not show a brown coloration.

After breaking the circuit the precipitate can be washed and it adheres so well that there is no need to remove it at the end of the analysis. After polishing with sea sand, the dish is again ready for use.*

By stronger currents (0.1 to 0.2 ampere) the platinum is deposited at ordinary temperatures in the form of platinum black. That the metal in this state is used for the preparation of platinized electrodes was mentioned on page 82.

The electrolytic determination of platinum may be used for the quantitative estimation of potassium and sodium (see these metals).

According to Julia Langness it is possible to deposit platinum rapidly under the following conditions.

According to the experience of A. Fischer in the author's laboratory, the method is not to be recommended.

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* If it is desired to remove the deposit, the electrode should be given a preliminary coating of copper or silver (pp. 172, 173). Then on heating with nitric acid the deposits will be loosened.

† J. Am. Chem. Soc., **29**, 459 (1907).

RAPID DEPOSITION OF PLATINUM FROM SULPHURIC-ACID SOLUTION.

	Experiments of J. Langness.†	
Electrode	Silvered dish and sieve anode	Silvered dish and sieve anode
Electrolyte	2.5 to 5 cc. H_2SO_4 (1 : 10)	2.5 cc. H_2SO_4 (1 : 10)
Volume	60 cc.	60 cc.
Quantity of metal	0.1 gm. as K_2PtCl_6	0.2 gm. as K_2PtCl_6
Temperature	Hot	Hot
Potential	5 to 10 volts	10 volts
Current strength	10 to 14 amp.	17 amp.
Revolutions	600	600
Time in minutes	3 to 7	5

Palladium.

At. Wt. = 106.7. Elec. Equiv. = 0.552 mg. for Pd^{++} ions. Elec. Potential = < -0.793 volt. Overvoltage of H_2 = 0.24–0.46 volt.

The experiments carried out in the author's laboratory by the older methods were not successful for the quantitative estimation of this metal. It was only when R. Amberg,* at the author's suggestion, experimented with a rapidly rotating anode that it was found possible to obtain a firmly adherent deposit of palladium.

If the palladium salt is soluble in water, enough sulphuric acid is added to the solution so that 120 cc. of electrolyte will contain about 30 per cent of concentrated acid and the electrolysis is carried out in a solution, which is not hotter than 65°, with an initial electromotive force of 0.75 volt; toward the end of the operation, a current of 1.15 volts is used but if the potential is increased above this value a spongy deposit will be obtained. About 0.3 gm. of palladium will be deposited quantitatively in 4 to 6 hours. As cathode the roughened platinum dish is used and as anode a platinum disk, made to revolve from 600 to 1000 times a minute.

To test the solution for palladium at the end of the electrolysis, a little of the electrolyte is treated with potassium iodide; a

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* Z. Elektrochem., **10,** 385, 853 (1904).

brown precipitate or coloration of palladous iodide, PdI, will be formed by palladium. The coloration does not disappear upon the addition of sulphurous acid; if this is the case, the color was due to free iodine.

If the test shows no palladium, the current is turned off, the liquid is poured out of the dish and the deposit, after the usual washing with water and alcohol, is dried at 110°.

For a satisfactory deposition of this metal it is important that the potential of the current does not rise above 1.15 volts. If the electrolysis is conducted with a current of ND_{100} = 0.05 to 0.04 ampere, the potential rises, after the greater part of the metal has deposited, to more than 1.15 volts. It is then necessary, by changing a front switch and a shunt resistance, to diminish the current strength enough so that the final potential is not over 1.15 volts. In this way the current is reduced to 0.01 or 0.02 ampere. If the voltage is allowed to exceed 1.15 volts, hydrogen is evolved at the cathode and a spongy deposit of palladium is formed (p. 88). When the current has been reduced to 0.01 or 0.02 ampere, the deposition of the metal is practically complete and the current is allowed to continue only until the electrolyte has cooled to about the temperature of the air.

Palladium salts which are insoluble in water are dissolved in as little concentrated sulphuric acid as possible and diluted with water and enough more sulphuric acid is added to give the proper acidity. The acid content of about 30 per cent sulphuric acid is the most suitable because this acid has the greatest conductivity as Grotrian* has pointed out. The presence of the palladium salt has little effect upon the conductivity of such a solution.

To remove the palladium deposit from the platinum dish, it is treated with a solution of potassium chloride, saturated at the room temperature, and, after heating to 70° or 80°, a little solid chromic-acid anhydride is added while the dish is kept in constant motion so that the air comes in contact with the metal. In this way the solution of the palladium is effected without dissolving much platinum.

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* Poggendorff's Ann., **151**, 378 (1874).

Rhodium.

At. Wt. = 102.9 Elec. Equiv. = 0.356 mg. for Rh^{+++} ions.

Rapid Precipitation of Rhodium from Sulphuric-acid Solution.

Julia Langness * used as electrolyte a solution of sodium-rhodium chloride, Na_2RhCl_6, which contained about 0.058 gm. of rhodium and 2.5 cc. of sulphuric acid (1 : 10). The solution was diluted with water to a volume of about 105 cc. and electrolyzed in a silver-coated platinum dish with a spiral anode making 600 revolutions per minute and a current of 8 or 9 amperes and 7 to 8 volts. The deposition of this amount of metal required 7 to 10 minutes.

By using a sieve anode (p. 56) it was found possible to deposit twice as much metal in the same time with a current of 7 volts and 15 amperes. In this case the volume of the solution was 60 cc.

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* J. Am. Chem. Soc., 29, 469 (1902).

Bismuth.

At. Wt. = 208.0 Elec. Equiv. = 0.718 mg. for Bi^{+++} ions.
Elec. Potential = < -0.393 volt.

Most methods proposed for the electrolytic determination of bismuth are more or less unreliable, partly owing to the difficulty in obtaining satisfactory, adherent deposits and partly owing to the tendency of some bismuth peroxide to deposit on the anode. Of the methods that have given satisfactory results with stationary electrolytes, the following one devised by O. Brunck * is to be recommended. If, however, a quick method as well as an accurate one is desired, it is better to stir the electrolyte.

The conditions under which Brunck obtained good results comprised the use of a platinum gauze electrode (p. 59), a maximum potential of 2 volts, a moderate amount of acid, and heating the solution before starting the electrolysis. A nitric-acid solution was used,† containing enough free acid to prevent the precipitation of basic salt upon dilution to a volume of about 100 cc. The quantity of acid must not exceed 2 per cent or the metal will be deposited in a crystalline condition such that there are losses during the washing. A larger quantity of acid may also cause the formation of bismuth peroxide. As a source of current which must not exceed a potential of 2 volts at any time, a single accumulator cell may be used, or several cells connected in parallel. The solution is heated nearly to boiling before turning on the current but the flame is removed after the electrolysis is started. If more than 0.1 gm. of bismuth is present in 100 cc. of the solution, the current density may be $ND_{100} = 0.5$ ampere, or even more, but if less than 0.5 gm. bismuth is present it is better not to use over 0.1 ampere. Here the current density at the start is understood. As the solution cools and as it becomes impoverished of metal ions, the current density naturally falls and at the last amounts to not more than a few hundredths of an ampere. It is not possible to have it otherwise if the work is to be carried out at a constant voltage. The electrodeposition of 0.3 gm. of

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* Ber., **35**, 1871 (1902).

† For practice either pure bismuth may be dissolved in nitric acid or basic bismuth nitrate may be dissolved in dilute nitric acid.

bismuth, however, does not require more than 3 hours. The presence of a little sulphuric acid does not have any appreciable effect upon the analysis.

The favorable results obtained with other metals, during the last few years, by keeping the electrolytes in constant motion led to the expectation that the deposition of bismuth could also be made more favorable by the use of the new method.* The results obtained were not satisfactory at first. Thus the method proposed by K. Wimmenauer† did not prove wholly successful in the hands of other experimenters.‡ It was only after Haber,§ Le Blanc and others had called attention to a new point of view which had hitherto been unnoticed in electro-analysis that it was found possible to work out the rapid electrodeposition of bismuth upon a scientific basis. The new feature consists in the measurement and control of the cathode potential under which the bismuth is deposited. The consideration of this electrical factor marks a new era in electro-analytical investigation.

Since the abandonment of purely empirical methods by which analyses were made with a certain number of galvanic elements, the path taken by investigation in this field has been characterized by a number of important innovations. Classen introduced the use of accumulators and measuring instruments and emphasized the importance of the current density in electrolysis. Kiliani, and after him Freudenberg, attempted to effect separations of metals by maintaining a certain difference in potential between the electrodes, a process which, in accord with the discovery, by Nernst and Caspari, of the overvoltage of hydrogen, must be modified and has not proved to be universally applicable. If, in such an analysis, only the potential difference between the electrodes is measured, the fact is not taken into consideration that this total difference in voltage is the sum of the drops in potential at the cathode and at the anode and that these two quantities are

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* General references to the literature covering the rapid electrodeposition and separation of bismuth in various solutions: Exner, J. Am. Chem. Soc., **25**, 896 (1903); A. Fischer and Boddaert, Z. Elektrochem., **10**, 945 (1904); H. J. S. Sand, J. Chem. Soc., London, **91**, 373 (1907); A. Fischer, Chem. Ztg., **31**, 25 (1907); Z. Elektrochem., **13**, 469 (1907); Smith and Kollock, J. Am. Chem. Soc., **27**, 1527 (1905).

† Z. anorgan. Chem., **27**, 1 (1901).

‡ Cf. A. Fischer and R. J. Boddaert, Z. Elektrochem., **10**, 945 (1904).

§ Z. phys. Chem., **32**, 194 (1900).

independent of one another. When the metal is deposited upon the cathode it is obvious that particular stress should be laid upon the drop in potential at this electrode, for it is possible that the reactions taking place at the two electrodes may change considerably during the electrolysis without there being any perceptible change in the potential difference between the two electrodes. In this way the cathode potential may become quite different from the value necessary for the satisfactory deposition of a metal. Many separations are, indeed, successful without taking these single potentials into consideration, but this is due either to the fact that large differences in the cathode potential have little effect upon the satisfactory deposition of the metal in question or that, owing to the addition of certain substances which have been found by experiment to be helpful, the nature of the electrolyte is such that the cathode potential is kept within the necessary limits throughout the process.

H. J. S. Sand has found that the control of the cathode potential is especially important for the successful analysis of a bismuth solution by electrolysis. At first sight the necessity of making such measurements during the progress of an analysis seems to introduce an inconvenient and time-consuming complication. When one considers, however, that, owing to the advantage gained by thoroughly stirring the electrolyte, the precipitation of 0.32 to 0.38 gm. of bismuth need not require more than 10 or 15 minutes, then the above objection is removed. Moreover, when the apparatus is once set up for measuring and regulating the cathode potential, it does not make any serious demands on the chemist.

In accordance with what has already been said, Sand's method for depositing bismuth can be easily explained. When the electric current is passed through an acid solution containing bismuth, then, as soon as the voltmeter registers a voltage higher than the discharge potential of bismuth ions, metallic bismuth will begin to separate upon the cathode and in a satisfactory condition. At the same time the ammeter registers a certain current strength and the single potential of the bismuth at the cathode must have a certain value; but what this exact value is we do not need to know. After a short time has elapsed, the solution becomes poorer in bismuth ions and then the cathode potential must rise in accordance with Nernst's formula (*cf.* p. 89), Since the cathode potential of bismuth is not much below that of hydrogen, which is taken as zero, this increase in potential will cause evolution of hydrogen and, as bismuth is influenced more than almost any other metal by this simultaneous discharge of hydrogen, the deposit will form in a spongy condition. To prevent this, it is necessary to keep the cathode potential lower than the discharge potential of hydrogen ions. The usual measuring instruments do not give enough information to accomplish this; the voltmeter only registers the total difference in potential between the electrodes and this may be influenced by the reactions taking place at the anode. It is necessary, therefore, to provide some means of measuring the drop in potential at the cathode and if we know the values which are favorable for a good deposition of metal, we are then able to keep the potential within the permissible limits.

A diagram of Sand's apparatus is shown in Fig. 47. *S* represents a beaker containing the bismuth solution and the cylinder-shaped platinum gauze electrodes *a*, *c* (see also Figs. 31 and 32). The electrodes are connected in the usual manner with the source of the current, *Q* (accumulators, p. 68) to be used in the analysis. The capillary tube of the auxiliary electrode *K* dips into the solution and the opening *e* is brought close to the cathode *c*. In this way a compound element is obtained, consisting on one side of the electrolyte of *S* and its pole *c*; the latter, as soon as the electrolysis is in progress, is represented by the bismuth deposit upon the cathode. On the other side, the mercury at the bottom of *K* forms the second pole and is in contact with the liquid in the apparatus *K* which is also contained in the capillary tubing. Thus

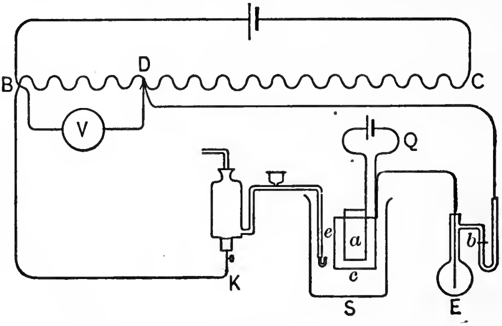

Fig. 47.

the two liquids are in contact at the opening *e* of the capillary (*cf.* p. 41).

If, now, we connect the mercury in *K* with the end *B* of the slide-wire bridge *BC*, which is rolled upon a cylinder, and on the other side connect the gauze electrode *c*, through the capillary electrometer *E*, with the sliding contact *D*, then we can compensate the electromotive force *Kec* by the opposite electromotive force that corresponds to the potential difference between *B* and *D*. To accomplish this it is merely necessary to move the sliding contact to a point *D* on the wire *BC* which causes the surface of the mercury in the capillary electrometer to rest at the zero point. The value of this electromotive force will be read directly in volts by inserting a voltmeter *V* between the points *B* and *D*. The way this compensating current is fed by a special accumulator is described on page 42.

The reading at the voltmeter does not give the single potential of the bismuth at the cathode *c* but it shows the difference in potential between the cathode *c* and the mercury in *K*. To compute the potential at *c* it would be necessary to know the potential of the mercury electrode *K*. It is not at all necessary to know this, however, for it suffices to know that the potential in the auxiliary electrode remains constant, for then any change in the reading of the voltmeter *V* will show that a change has taken place in the potential at *c*.

It is necessary, then, to determine experimentally what the reading of the voltmeter should be to cause the bismuth to deposit in a satisfactory condition. If this potential is once known, it is only a question of carrying out the electrolysis so that the potential at the cathode remains constant, or rather that it does not vary except within the allowable limits. To keep the potential absolutely constant is out of the question here, as in all other methods.

The above description, based upon the sketch shown in Fig. 47, will enable one to understand the picture of the apparatus shown in Plate II. Details of the connections will be evident from a study of Fig. 48, where the lettering corresponds to that used in Plate II (back of the book).

The three electric circuits shown in Fig. 48, which are the same as those referred to in Fig. 47 although the lettering is different, are as follows:

1. The wires from the main circuit to the accumulator *A* and the slide-wire bridge *C* (in which the commutator switch *B* is also included) are shown by the heavy black lines. This circuit is *AaCbBcA*.

2. The circuit which branches off from the lead wires and contains the voltmeter *E* (also a resistance *D*) is shown by heavy dashes and is *CdDeEfC*.

3. The circuit which contains the auxiliary electrode *L* and the electrolytic cell *K* is shown by dotted lines *CgLKhikGlmHnC*.

In the last circuit is found the capillary electrometer *G*. This instrument must be short circuited when not in use. There is, therefore, a key *H* connected with the last of the above-mentioned circuits, which is arranged so that when the capillary electrometer is not being used the short circuit *GlmHokG* is formed. If, however, it is desired to make a measurement, the finger is pressed against the key of *H* and then the connection *o*, represented by heavy dots and dashes in Fig. 48, is broken and the circuit becomes that given above.

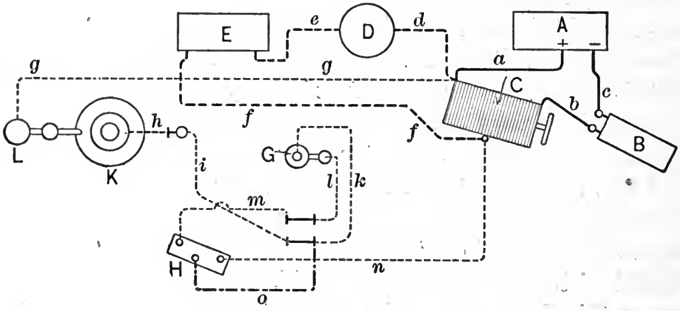

FIG. 48.

The bismuth determination is carried out as follows:* The solution, containing 0.2 to 0.3 gm. of bismuth and about 2.5 cc. of nitric acid (sp. gr. 1.4), is in the beaker *S* (Fig. 47). It is heated and a solution of 8 gms. sodium tartrate in water is added

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* The description given here is based upon that published by Sand. A. Fischer has tested the method in the author's laboratory under the conditions described by Sand and has obtained good results. The apparatus used in these experiments differs from that of Sand inasmuch as the two electrodes were stationary and the electrolyte was kept in motion by an independent stirrer (*cf.* p. 66). The capillary electrometer may be either to the right or to the left of *K*.

with enough more water to make the total volume 100 cc. The anode *a* and the weighed cathode *c* are placed in the solution and connected with the binding posts but the current is not yet turned on. By means of a small flame beneath the beaker, the temperature of the liquid is kept practically constant through the entire operation but it is not necessary to use a thermometer.

After the stopcock of the auxiliary electrode has been turned so that a few drops of sodium-sulphate solution run out, in order to be certain that this solution fills the entire capillary tube, the cock is turned back and the capillary tubing is sunk into the solution to be analyzed so that its end *e* lies very close to the cathode (Fig. 47). The wire stem of the cathode (Fig. 32) is connected with the capillary electrometer and the remaining connections are made in accordance with Fig. 48 and Plate II.

When everything is ready, the stirrer is set in motion (900 to 1000 revolutions per minute) and the current for the analysis is turned on (Fig. 47; see also Fig. 39). The bismuth at once begins to deposit upon the cathode. The sliding contact *D* is now moved, by the aid of the knob on the cylinder (Plate II), until the voltmeter registers about 0.63 volt, and the position of the mercury thread in the capillary electrometer is watched to see whether the surface of the mercury is at rest at *b* (Fig. 47) when the key *H* (Plate II) is pressed. By slightly changing the sliding contact *D* it is easy to bring the mercury to the zero position.

Under these conditions the deposition of the bismuth takes place in the most favorable manner and it now is only a matter of keeping the cathodic potential as nearly constant as possible. According to the explanation on page 41, it is evident that the potential will tend to rise and this must be offset by lessening the strength of the current, for the principle of the method lies in carrying out the analysis at a practically constant potential. During the ten or fifteen minutes required for the analysis, it is necessary to keep diminishing the current until toward the end only about 0.2 ampere is used, but it is permissible to allow the potential to rise as high as 0.9 volt.

When the potential and the current strength have reached their constant final values, *i.e.*, when the former stops rising so that it is no longer necessary to diminish the current, the greater part of the metal will have been deposited. If now the analysis is continued for about half as long again as the time from the start of the electrolysis, one may be certain, from theoretical reasons, that all the metal will be precipitated. To make sure of this, however, a little of the liquid is removed from the beaker and tested with ammonium sulphide.

A good way to conduct the washing of the deposited metal is first to remove the auxiliary electrode, without interrupting the current, then to stop the stirrer and quickly remove the beaker containing the electrolyte from under the electrodes, replacing it with a beaker of distilled water. By starting the stirrer again, a thorough washing of the deposit is obtained in a few seconds, for in this way the water is forced very energetically through the meshes of the gauze electrode. The stirrer is now stopped and the current turned off; it is then only necessary to rinse off the cathode once with distilled water, dip it in alcohol, dry and weigh.

After the capillary tube of the auxiliary electrode has been rinsed with water, a few drops of sodium-sulphate solution are allowed to flow into it, as described on page 41, to remove any liquid that may have diffused into the tubing from the beaker.

In the above directions, it was recommended to allow the current to pass through the solution for half as long again as the time between the start of the electrolysis and the point where the voltage and amperage had reached their final values. According to the explanation on page 89, the concentration of the electrolyte will have been diminished to an immeasurably small value as soon as the potential has been raised about 0.2 volt. It is well, however, to let the current act a little longer.

Another method for determining bismuth electrolytically, and one suitable for small quantities of this element, will be given under the section on the analysis of commercial copper.

Antimony.

At. Wt. = 120.2. Elec. Equiv. = 0.415 mg. for Sb^{+++} ions.
Elec. Potential = < − 0.463 volt.

The only reliable method for the electrolytic determination of antimony is from a solution of the thio salt.* At the same time a separation of antimony from tin and arsenic may be made by carrying out the special conditions described in the section of this book dealing with separations. The objection to the method, however, is the fact that if the electrolysis is continued too long, *e.g.*, overnight, polysulphides are formed from the sodium sulphide in the solution and these polysulphides exert a solvent effect upon the metallic antimony. The chemical and electrolytic behavior of the antimony in this determination will be explained and ways and means will be shown for meeting the above objection.

Antimony pentasulphide dissolves in sodium sulphide as represented by the equation:

$$Sb_2S_5 + 3\,Na_2S = 2\,Na_3SbS_4,$$

and the sodium thioantimonate is dissociated thus:

$$Na_3SbS_4 \rightleftarrows 3\,Na^+ + SbS_4^{---}.$$

The antimony is present, therefore, as a component of the complex SbS_4^{---} anion and it is to be expected, therefore, that the antimony in this negatively charged complex will at first migrate to the anode, when the current is turned on. To study the migration relations of antimony during the electrolysis, H. Ost and W. Klapproth † separated the region of the anode in the cell from the cathode region by interposing a diaphragm of porous clay and with such an apparatus the following experiments were performed.

1. First, the electrolyte was distributed uniformly in the anode and cathode compartments and subjected to electrolysis; as a result all the metal in the cathode compartment was deposited upon the cathode while the anode compartment contained practically all the antimony that was originally present there. Thus no antimony ions migrated from the anode compartment into the cathode compartment.

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* Methods of A. Classen: Classen and v. Reis, Ber., **14,** 1622 (1881); **17,** 2467 (1884); **18,** 1104 (1885); Classen, *ibid.*, **27,** 2060 (1894).

* Z. angew. Chem., **1900,** 827.

2. The entire antimony solution was placed in the cathode compartment and the anode compartment was filled with pure sodium-sulphide solution. The result of the electrolysis was a quantitative deposition of the antimony upon the cathode and no antimony solution reached the anode compartment.

3. As a final experiment, the entire antimony solution was placed in the anode compartment and the cathode compartment was filled with sodium-sulphide solution; under these conditions there was no trace of antimony deposition but antimony sulphide was deposited upon the anode.

The influence of the sodium-sulphide solution was also studied. If at the start the antimony is all present in the cathode compartment together with an excess of sodium sulphide, then, as in the second experiment, all the antimony is deposited upon the cathode; the potential of the bath is low on account of the high concentration of sodium sulphide. If the solution, however, contains but little sodium sulphide, then the potential of the bath becomes high and a little of the antimony passes through the diaphragm and deposits upon the anode as antimony sulphide.

From these experiments it is apparent that under the usual experimental conditions, *i.e.*, in the presence of considerable sodium sulphide, the antimony neither migrates from the anode into the cathode space nor does it migrate in the opposite direction. In other words, it does not take part at all in the conductance of the current through the solution. The action of the current, according to Ost and Klapproth, consists essentially of the decomposition of sodium sulphide:

$$Na_2S = 2\,Na + S,$$

and the deposition of antimony upon the cathode is really the result of a secondary reaction, which is the action of the discharged sodium ions upon the sodium thioantimonate:

$$Na_3SbS_4 + 5\,Na = Sb + 4\,Na_2S.$$

As regards the reactions at the anode, it has been found that in the first stages of the electrolysis only sulphur ions from the sodium sulphide are discharged there and the sulphur, as fast as it is set free, combines with the sodium sulphide to form sodium polysulphide:

$$Na_2S + S = Na_2S_2.$$

Later on, oxygen is liberated at the anode which also acts upon sodium hydrogen sulphide * to form polysulphide: †

$$6\,NaSH + 3\,O = 3\,Na_2S_2 + 3\,H_2O.$$

This polysulphide gradually diffuses during the progress of the analysis, and if the space around the cathode is not separated from the rest of the solution it begins to dissolve the deposited antimony as soon as it reaches the cathode:

$$2\,Sb + 3\,Na_2S_2 = 2\,Na_3SbS_3.$$

This was a frequent cause of failure in antimony determinations when the current was passed through the cell for too long a time, and, to prevent the diffusion of the polysulphide, Ost and Klapproth recommended that the cell be separated into two compartments by a diaphragm. In this way good results were obtained. This complication of the apparatus is unnecessary, however, if some substance is added to the bath which acts upon the polysulphide and reduces it to monosulphide.

Lecrenier ‡ used sodium sulphite for this purpose. It reacts with polysulphides to form thiosulphate and monosulphide:

$$Na_2S_2 + Na_2SO_3 = Na_2S_2O_3 + Na_2S.$$

Quite independent of one another, Hollard and Bertiaux, as well as A. Fischer, have used potassium cyanide for the same purpose since the year 1900. By this salt, the polysulphide is reduced to monosulphide and the cyanide is changed to thiocyanate:

$$Na_2S_2 + KCN = KCNS + Na_2S.$$

Sodium hydrosulphite has also been tried by A. Fischer and found to work satisfactorily but neither this reagent nor the above-mentioned sodium sulphite has any advantages over potassium cyanide. §

In recent years the electrolytic determination of antimony from sodium-sulphide solutions has been examined critically by a num-

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* NaSH is formed by the hydrolysis of some of the sodium sulphide: $Na_2S + H_2O = NaHS + NaOH$.

† Some thiosulphate is also formed but it does no harm:

$$Na_2S_2 + 3O = Na_2S_2O_3.$$

‡ Chem.-Ztg., **13**, 1219 (1889).

§ The potassium cyanide has the advantage of converting traces of copper into complex ions which are not decomposed during the analysis.

ber of investigators * and the general opinion, obtained as a result of such studies, is that the method usually gives results that are a little higher than the truth and that the positive error is apparently caused by small quantities of oxygen and of sulphur present in the antimony deposit.† It has been found that when the electrolysis is carried out in hot solutions and with high current density the results are a little higher than when the analysis is made at room temperature with a weaker current. According to several authorities, the positive error amounts to from 1 to 1.5 per cent ‡ and for this reason Henz proposed that a deduction of 1.5 per cent be made upon the weight of deposit actually obtained.

At the author's suggestion, Dr. Scheen § has carried out some experiments to ascertain the cause of these high results and he has found that the error is really due to inclusions which are dependent upon the nature of the cathode surface. It was mentioned on page 58 that a rough platinum surface was more likely to give rise to this sort of an error and it has been found that gauze electrodes are particularly bad in this respect. The facts mentioned by other authors were confirmed, that the temperature of the electrolyte should not exceed 65° to 70° and that the presence of considerable alkali hydroxide tends to increase the positive error. The temperature plays a part in this behavior, because above 70° the deposit is rather spongy and has a greater tendency to take up foreign substances. If the electrolyte contains considerable alkali hydroxide, the deposit will retain an alkaline odor even after the most careful washing with water and alcohol.

The author originally recommended polished platinum dishes for this determination although they will not hold firmly much more than from 0.1 to 0.15 gm. of antimony deposit. For this reason he was led to adopt dishes with the inside surface roughened. The experiments performed by Dr. Scheen with both smooth and roughened dishes have shown, however, that correct results

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* F. Henz, Z. anorg. Chem., **37,** 1 (1903); F. Foerster and J. Wolf, Z. Elektrochem., **13,** 205 (1907); H. J. S. Sand, *ibid.*, 326; J. M. M. Dormaar, Z. anorg. Chem., **53,** 349 (1907).

† Foerster was inclined to believe that a solid solution of antimony oxide and of antimony sulphide in metallic antimony was formed.

‡ If the electrolyte contains more than 3 per cent of alkali hydroxide, the positive error may be 3 per cent of the weight of the deposit.

§ Z. Elektrochem., **14,** 257 (1908).

can be obtained with the former, whereas, with the latter, or with gauze electrodes of various designs, the results are too high. When most accurate results are desired, therefore, roughened dishes or gauze electrodes should not be used. Treatment of the dishes with dilute aqua regia serves to etch them very slightly and such dishes will hold a deposit of as much as 0.3 gm., although it is better not to have more than 0.2 gm. of antimony in the solution.

Procedure for Depositing Antimony from a Sodium-sulphide Solution.

For this method * it is immaterial whether the dissolved antimony is present in the trivalent or quinquevalent condition. In the course of a chemical analysis, the antimony is usually obtained as the trisulphide or pentasulphide, either by direct precipitation or as a result of a separation from other sulphides.†

The antimony sulphide is dissolved in about 80 cc. of a solution which has been saturated with crystallized sodium sulphide at the room temperature (the specific gravity of such a solution is 1.14), 30 cc. of a freshly prepared potassium-cyanide solution are added, and the mixture is diluted with water to a total volume of 120 to 140 cc.

The solution is electrolyzed at a temperature of 65° (not over 70° in any case) with a current of 1.2 to 1.3 amperes.‡ The electrolysis usually requires about 2 hours. The completeness of the deposition may be tested as described under Copper (p. 125) and Lead (p. 194) by diluting with a little water and observing

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* For practice, 0.2 to 0.3 gm. of metallic antimony is pulverized very finely and dissolved by heating in a narrow test tube with about 1 cc. of concentrated sulphuric acid. The excess of acid is driven off and the cold residue dissolved in a saturated solution of sodium sulphide.

† If the antimony is present in the form of a precipitate which may contain members of the copper group, a separation from the latter is obtained by warming the precipitate with sodium-sulphide solution. In this case, there is always some polysulphide formed, as is shown by the yellow color of the solution and before adding the prescribed quantity of potassium cyanide, enough of this reagent should be added to decolorize the solution.

‡ The potential should be 1.1 to 1.4 volts and must not exceed 1.7 volts. Periodic changes will take place in the voltage during the analysis. K. Koelichen studied this phenomenon (Z. Elektrochem., **7**, 629 (1901)) and found it due to the alternating deposition and solution of a thin layer of sulphur on the anode.

after about 10 minutes whether any further deposit is obtained on the freshly exposed surface.

When the deposition is complete, the current is turned off, the liquid poured out of the dish, which is washed with water and with alcohol, dried at 80° or 90° in an air bath and weighed after cooling in a desiccator (*cf.* p. 120).

The antimony may be easily removed from the dish by heating it with a mixture of nitric and tartaric acids.

If it is not a question of great accuracy, or if it is desired to use a platinum gauze cathode, the antimony sulphide may be dissolved in about 80 cc. of a saturated sodium-sulphide solution, 30 cc. of potassium-cyanide solution added, as above, and the contents of the small beaker diluted with water until the gauze electrode is completely immersed. The rest of the analysis is carried out as before.

It was formerly recommended to prepare the sodium-sulphide solution in the laboratory from hydrogen sulphide and pure sodium hydroxide, but it is now possible to buy pure sodium sulphide and thus the somewhat tedious operation may be avoided.

If the antimony solution was prepared by the method described on page 157, footnote 1, it may contain tin, arsenic and traces of copper. The fact that copper has no disturbing effect has been mentioned (p. 155). The method of carrying out the analysis when tin or arsenic is present will be given under the separations.

Tin.

At. Wt. = 118.7. Elec. Equiv. = 0.614 mg. for Sn^{++} ions. Elec. Potential = $< +0.192$ volt. Overvoltage of H_2 = 0.43–0.53 volt.

Tin deposits are often difficult to remove completely from the electrode. After treatment with concentrated hydrochloric acid, a dark stain (probably of Sn-Pt alloy) is likely to remain. This stain can be removed by placing the electrode in molten potassium pyrosulphate. Henz states that treatment with a mixture of nitric and oxalic acids is a more rapid means of dissolving a tin deposit. If a dark residue remains it may be removed by Bunsen's method, which consists of treating with zinc and dilute hydrochloric acid followed by concentrated hydrochloric acid. To avoid any difficulty in cleaning the electrode, it is perhaps best to deposit a thin film of copper on the platinum before using it for the tin determination.

Tin hydroxide is amphoteric. In very dilute solution, particularly when in the quadrivalent state, there is a marked tendency toward hydrolysis, with the resulting precipitation of hydrated tin oxide, unless the tin is in the form of a complex ion. From nitric-acid solutions, the precipitation of the hydrated oxide (metastannic acid) may be made complete.

There are two methods which have proved satisfactory for the electrolytic determination of tin; the electrolysis of a solution containing the complex ammonium stannic oxalate and the electrolysis of ammonium thiostannate.* The latter method has proved especially advantageous in the rapid electro-analysis as well as in the determination of tin present as metastannic acid and contaminated with copper or other metals whose sulphides are insoluble in ammonium sulphide (*cf.* Bronzes).

Deposition of Tin from Acid-oxalate Solution.

Stannic oxide (also the sulphide) as obtained in the course of analytical operations (but not cassiterite) may be dissolved by heating it with a solution of ammonium oxalate or of acid ammonium oxalate. If the solution of the normal oxalate is subjected to the action of the electric current, the tin is at first deposited upon the cathode in a bright metallic form but as the ammonium oxalate is gradually oxidized at the anode to ammonium carbonate and carbon dioxide,

$$(NH_4)_2C_2O_4 + O = (NH_4)_2CO_3 + CO_2,$$

the solution becomes alkaline (owing to hydrolysis of ammonium carbonate) and stannic acid separates. The principal condition for the quantitative electrodeposition of tin is, therefore, to keep the solution acid with oxalic acid until the end.

F. Henz † found it better to liberate the oxalic acid from the ammonium oxalate rather than to add fresh oxalic acid from time to time. The sulphuric acid is added after the electrolysis has been in progress for some time, when some of the ammonium oxalate has undergone the above reaction. Thus, besides setting

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* Methods of A. Classen: Classen and v. Reis, Ber., **14,** 1622 (1881); Classen, *ibid.*, **17,** 2467 (1884); **18,** 1104 (1885); Bongartz and Classen, *ibid.*, **21,** 2900 (1888); Classen, *ibid.*, **27,** 2060 (1894).

† Z. anorg. Chem., **37,** 39 (1903).

free oxalic acid, more or less ammonium sulphate is formed and this salt has a favorable effect.

To carry out the analysis, the solution of the tin salt is treated with 100 cc. of a solution containing 3.6 gms. of ammonium oxalate and an equal weight of free oxalic acid, and electrolyzed with a current of 0.2 to 0.6 ampere (corresponding to 2.7 to 3.8 volts) at the room temperature. After about 2 hours, 8 cc. of sulphuric acid (1 : 1) are added. The precipitation of about 0.3 gms. of tin requires from 8 to 10 hours. The tin deposits upon the electrode, which has been previously plated with copper, in the form of a glistening, metallic layer that adheres well. Some authorities have claimed that only a little tin will adhere to the cathode, but Bongartz and Classen* have shown that deposits weighing as much as 1 gram can be obtained satisfactorily. After breaking the circuit, the cathode is washed, in the usual manner with water and alcohol, and dried at 80° to 90°.

The experiments of M. Heidenreich in the author's laboratory have shown that about 0.3 gm. of tin may be deposited in 4 to 4.5 hours by a current of ND_{100} = 1 to 1.5 amperes, if the electrolysis is carried out at a temperature of 60° to 65°. In this case the washing must take place before the current is turned off. Like antimony, tin is often obtained in the course of a chemical analysis as dissolved alkali thio-salt. To change such a solution into one of oxalic acid, Henz acidifies it with acetic acid and then, without filtering off the precipitated stannic sulphide, adds a boiling hot solution of ammonium oxalate and oxalic acid (of the concentration stated above), using 100 cc. for each 0.1 gm. of tin. The stannic sulphide dissolves and the solution is turbid only with precipitated sulphur which has no effect upon the electrolysis.

If this last solution is electrolyzed, after cooling to room temperature, with a current of ND_{100} = 0.2 to 0.3 ampere (corresponding to 2 or 3 volts), the greater part of the tin will be deposited in 6 hours. Then 8 cc. of sulphuric acid (1 : 1) are added and the electrolysis is continued. After 24 hours from the start, all the tin will have been deposited. The current is broken, the cathode washed with water and alcohol and dried at 80–90° before weighing.

If, in the necessary preparation of the electrolyte, the volume of the tin solution becomes too large to be contained in the usual platinum dish, the electrolysis is carried out in a beaker and a gauze

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* Ber., **21,** 2900 (1888).

cathode is used. In this case, when the electrolysis is finished, the electrodes are quickly raised from the acid solution and transferred to a beaker containing distilled water.

If the electrolysis is carried out at ordinary temperatures, the long time is recommended because there is no satisfactory test for traces of tin in oxalic-acid solution and the color of the metal is so similar to that of platinum that it is hard to tell whether there is any slight deposit on a freshly exposed cathode surface.

If, however, the tin solution is heated to 60° at the start and the sulphuric acid is added after 3 hours, one may feel certain after another 5 hours that as much as 0.2 gm. of tin will have been precipitated quantitatively. It is necessary to keep the deposit thoroughly wet throughout the electrolysis, adding water from time to time to replace that lost by evaporation.

If the thiostannate solution is one from which antimony has just been determined by electrolysis, the solution will contain hardly any polysulphide because the chief requirement of a successful antimony determination is the absence of polysulphide. If, however, the solution is yellow colored, it is heated before the addition of the acetic acid, and freshly prepared potassium cyanide is added, drop by drop, until the solution becomes colorless. Otherwise, too much sulphur is precipitated upon the addition of acetic acid, and it is hard to tell whether the stannic sulphide is dissolved completely by the addition of ammonium oxalate and oxalic acid.

Rapid Deposition of Tin from Ammonium-sulphide Solution.*

Experience has shown that the electrolysis of an ammonium thiostannate solution often yields spongy deposits. If the platinum cathode is given a thin coating of copper (see Zinc) and then a thin coating of tin (best by the electrolysis of an acid solution of ammonium stannic oxalate, p. 160) the deposit of tin obtained from the thiostannate solution is very satisfactory. This is due to the overvoltage which hydrogen shows toward tin (p. 82).

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* General references to the rapid electrodeposition of tin in various solutions: Medway, Am. J. Sci., [4], **18**, 56, 180 (1904); Z. anorgan. Chem., **42**, 114 (1904); Exner, J. Am. Chem. Soc., **25**, 896 (1903); A. Fischer, Z. anorgan. Chem., **42**, 382 (1904); A. Fischer and Boddaert, Z. Elektrochem., **10**, 945 (1904); L. F. Witmer, J. Am. Chem. Soc., **29**, 473 (1907); Smith and Kollock, J. Am. Chem. Soc., **27**, 1527 (1905).

	Experiment performed by A. Fischer at Aachen.
Electrode	Gauze electrode and lattice stirrer
Electrolyte contained	16 cc. $(NH_1)_2S$ [*] and 20 cc. Na_2SO_3 (40 per cent)
Volume	120 cc.
Quantity of metal	0.2 gm. as $SnCl_4.2\ NH_4Cl$
Temperature	60°
Voltage of the bath	3.2 to 4 volts
Current density	5.5 amperes
Number of revolutions	About 800
Time in minutes	25

The metal is washed with alcohol, then with carbon disulphide and finally with alcohol.

The rapid electrodeposition of tin with the aid of magnetic stirring is described on page 78.

Arsenic.

All experiments with regard to the electrolytic determination of arsenic have proved unsatisfactory. This is even true of the method proposed by B. Neumann [†] which consisted in electrolyzing arsenious acid in fuming hydrochloric acid with lead or silver anodes and a potential of about one volt. This proves, it is true, the possibility of quantitatively depositing the arsenic as metal on the cathode but the experiment is such a tedious one that it has no practical significance.

The section of this book on Metal Separations will show how arsenic may be separated from other elements by means of the electric current.

Recently, experiments have been made which show that the Marsh test can be carried out satisfactorily for forensic purposes in such a way that the hydrogen necessary for the formation of arsine is formed, not by the action of acid upon zinc but by the electrolytic decomposition of the acid. In this way there is no danger of getting a test from the arsenic likely to be present in zinc. Here, it will suffice to refer to the literature on the subject.[‡]

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[*] The ammonium-sulphide solution is prepared from aqua ammonia, sp. gr. 0.91.

[†] Chem.-Ztg., **30,** 33 (1906).

[‡] T. E. Thorpe, J. Chem. Soc., London, **83,** 974 (1903); H. J. S. Sand, *ibid.*, **85,** 1018 (1904); S. R. Trotmann, J. Soc. Chem. Ind., **23,** 117 (1904). See also Treadwell-Hall, "Quantitative Analysis."

Tellurium.

At. Wt. = 127.5. Elec. Equiv. = 0.661 mg. for bivalent Te.

G. Pellini * has obtained satisfactory results from a chloride solution to which ammonium tartrate has been added.

Procedure. Weigh 0.1 to 0.02 gm. of the dioxide into a platinum dish which has been sand-blasted on the inside and dissolve the sample in 5 cc. of concentrated hydrochloric acid. Dilute the solution with 100 to 125 cc. of a cold, saturated solution of ammonium tartrate in water and then add pure water till the total volume is about 170 cc. Heat the solution to 60° and electrolyze, using the dish as cathode, with a current of ND_{100} = 0.02 to 0.01 ampere and 1.85 to 2.2 volts e.m.f. When, at the end of about 9 hours, a portion of the solution gives no brown precipitate of tellurium upon treatment with stannous chloride and hydrochloric acid, wash the deposit with water which has been boiled to remove dissolved oxygen and cooled in a current of carbon dioxide. Finally rinse with alcohol and dry at 90° for a few minutes.

Rapid Deposition of Tellurium.

Larger quantities of tellurium (0.06 to 1.2 gms.) were determined by the same author in well-stirred electrolytes. Starting with metallic tellurium, the solution obtained by oxidation with nitric acid was evaporated, the tellurous acid dissolved on the water bath in 10 cc. of sulphuric acid, and 30 to 40 cc. of a saturated solution of ammonium-acid-tartrate added. The tellurous-acid solution was further diluted with the same solution to 250 cc. and after heating to 60° the electrolysis was carried out with a current of ND_{100} = 0.12 to 0.09 ampere at 1.8 to 1.2 volts. The cathode used by the author was a platinum cylinder roughened on the inside. The stirrer was made to revolve from 800 to 900 times per minute. The deposited tellurium was washed and dried as described above.

Gallo † found that the above method was not wholly satisfactory for relatively large quantities of tellurium. He recommended the following procedure.

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* Gazz. chim. ital., **34,** I. 128 (1904).

† Atti d. Reale Accad. dei Lincei, Roma [5], **13, I,** 713 (1904).

Dissolve the metal in concentrated sulphuric acid, using a platinum dish which has been roughened on the inside by sand blasting. Evaporate till fumes of sulphuric acid are evolved, and but little free acid remains. Cool, add a few cubic centimeters of boiled water, free from carbonic acid, and then dilute to 150 cc. with 10 per cent sodium pyrophosphate solution. Electrolyze with a current of ND_{100} = 1.8 to 2 volts at 1.8 to 2 volts. About 25 mgms. of metallic tellurium will be deposited per hour.

GROUP II.

This group includes the metals indium, cadmium, and zinc. The exact position of indium in the voltage series is in doubt. The metals cadmium and zinc are considerably above hydrogen in the series but, thanks to the overvoltage which they show toward the evolution of hydrogen, it is possible to deposit them from slightly acid solutions. The elements will be discussed in the order of their importance.

Zinc.

At. Wt. = 65.37. Elec. Equiv. = 0.339 mg. for Zn^{++} ions. Elec. Potential = + 0.770 volt. Overvoltage of H_2 = 0.70 volt.

Zinc may be deposited quantitatively either from acid or from alkaline solutions. Many methods have been proposed of which only a few of the best will be mentioned.

On account of slight oxidation, the values obtained by all electrolytic methods for the determination of zinc are likely to be a little high unless special pains are taken to prevent such oxidation.

Deposition of Zinc from Alkaline Solutions.

Beilstein and Jawein in 1879 successfully deposited zinc from a potassium-cyanide solution. This method is seldom used to-day because it is simpler and quicker to use an alkaline solution without any potassium cyanide.* G. Vortmann† added alkali tartrate to the alkaline solution and stated that the deposits adhered well irrespective of whether little or much caustic-soda solution were present. After R. Amberg,‡ on the basis of work carried out in the author's laboratory by Millot and v. Foregger, had found that the electrolytic deposition of zinc was possible from an alkaline solution without the addition of any other chemical, F. Spitzer§

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* A modification of the potassium-cyanide method used for the electrolytic separation of zinc from iron will be given in Part III.

† Monatsh. Chem., **14**, 536 (1903).

‡ Ber., **36**, 2489 (1903).

§ Z. Elektrochem., **11**, 391 (1905).

succeeded in simplifying the method by proving that the large excess of caustic alkali recommended by Amberg was unnecessary. Amberg had recommended that not less than 40 gms. of potassium hydroxide should be used for 0.5 gm. of zinc but Spitzer found that accurate results were obtained if the quantity of alkali added was large enough to keep the solution clear during the progress of the analysis, and, to accomplish this, at least 10 molecules of NaOH are necessary for 1 molecule of $ZnSO_4$.

Spitzer's directions, therefore, were to add enough sodium hydroxide to the zinc-sulphate solution * to make a permanently clear solution. It is not necessary to measure the alkali very carefully for Amberg's work has shown that an excess of this reagent does no harm. A convenient strength of the caustic alkali is 160 gms. NaOH in a liter (4-normal). The quantity of zinc used in an analysis may be from 0.16 to 0.32 gm. As cathode a

RAPID DEPOSITION OF ZINC FROM ALKALINE SOLUTION.

	Experiments performed by						
	A. Fischer.				Exner.	Ingham.	
Electrode	Dish and rotating disk	Gauze electrode and lattice stirrer			Dish and rotating spiral		
Electrolyte contained	20 gm. KOH	Enough NaOH to form the zincate			5 to 12 gms. NaOH	6 gms. NaOH	6 gms. NaOH
Volume	125 cc.	100 cc.	100 cc.	100 cc.	125 cc.	....	....
Quantity of metal	0.23 gm. as sulphate	0.2 gm. as sulphate	0.4 gm. as sulphate	0.4 gm. as sulphate	0.5 gm.	0.25 gm.	0.48 gm.
Temperature	95°	Cold at the start; during the analysis the temperature rises to 60°			Hot	Hot	Hot
Potential	3 volts	4 volts	3.9 to 4 volts	4.1 volts	5 to 6 volts	8 volts	6 volts
Revolutions	600–800	800–1000	800–1000	800–1000	600–800	230	230
Time	15 min.	30 min.	20–15 min.	5 min.	15 min.	20 min.	30 min.

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* For practice, zinc vitriol, $ZnSO_4.7H_2O$, may be used.

Winkler's platinum gauze electrode, which is given a preliminary coating of silver, is used (see below). With such an electrode about 0.3 gm. of zinc can be deposited quantitatively at ordinary temperatures with a current of 0.8 ampere in 2 hours. The current may be reduced to 0.3 ampere if it is not desired to carry out the analysis quickly. The potential difference between the electrodes with the above current is about 4 volts. The deposit may be washed after turning off the current and the same electrode, with its zinc deposit on it, may be used for several analyses. After washing with alcohol, the electrode is dried at 70° to 80°.

In technical laboratories electrodes of amalgamated brass gauze have been used on account of their cheapness (*cf.* p. 178).

The deposition of zinc from ammoniacal and from alkaline tartrate solutions will be described under the separation of nickel from zinc.

The above table shows that zinc can be determined rapidly from alkaline solutions even when the conditions are varied considerably.*

Spear and Strahan † recommend the determination of zinc from alkaline solutions but have obtained the best results under conditions somewhat different from those given above. Their method is as follows: About 0.4 gm. of zinc, present as sulphate, is treated with an aqueous solution of 10 to 25 gms. KOH and the total volume of the electrolyte made up to 125 cc. The solution is brought nearly to boiling and electrolyzed with a current of ND_{100} = 3 amperes. As anode a platinum spiral is used and it is placed *above* (not at the side) the rotating cathode. The latter is preferably made of nickel gauze, 30 meshes to the inch, which is bent over (dome shaped) at the top but does not extend to the stout wire stem of the same metal. Seven to eight minutes before the end of the experiment, which should require from 30

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* General references on the rapid electrolytic determination of zinc from various solutions: Medway, Am. J. Sci., [4], **18,** 56 (1904); Z. anorg. Chem., **42,** 114 (1904). Exner, J. Am. Chem. Soc., **25,** 896 (1903). Exner, *ibid.*, **26,** 1269 (1904). A. Fischer and Boddaert, Z. Elektrochem., **10,** 945 (1904). Perkin, Chem. News, **93,** 283 (1906). Price and Judge, *ibid.*, **94,** 18 (1906). A. Fischer, Chem.-Ztg., **31,** 25 (1907). E. F. Smith and Kollock, J. Am. Chem. Soc., **27,** 1255 (1905). H. J. S. Sand, J. Chem. Soc., London, **91,** 373 (1907).

† J. Ind. Eng. Chem., **4,** 889 (1912).

to 45 minutes, the anode and sides of the beaker are washed down with a little water. Then, after electrolyzing a minute longer, the solution is cooled to below 25°, using ice if necessary. When the solution is cold, the beaker is lowered without interrupting the current and, before stopping the stirrer, the cathode is carefully washed with water, then with alcohol, and finally with ether that has been *recently dried over sodium and freshly distilled.* The ether is at once removed by gentle heating and the electrode weighed after standing a short time in a desiccator.

Spear and Strahan obtained excellent results by this method. Nitrates and ammonium salts must be absent or the deposition of the zinc will be incomplete. The original solution should not contain much free sulphuric acid, as zinc-potassium sulphate is not very soluble in concentrated alkali solutions. High results are often due to the formation of hydroxide on the cathode. This may be due to exposure of the cathode to the air or to the gases arising from the anode, to stopping the electrolysis while the solution is still warm, to incomplete removal of caustic alkali before washing with alcohol, to the use of ether containing water and oxides that attack zinc, or to letting the ether evaporate spontaneously in a desiccator. There is always a weighable amount of zinc hydroxide formed but this positive error is almost exactly compensated in the above method by slight zinc losses which take place during the washing with water.

Rapid Deposition of Zinc in Ammoniacal Solution.

L. H. Ingham * has found that the deposition of zinc from an ammoniacal solution, which is successful with stationary electrolytes only under special conditions, gives good results if the electrolyte is kept in motion. The presence of ammonium chloride in the solution has a favorable effect, rather than otherwise, because it serves to increase the conductivity of the electrolyte. As cathode a silvered platinum dish and as anode a platinum spiral of about 50 mm. diameter is used. The latter is arched slightly to make it correspond to the surface of the stirred liquid and is made to revolve about 230 times in a minute. From a solution containing 0.24 gm. of zinc sulphate, with 5 cc. of hydrochloric acid (sp. gr. 1.21) which is neutralized with ammonia (sp. gr. 0.95),

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* J. Am. Chem. Soc., **26**, 1280 (1904).

and the solution treated with one gram of ammonium chloride in addition, the zinc is quantitatively deposited upon the cathode in 20 minutes with a current of 5 amperes and 5 volts. There is no injurious effect of the chlorine at the anode. This method has given good results in the analysis of zinc-sulphide ores (see Part IV).

Deposition of Zinc from Acid Solution.

Before the significance of the overvoltage of hydrogen was recognized, it was regarded as futile to attempt the electrolysis of zinc in an acid solution (*cf.* p. 174). Although it is possible to deposit zinc electrolytically from a fairly acid solution upon a zinc cathode, and such an electrode exists as soon as a layer of zinc has been formed upon the platinum, yet the reaction comes to an end as soon as the concentration of zinc ions has become diminished, while that of hydrogen ions is increased to the point where less work is needed by the current to discharge the hydrogen ions than to discharge the zinc ions. To counteract this tendency, the concentration of free acid must be kept very low, by using an acid such as acetic, tartaric, formic, etc., and by adding a salt of the same acid to the electrolyte bath. In this way the deposition of zinc can be made quantitative.

(a) *The solution contains sodium acetate and acetic acid.* The electrolysis of zinc solutions containing these substances was recommended by Riche, Parodi and Mascazzini, as well as by Rudorff and has been tested by F. Spitzer.* By using a gauze electrode, good deposits are obtained with a current strength of 0.5 ampere if the solution containing about 0.16 gm. of zinc in 100 cc. is treated with a solution of 5 gms. sodium acetate and acidified with 0.3, or 0.5 cc. at the most, of glacial acetic acid. The analysis is carried out at the ordinary temperature and requires from 2 to 2.5 hours.

Too high a current density or too much acetic acid causes an uneven deposit; a branching, crystalline growth is obtained which easily falls off the electrode. To make sure that the acidity of the solution is not too great, any free acid originally present in the solution is neutralized by the cautious addition of caustic-soda solution, before adding the sodium acetate.

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* Z. Elektrochem., **11**, 404 (1905).

Rapid Deposition of Zinc from Acetic-acid Solutions.

It is technically very important to have a rapid and reliable method for the determination of zinc. The extent to which this problem has occupied the attention of different investigators is shown by the monograph of H. Nissenson.* This author believes that the rapid electrolytic methods for determining zinc will eventually replace the volumetric methods generally used where a great many zinc determinations have to be made. The chief advantage of the volumetric methods lies in the rapidity at which the analyses are carried out but the objection to them is that the end point depends upon an accurate judgment of a color shade, so that an operator can be certain of his results only when he has had constant and recent practice with the determination. The results obtained by H. J. Sand, which are taken from the paper referred to on page 42, will be given here in detail.

All the electrolytes used by this investigator contained a little free acetic acid and also some alkali sulphate, because this salt is almost always present in the analysis of zinc ores. The excess of sulphuric acid was neutralized in some cases by the addition of a large excess of ammonia and in other cases by sodium hydroxide; but, at the last, enough acetic acid was always added to make the solution slightly acid. As it has been shown that it is hard to deposit the last traces of zinc when the electrolyte is at a temperature above 30°, it was necessary to keep the electrolytic cell surrounded by cold water in order to prevent the solution becoming heated by the passage of the current.

All these experiments were carried out with Sand's electrodes (p. 66) and the cathode was first covered with a copper deposit.

In experiments 2, 3 and 4 the auxiliary electrode was used (*cf.* p. 40). The volume of the electrolyte was about 85 cc. in all cases and the stirrer made between 300 and 800 revolutions per minute.

In experiments 4, 5 and 7 the first values for zinc were obtained after 20 minutes and the second values were obtained by continuing the electrolysis until the weight of the cathode became constant, which required 10 minutes more. It will be noted that most of the results are a little too high (*cf.* p. 168).

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* Die Bestimmungsmethoden des Zinks, Stuttgart, 1907.

RAPID DEPOSITION OF ZINC FROM ACETIC-ACID SOLUTION, ACCORDING TO SAND.

	1	2	3	4	5	6	7
Electrolyte contained	1.5 cc. H_2SO_4, 3.3 gms. NaOH, 1.5 cc. $HC_2H_3O_2$*	1.25 cc. H_2SO_4, 6.6 gms. NaOH, 9 cc. $HC_2H_3O_2$	3 cc. H_2SO_4, 5.5 gms. NaOH, 1.25 cc. $HC_2H_3O_2$	1.25 cc H_2SO_4, 10 cc. conc. NH_4OH, 8 cc. $HC_2H_3O_2$	1.25 cc. H_2SO_4, 10 cc. conc. NH_4OH, 8 cc. $HC_2H_3O_2$	1.25 cc. H_2SO_4, 3.5 cc. conc. NH_4OH, 1.5 cc. $HC_2H_3O_2$, 2.5 gms. $NH_4C_2H_3O_2$	1.25 cc. H_2SO_4, 4.5 cc. conc. NH_4OH, 2.5 cc. $HC_2H_3O_2$, 2.5 gms. $NH_4C_2H_3O_2$
Quantity of metal	0.6175 gm.	0.4943 gm.	0.2529 gm.	0.4943 gm.	0.4943 gm.	0.4943 gm.	0.4943 gm.
Weight of deposit	0.6168 gm.	0.4957 gm.	0.2540 gm.	0.4944 gm. 0.4957 gm.	0.4946 gm. 0.4953 gm.	0.4944 gm.	0.4938 gm. 0.4945 gm.
Potential	4 to 4.5 volts	3.8 to 4 volts	3.6 to 4.2 volts	3.8 to 4.3 volts	3.8 to 4.3 volts	....	3.6 to 4.2 volts
Auxiliary electrode	....	1.45 to 1.7 volts	1.5 to 1.55 volts	1.5 to 1.55 volts	....	....	....
Current strength	3 amperes	3 amperes	3 to 4 amperes	3 amperes	3 amperes	3 amperes	3 to 4 amperes
Time	30 minutes	18 minutes	13 minutes	20+10 minutes	20+10 minutes	30 minutes	20+10 minutes

* Glacial acetic acid was used in all cases.

RAPID DEPOSITION OF ZINC FROM ACETIC-ACID SOLUTION.

	Experiments performed by			
	A. Fischer.	Exner.	Ingham.	A. Fischer.
Electrode	Dish and rotating disk	Dish and rotating spiral	Dish and rotating spiral	Gauze electrodes and lattice stirrer
Electrolyte contained	1 to 3 gms. of sodium acetate and 0.2% of acetic acid (30%)	1 to 3 gms. of sodium acetate and 0.2% of acetic acid (30%)	3 gms. sodium acetate and 4 to 6 cc. of acetic acid (30%)	1.25 cc. of conc. H_2SO_4, 3.5 cc. of conc. NH_4OH, 1.5 cc. of glacial $HC_2H_3O_2$, 2.25 gms. of $NH_4C_2H_3O_2$
Volume	125 cc.	125 cc.	125 cc.	100 cc.
Quantity of metal	0.25 to 0.5 gm. as sulphate	0.25 to 0.5 gm. as sulphate	0.25 to 0.5 gm. as sulphate	0.4 gm. as sulphate
Temperature	20°	Hot	Hot	Under 30°
Potential	6.5 to 8.7 volts	10 to 8 volts	12 to 17 volts	3.9 to 4.2 volts
Revolutions	600 to 800	600 to 800	230 to 560	1200
Time	15 min.	10 to 15 min.	10 to 15 min.	30 min.

(b) *The solution contains ammonium oxalate and free oxalic acid or tartaric acid.** The zinc salt is dissolved by warming with as little water as possible, about 4 gms. of ammonium oxalate are added and complete solution is effected by heating, adding a little more water if necessary.† The clear solution is transferred to a platinum dish, which has been coated with either copper or silver (see below), diluted to 120 cc., heated to 50° or 60° and electrolyzed with a current of 0.5 to 1 ampere and 3.5 to 4.8 volts.

The author has found by experiment that a dense, metallic deposit is formed only by keeping the solution acid during the electrolysis. For acidifying, a cold saturated solution of oxalic acid or, better, a solution of 3 gms. of tartaric acid in 50 cc. of

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* The method has been credited to Reinhardt and Ihle, but was previously used by the author; *cf.* Classen and v. Reis, Ber., **14,** 1662 (1881) and Classen, *ibid.*, **27,** 2060 (1894).

† The addition of ammonium oxalate to a dilute solution of zinc salt causes a precipitate of zinc oxalate to form which is not entirely converted to ammonium zinc oxalate by a dilute solution of ammonium oxalate.

water,* is employed. After electrolyzing for from 3 to 5 minutes, the acid solution is permitted to flow in drops (about ten to the minute), from a burette with a fine outlet, upon a watch glass covering the dish. The acid runs slowly into the solution through a perforation in the watch glass.

The reduction requires about 2 hours. When all the zinc has been deposited, as shown by warming a little of the solution with potassium ferrocyanide and finding no brownish precipitate formed, the deposit is washed with water without breaking the circuit, rinsed with alcohol, and dried at 70° to 80° in an air bath.

If the zinc is deposited directly upon a platinum surface, then on dissolving the deposit in dilute hydrochloric or sulphuric acid, a dark coating of platinum black usually remains which can be removed best by igniting the dish and again treating it with acid. Since the dish is appreciably attacked by this operation, it is advisable, before weighing the dish, to precipitate upon it a thin coating of copper or, better, silver.

A bright, thick coating of copper can be obtained in a few minutes if a saturated solution of copper sulphate is treated with an excess of ammonium oxalate to form the double salt, acidified with oxalic acid, warmed to 70° to 80°, and the copper precipitated by a current of 1 ampere. The preparation of the double salt in a beaker and the transfer of the clear hot solution to the platinum dish is to be recommended.

For silvering the dish it is best to precipitate the silver from a solution containing potassium cyanide (see p. 133).

Von Miller and Kiliani have modified the oxalate method as follows. In the copper-plated platinum dish, 4 gms. of potassium oxalate and 3 gms. of potassium sulphate are dissolved and to this aqueous solution (not the reverse) the zinc nitrate or zinc sulphate (but not chloride) solution is added after it has been carefully neutralized with caustic potash. The mixture is electrolyzed at the room temperature with a current of $ND_{100} = 0.3$ ampere. The electrolysis requires from 2 to 3 hours. By stirring the electrolyte, the current density may be increased to 0.5 ampere and the time diminished.

The solution must not contain any ammonium salts or chloride. The latter, especially, causes a spongy deposit to be obtained.

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* Nicholson and Avery, Z. Elektrochem., **3,** 150 (1896), prefer to acidify with formic acid.

Cadmium.

At. Wt. = 112.4. Elec. Equiv. = 0.582 mg. for Cd^{++} ions. Elec. Potential = + 0.770 volt. Overvoltage of H_2 = 0.70 volt.

Deposition from Sulphuric-acid Solution.

The electrolytic deposition of cadmium from a solution containing a considerable quantity of free sulphuric acid would at one time have been regarded as theoretically impossible. Cadmium, like zinc, belongs to the class of metals of which the discharge potential is greater than that of hydrogen ions (*cf.* p. 81), thus, in an acid solution, hydrogen should be liberated before the cadmium ions are discharged, or, in a weakly acid solution, there might be a simultaneous discharge of cadmium and hydrogen ions. Owing to the bad effect of hydrogen upon the nature of the deposit (*cf.* p. 22), there would seem to be little prospect of obtaining a satisfactory deposit of cadmium by the electrolysis of an acid solution.

The placing of cadmium among the metals which are positive with respect to hydrogen is justifiable, or, in other words, the discharge potential of cadmium is higher than the potential of hydrogen, only when the hydrogen or cadmium ions are in contact with a platinum cathode. After Nernst and Caspari* showed that it requires a higher electromotive force to discharge hydrogen ions in contact with a metal other than platinum (for example, cadmium) the possibility of cadmium ions being discharged before hydrogen ions became apparent and experiments with cadmium in weakly acid sulphate solutions were renewed. Even before this was understood, Luckow succeeded in depositing cadmium quantitatively from a dilute sulphuric-acid solution. Since the discovery of the overpotential of hydrogen towards metals other than platinum, the cadmium deposition has been explained very easily. At the beginning of the electrolysis, the concentration of cadmium ions is sufficient to cause deposition of cadmium upon the platinum electrode even though some hydrogen may be evolved at the same time, and when this layer of cadmium has formed upon the surface of the platinum, the overvoltage of hydrogen is such that from now on the cadmium will deposit more readily than hydrogen ions will be discharged. Balachowsky has obtained good results using as cathode a platinum

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* Z. physik. Chem., **30**, 89 (1899).

dish which was first plated with silver or copper before beginning the electrolysis of the cadmium solution. For the same reason, Hollard and Bertiaux recommended the formation of a preliminary deposit of cadmium.

P. Denso* succeeded in obtaining a satisfactory deposition of cadmium by using gauze cathodes without any preliminary preparation. The cadmium-sulphate solution was 0.05 normal in respect to free sulphuric acid (about 0.25 per cent H_2SO_4) and was electrolyzed overnight with a current of 0.045 to 0.25 ampere at a potential of 2.6 to 3.3 volts. In this way 0.21 gm. of cadmium was obtained in a weighable form.

In a solution which was normal in respect to free sulphuric acid, it was possible to deposit 0.1 gm. of cadmium in 3 hours with a current of 0.16 ampere at 2.6 volts. The same quantity of metal in a double-normal acid solution (about 10 per cent free H_2SO_4) required 5 hours with a current of 0.29 ampere at 2.7 volts.

The deposit of cadmium must be washed with water before breaking the circuit.

Hollard,† realizing the significance of the overpotential of hydrogen with respect to the deposition of metal, covers the platinum gauze electrode with a layer of cadmium before beginning the analysis. This is done most conveniently by electrolyzing with a current of 0.4 ampere a cadmium-sulphate solution to which 8 gms. of potassium cyanide and 4 gms. of sodium hydroxide have been added. In this way a beautiful, silver-white coating of cadmium is obtained. After washing, drying and weighing the electrode, it possesses the requisite surface to obtain a quantitative deposit of metal from very dilute cadmium solutions.

The solution of cadmium sulphate is treated with 5 cc. of concentrated sulphuric acid, a solution containing 10 gms. of sodium sulphate is added, and, after diluting to a volume of 300 cc., the electrolysis is carried out with a current of 1 ampere.

If more than 0.1 gm. of cadmium is present in 300 cc. of solution the preliminary plating of the cathode with a layer of cadmium is unnecessary because in such cases the original concentration of cadmium ions is sufficient to prevent any injurious effect of the hydrogen ions (*cf.* p. 174).

Holland explains the favorable effect obtained by adding the sodium sulphate. He assumes that the hydrogen ions form a com-

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* Z. Elektrochem., **9,** 468 (1903).

† Bull. soc. chim., **29,** 217 (1903).

plex compound with the salt and are rendered less harmful thereby. The result of conductivity measurements confirms the assumption that a complex compound is formed. Hollard found that the sum of the conductivities of the sodium-sulphate solution and of the sulphuric acid, when measured separately, was greater than the conductivity of the solution containing the mixture of sodium sulphate and sulphuric acid. The difference was more than could be accounted for by the mutual effect of sodium sulphate and of sulphuric acid upon the electrolytic dissociation of the original molecules.

The electrodeposition of cadmium from sulphuric-acid solutions serves to afford a separation of this metal from zinc and from iron, as will be shown later.

Deposition of Cadmium from Alkaline Cyanide Solutions.

According to the present status of electro-analytical practice, the method first recommended by Beilstein and Jawein* and subsequently improved by E. Rimbach† for depositing cadmium from the solution of the complex cyanide is quite generally preferred. The metal obtained from such a solution has a silver-white color, whereas it is more grayish when obtained otherwise, and the cathode never requires any special preparation, as in the methods just described. The disadvantages lie in the general unpleasantness of working with cyanide solutions when other determinations are to be carried out in the solution after the removal of the cadmium, and the further fact that the electrolysis requires a comparatively long time.

If the time factor is not important, and if it is not going to be necessary to remove the excess of potassium cyanide from the electrolyzed solution, the electrolysis may be carried out overnight and in the following manner:

The solution of cadmium sulphate, or chloride, is treated, in case it contains free acid, with enough caustic-potash solution to neutralize all the acid and then a solution of pure potassium cyanide is added until the precipitate, which is first formed, disappears entirely. A large excess of potassium cyanide should be avoided. The solution is then electrolyzed with a current of $ND_{100} = 0.3$ to 0.4 ampere, which is strengthened to about 1 ampere after the greater part of the metal has been removed.

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* Ber., **12**, 759 (1879).

† Z. anal. Chem., **37**, 284 (1898).

According to the quantity of cadmium and the strength of current used, the electrolysis may require 12 hours or longer. Heating the solution to 50° or 60° hastens the process.

At the last, the solution is tested for cadmium by heating under the hood a little of the liquid with dilute sulphuric acid until all the hydrogen cyanide has been expelled and then adding an excess of hydrogen-sulphide water. If no yellow precipitate or yellow coloration is noticeable, the solution is free from cadmium * and the deposit should be washed with water before breaking the circuit. It is finally washed with alcohol and dried as described under Copper.

The following table gives the conditions which have given good results in the

RAPID DEPOSITION OF CADMIUM FROM ALKALI-CYANIDE SOLUTION.†

	Experiments performed by			
	Exner.	Davison.		Flora.
Electrode	Dish and rotating spiral	Dish and rotating spiral	Dish and rotating spiral	Rotating crucible as cathode
Electrolyte contained.	2 gms. KCN and 5 gms. NaOH	4 gms. KCN and 2 gms. NaOH	5 gms. KCN and 1 gm. NaOH	0.5 to 1.5 gms. KCN and 0.5 to 1.5 gms. NaOH
Volume	120 cc.	90 to 125 cc.	90 to 125 cc.	65 to 70 cc.
Quantity of metal	0.55 gm. as sulphate	0.35 gm. as nitrate	0.35 to 0.45 gm. as nitrate	0.1 to 0.15 as sulphate or nitrate
Temperature	Hot	Hot	Hot	Room temperature
Potential	8 volts	4 volts	5.5 volts	7.6 to 8 volts
Revolutions	600	600	600	600
Time in minutes	10 to 15	15	20	30 to 45

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* It should be remembered that the test will not be obtained if the solution is too acid.

† General references to the literature on the rapid electrodeposition of cadmium in various solutions: Medway, Am. J. Science [4], **18,** 56 (1904); Z. anorg. Chem., **42,** 114 (1904). A. Fischer and Boddaert, Z. Elektrochem, **10,** 945 (1904). Flora, Z. anorg. Chem., **47,** 1, 13, 20 (1905). Exner, J. Am. Chem Soc., **25,** 896 (1903). Davison, Thesis, U. of Pa., 1906. H. J. S. Sand, J. Chem. Soc., London, **91,** 373 (1907). Smith and Kollock, J. Am. Chem. Soc., **27,** 1527 (1905).

Deposition of Cadmium from Oxalate Solution.*

The metal may be obtained in compact form, with a bright metallic luster, by the electrolysis of a hot solution of the complex ammonium cadmium oxalate in the presence of free oxalic acid. The cadmium salt is dissolved in a weighed platinum dish by heating it with 20 to 25 cc. of water. When all the salt has dissolved, a hot, filtered solution of 10 gms. ammonium oxalate in 80 to 100 cc. of water is added and the electrolysis is carried out with a current of ND_{100} = 0.5 to 1 ampere at a potential of 3 to 3.4 volts. During the entire time the solution is kept at a temperature of 70° to 75°. As soon as the action of the current has begun, a few cubic centimeters of an oxalic-acid solution, saturated at the room temperature, are poured upon the watch glass which covers the dish, and the electrolyte is kept slightly acid by the addition from time to time of a little of this solution. The end of the reaction is determined by removing a little of the solution with a piece of glass tubing, acidifying it with hydrochloric acid and adding hydrogen sulphide. The metal must be washed with water without interrupting the current. The largest quantity of metal which can be deposited satisfactorily in this way is 0.15 to 0.16 gm. and the time required is about three hours.

The method has proved satisfactory in analytical practice. If the cadmium is present as sulphide, about 0.5 gm. of it is dissolved in hydrochloric acid, the solution is evaporated to dryness and the residual cadmium chloride is treated as described. Instead of using a platinum dish as cathode, good results can be obtained and larger quantities of metal deposited by using a brass gauze cathode, of the shape recommended by Winkler (p. 59), which has been amalgamated. Paweck,† who first used this kind of an electrode, amalgamated it by first dipping the gauze in nitric acid to clean it, washing it with water, and then using it as cathode for 45 minutes to an hour with a current of 0.1 to 0.2 ampere in a solution containing about 0.6 gm. of mercuric chloride, 5 cc. of concentrated nitric acid and 200 cc. of water; a platinum wire was used as anode. The quantity of mercury deposited in this way upon the brass gauze must not, of course, be so large that it will drop off in handling the electrode. The amalgamated electrode is raised

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* A. Classen and v. Reis, Ber., **14,** 1628 (1881); A. Classen, *ibid.*, **17,** 2060 (1884).

† Z. Elektrochem., **5,** 221 (1898).

quickly from the bath and washed successively with dilute hydrochloric acid, water and absolute alcohol. It must be dried very carefully, by placing it at some distance above a hot asbestos plate, and then kept in a desiccator until it is weighed.

After the cadmium has been deposited upon such an amalgamated electrode, it must be washed and dried as before. After it has been weighed, the electrode is placed in quite concentrated hydrochloric acid, and, when the evolution of gas has stopped, washed and dried as above; it is then ready for use again. Thus a large number of analyses may be carried out with the same electrode after it has been once amalgamated.

Besides the above three distinctly different ways for determining cadmium electrolytically, quite a number of other methods have been proposed some of which do not give satisfactory results, and the others possess no advantages over those that have been given. Some of these methods are mentioned in the footnote.*

Indium.

At. Wt. = 114.8. Elec. Equiv. = 0.397 mg. for In^{+++} ions.

Rapid Deposition from Formic-acid Solution.

L. M. Dennis and W. C. Geer † have obtained excellent deposits of indium upon platinum and found the determination sufficiently accurate to use for determining the atomic weight of this element.

Yellow indium oxide is dissolved on the water bath in six times its weight of normal sulphuric acid, carefully avoiding an excess of acid. To the resulting solution, 25 cc. of formic acid (sp. gr. 1.2) are added, then 5 cc. of ammonia (sp. gr. 0.908) and the solution is diluted to 200 cc. The quantity of metal in the electrolyte may vary within wide limits (0.2 to 1.5 gms.) and likewise the current density (ND_{100} = 9 to 12 amperes). The results are equally good whether the indium is deposited upon a rotating crucible, upon a platinum dish, or upon a stationary platinum-

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* D. L. Wallace and E. F. Smith use an acetate solution and also a phosphate solution, Z. Elektrochem., **4**, 259 (1898); **5**, 167 (1898). Balachowsky adds acetic acid, urea, formaldehyde and acetaldehyde to the bath, Z. Elektrochem., **7**, 272 (1900). See also Separation of Cadmium from Silver.

† Ber., **37**, 961 (1904).

foil electrode. Apparently air has no effect upon the deposit. A. Thiel * found that after the indium was dissolved off the electrode, the platinum was attacked, as in the determination of zinc; but Dennis and Geer noticed the formation of platinum black only when too little formic acid was used in the electrolysis of indium chloride.

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* Ber., **37**, 176 (1904).

GROUP III.

The metals of this group, iron, nickel, and cobalt, are above hydrogen in the voltage series and do not show enough over voltage toward the evolution of hydrogen to permit their deposition from acid solution except in the form of amalgams or from solutions of weak organic acids which are susceptible to anodic oxidation. While the acid is oxidized at the anode, the acidity is decreased at the cathode if hydrogen ions are discharged.

Iron.

At. Wt. = 55.84. Elec. Equiv. = 0.29 mg. for Fe^{++} ions. Elec. Potential = + 0.340 volt. Overvoltage of H_2 = 0.08 volt from an alkaline solution.

Of the many methods proposed for the electrolytic determination of iron, the best is that of the deposition of the metal from a solution of the complex ammonium ferro-oxalate or of ammonium ferri-oxalate.* Some authors have raised the objection that the metal deposit will contain carbon but the daily experience of the author during the last 25 years has proved that, if the work is properly carried out, the iron deposit is entirely free from carbon and the results are quantitatively correct. S. Avery and Benton Dales† were the first to assert that an iron deposit obtained by the ammonium-oxalate method was contaminated with carbon. As a result of this assertion, H. Verwer and F. Groll,‡ in the author's laboratory subjected the method to the closest scrutiny and the results of their studies showed that the use of ammonium oxalate in the electrolysis of iron salts does not cause a simultaneous deposition of carbon, either as such or as carbide, and that the iron is deposited quantitatively.

By further investigation, however, Verwer § found that the deposit may contain carbon in case the electrolysis is prolonged

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* A. Classen and v. Reis., Ber., **14,** 1622 (1881).

† *Ibid.*, **32,** 64 (1899).

‡ *Ibid.*, **32,** 806 (1899).

§ Chem.-Ztg., **25,** 792 (1901).

beyond the time necessary for the complete removal of the iron. The author's directions, if strictly followed, will not give rise to this error. Verwer's experiments showed that the deposition of carbon was not due to the use of too high a voltage but rather to the formation of carbonate at the anode (*cf.* p. 51) and the subsequent reduction of $CO_3^=$ at the cathode. In this way free carbon is deposited upon the iron. This can be shown by the following experiment. If a number of deposits of iron are made and the current stopped each time before all the iron is removed from the solution, careful examination of the deposits will fail to reveal the presence of any carbon. If now an electrode with an iron deposit upon it is used as cathode in an ammonium-carbonate solution, or in an ammonium-oxalate solution from which all the iron has been removed by 12 hours electrolyzing, then the deposit will become strongly contaminated with carbon.

Other experimenters have also obtained good results with the method. Thus Schudl,* in using electrolytic iron for the standardization of a potassium-permanganate solution, found that the results obtained compared favorably with values obtained by other methods. A. Neuburger † obtained similar results.

If to the oxalate solution such substances as tartaric acid or citric acid (E. F. Smith) are added, then the iron deposit is more likely to contain carbon.

The solution in which the iron is to be determined may contain a ferrous or ferric salt. If a solution of a ferrous salt is treated with ammonium oxalate, there is produced a deep, yellowish-red precipitate of ferrous oxalate, soluble in an excess of the reagent to a yellowish-red solution of ammonium ferro-oxalate.

Ferric salts are not precipitated but if the yellow solution of ferric chloride is treated with sufficient ammonium oxalate, a solution of ammonium ferri-oxalate results which has a light green color. It is interesting to note that the complex ferrous oxalate forms a yellow solution and the complex ferric oxalate a green one, whereas the color of ferrous chloride is green and that of ferric chloride is yellow.

If the solution of ammonium ferri-oxalate is subjected to electrolysis, first of all the corresponding ferrous salt is formed by reduction and the latter eventually gives a deposit of iron on the

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* *Cf.* Treadwell-Hall, "Quantitative Analysis."

† Z. Elektrochem., **11**, 77 (1904).

cathode; thus the solution changes from yellow into red and finally becomes colorless. It is evident, too, that the electrolysis will take place more quickly on starting with the ferrous salt because otherwise some of the current is used up in accomplishing the preliminary reduction (*cf.* the rapid determination of iron, below).

The electrolysis of the ammonium double oxalates takes place smoothly without any intermediate formation of insoluble iron compounds. Only when nitrates are present are flocks of ferric hydroxide sometimes observed. Nitrates, therefore, must be removed before the electrolysis by evaporating with sulphuric acid. The greater part of the excess acid is expelled, and then, after diluting and boiling until all the sulphate has dissolved, the last traces of the free acid are removed by neutralization with ammonia. The ammonium sulphate thus formed has a favorable effect upon the analysis and increases the conductivity of the solution.

If the solution contains free hydrochloric acid it is best to remove it by evaporating on the water bath. Chlorides, however, do not exert a harmful effect.

Procedure. If the solution to be electrolyzed does not contain more than 1 gm. of iron,* from 6 to 8 gms. of ammonium oxalate are dissolved by heating with as little water as possible in a platinum dish, and, while constantly stirring, the iron solution is gradually added.† The solution is then diluted with water to a volume of 100 to 150 cc. and the platinum disk, which is to serve as anode, is immersed in the solution until it is just covered by the liquid. The temperature of the electrolyte does not matter much in this case and the analysis may be carried out at the laboratory temperature or at 65°. In the former case the current

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* Ferrous ammonium sulphate, $FeSO_4.(NH_4)_2SO_4.6\,H_2O$, may be used for practice. The salt is easily obtained pure and contains exactly one-seventh iron. The salt should be dissolved in water containing a few drops of sulphuric acid.

† It is not advisable to add the ammonium oxalate to the ferrous solution because ferrous oxalate will be precipitated and can be dissolved only by long heating with an excess of oxalate solution. If only ferric salts are present, there is no need of taking the above precaution as no precipitate forms.

Potassium oxalate cannot be used instead of ammonium oxalate, as it becomes partly changed to potassium carbonate during the electrolysis and forms a precipitate of basic ferrous carbonate.

density should be $ND_{100} = 1$ to 1.5 amperes and in the latter case, 0.5 to 1 ampere. The corresponding potential difference between the electrodes is from 4 to 2 volts.

After the solution has become perfectly colorless, a little of it is heated with a drop of nitric acid (to oxidize any iron to the ferric condition), an excess of hydrochloric acid is added and a liberal quantity of potassium thiocyanate solution.* If no red coloration is obtained by this test, the current is turned off, the solution at once poured out and the dish is washed several times with cold water and finally with alcohol. It is dried at 70° to 80° and weighed after cooling in a desiccator.

The iron deposit has a lustrous, steel-gray color, adheres firmly to the dish, either on a polished or roughened surface, and can be kept all day in the air without oxidation.

The conditions for the rapid electrolysis of an oxalate solution are given in the following table.

RAPID DEPOSITION OF IRON FROM OXALATE SOLUTION.†

	Experiments performed by	
	A. Fischer at Aachen.	Exner.
Electrode	Dish and rotating disk	Dish and rotating spiral
Electrolyte contained	7 to 7.5 gms. of ammonium oxalate and 1 cc. of a saturated solution of oxalic acid	
Volume	120 cc.	125 cc.
Quantity of metal	0.2 gm. as Mohr's salt	0.25 gm. as ferric alum
Temperature	85°	Hot
Potential	6 to 7 volts	7.4 to 7.5 volts
Current strength	7 amp.	7 amp.
Revolutions	600	800
Time	30 min.	25 to 35 min.

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* It is to be remembered that oxalates tend to prevent the above test for iron. The original oxalate content is, however, considerably reduced by the action of the current and the test will be obtained with traces of iron if an excess of hydrochloric acid and considerable potassium thiocyanate are used.

† General references to the literature on the rapid electrolytic determination of iron: Exner, J. Am. Chem. Soc., **25,** 896 (1903). A. Fischer, Chem.-Ztg., **31,** 25 (1907). E. F. Smith and Kollock, J. Am. Chem., Soc., **27,** 1255, 1527 (1905). Frary, Z. Elektrochem., **13,** 308 (1907); Z. angew. Chem., **20,** 1897 (1907).

According to the time required in the above experiments it would appear that it makes no difference whether the iron is originally present as ferrous or as ferric salt, whereas with stationary electrolytes more time is required with the latter. The iron deposits obtained by the rapid method are perfectly free from carbon if the current is not continued too long after all the iron is deposited. A. Fischer begins adding a little oxalic acid after the analysis has been in progress about 15 minutes and then adds 0.2 cc. every 3 minutes.

For rapid analysis by the aid of magnetic stirring, see page 78.

Nickel.

At. Wt. = 58.68. Elec. Equiv. = 0.304 mg. for Ni^{++} ions. Elec. Potential = + 0.228 volt. Overvoltage of H_2 = 0.03–0.21 volt.

Numerous methods have been proposed for the electrolytic determination of nickel, but here only the deposition from ammoniacal and from oxalate solutions will be discussed.

Deposition of Nickel from Ammoniacal Solution.

This method was first proposed and tested by W. Gibbs in 1864. H. Fresenius and Bergmann * determined the best conditions for carrying out the electrolysis and since that time the electrolytic determination of nickel has been regarded as one of the most satisfactory methods for determining this element. It is important that a large excess of ammonia be present; this condition, which has been recognized in practice for a long time, has been explained by Foerster † on the basis of the theory of electrolytic dissociation. In the ammoniacal solution of nickel sulphate, for example, the metal is present as complex nickel-ammonium sulphate, $[Ni(NH_3)_4]SO_4$, and this salt is dissociated primarily into $SO_4^{=}$ and the complex nickel-ammonia cation, $[Ni(NH_3)_4]^{++}$. Like all complex ions, the latter itself undergoes a slight dissociation and there is, therefore, the following state of equilibrium in the solution

$$Ni^{++} + 4\,NH_3 \rightleftarrows [Ni(NH_3)_4]^{++}.$$

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* Z. anal. Chem., **19**, 320 (1880).

† Z. angew. Chem., **19**, 1884, 1889 (1906).

Inasmuch as hydroxyl ions are present in an ammoniacal solution, there is a tendency for nickel hydroxide to precipitate in case the concentration of the Ni ions becomes sufficiently great at any time. The concentration of Ni ions, however, can be kept as low as one pleases by making the ammonia content high. Under these conditions the nickel ions are discharged at the cathode in a metallic condition, whereas, if insufficient ammonia is present, a dark-colored deposit containing oxide is obtained.

There is often a tendency for the deposit to scale off the cathode. This is avoided by the use of a platinum gauze cathode.

If a solution of nickel sulphate containing free sulphuric acid is to be analyzed, it is neutralized with ammonia, sp. gr. 0.9, and 24 cc. are added in excess; the clear, blue solution thus obtained is diluted to 100 cc. In the liquid, which should preferably contain not more than 0.1 gm. of nickel, from 4 to 5 g. of ammonium sulphate are dissolved to increase the conductivity, and the electrolysis is conducted with a current of 0.7 to 1.0 ampere with a gauze cathode. The deposition of the nickel is then accomplished in about 45 minutes. The solution is proved to be free from nickel by testing a portion of it with ammonium sulphide or with potassium thiocarbonate; with the former reagent a brown coloration is obtained and with the latter a pink one. The current is turned off and the electrode washed and dried in the usual manner. The deposit is bright and lustrous, hardly to be distinguished from the platinum.

Until recently the electrolysis of a nitrate solution has led to bad results; it was usual, therefore, to evaporate nitrate solutions with sulphuric acid before adding water and ammonia. A. Thiel * has shown, however, that it is possible to electrolyze a solution containing nitrate if certain precautions are taken. This fact is of importance in those cases where the separation of copper and nickel in a nitric-acid solution is involved as it enables one to avoid the time-consuming operation of evaporating with sulphuric acid.

Thiel first convinced himself that the poor deposits obtained with the use of solutions containing nitrate were due, as A. Windelschmidt † had previously recognized, less to the presence of nitrate than to the presence of nitrite. The nitrous acid is formed either in the solution of an alloy in nitric acid or during the progress of the electrolysis. After it was found that simply boil-

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* Z. Elektrochem., **14**, 201 (1908).

† Dissertation, Münster, 1907.

ing the acid solution sufficed to free it from nitrous acid, other difficulties were encountered due to the fact that under certain conditions the platinum anode is attacked by the ammoniacal solution. In such cases the weight of the nickel is found to be too high. Thiel succeeded in overcoming this difficulty by employing, instead of the spiral platinum anode, a straight wire of passive iron. An iron wire of 1.5 mm. diameter is cleaned with hydrochloric acid and made passive by dipping it for a short time in nitric acid (sp. gr. 1.4) and immediately washing it with water and with alcohol. The dull surface of the metal is unchanged for a long time on exposure to the atmosphere. A straight wire is better in this case than a spiral, because the ferric hydroxide, with which the wire gradually becomes coated during the electrolysis, is more likely to scale off from a spiral and this might lead to contamination of the deposit.

The analysis is carried out as follows: The nitric-acid solution of nickel is boiled to expel traces of nitrous acid and, after cooling, it is neutralized with ammonia. Enough more of the reagent is added so that in 200 cc. of electrolyte about 80 cc. of ammonia (sp. gr. 0.91) will be present. If insufficient ammonia is present, some oxide is deposited with the nickel. As cathode the cylinder of platinum gauze (Fig. 24, p. 60) is used and as anode the passive iron wire. The current density is $ND_{100} = 5$ amperes and the potential difference between the electrodes is 14 volts at the start. It is not necessary to heat the beaker with a flame and, in fact, this is not advisable on account of the large losses of ammonia that will then result by evaporation. Owing to the high current density used, the electrolyte becomes heated to about 70° and the potential of the bath sinks to about 10 volts.

The electrolysis is continued until the solution is absolutely colorless and there is a strong liberation of gas at the cathode; this takes place with 0.1 to 0.3 gm. of nickel at the end of 45 or 50 minutes. Then, without breaking the circuit, the cathode is gradually raised from the solution while washing it with a stream of water from a wash bottle. The electrode is dried in the usual way before weighing it. The anode is replaced by a fresh piece of passive iron wire, the cathode is again put in the solution and the electrolysis is continued for 5 minutes more. The cathode is washed, dried and weighed and if this weight is not the same as before the process is repeated again. Thiel found that the second weighing was usually a few tenths of a milligram lower than the first but that the third weighing was usually the same as the second. The last weight obtained was regarded as correct.

The deposited nickel is dull gray; duplicate analyses agree well.

This method of continuing the electrolysis until two consecutive weighings agree is recommended by Thiel because the test for nickel with ammonium sulphide is not reliable in a strongly ammoniacal solution.

The very sensitive reaction for nickel that depends upon the formation of nickelic hydroxide by the action of bromine and caustic alkali gives reliable results only in the absence of ammonium salts. A few cubic centimeters of the solution, therefore, may be evaporated to dryness on a large porcelain crucible cover, the ammonium salts expelled by gentle ignition and the residue barely moistened with aqua regia and dissolved in water. This solution is treated with caustic potash solution and bromine vapors are brought in contact with it. As little as 0.00004 gm. of nickel will at once give a black precipitate; one tenth as much nickel will be shown when the solution turns yellow owing to the absorption of bromine.

Chloride solutions also were regarded as unsuitable for the electrolytic determination of nickel in ammoniacal solution until F. Oettel * showed that satisfactory deposits could be obtained from them. Ammonium chloride is added to the electrolyte to increase its conductivity, about 10 gms. being used for 1 gm. of nickel; a larger quantity of the salt does no harm. The quantity of free ammonia present, sp. gr. 0.92, must reach at least 20 per cent by volume, as otherwise a black deposit of nickel oxide will be obtained upon the anode and some oxide will be present in the nickel on the cathode. With a current density of $ND_{100} = 0.4$ ampere, 1 gm. of nickel is usually deposited in 7 or 8 hours and as cathode the gauze electrode has proved most satisfactory. The end of the electrolysis is determined by one of the several tests that have been given.

A number of investigators have studied the rapid electrodeposition of nickel and some of the results obtained in ammoniacal solutions are given in the table on page 189.

Concerning the deposition with magnetic stirring, see page 78.

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* Z. Elektrochem., **1,** 194 (1894).

RAPID DEPOSITION OF NICKEL FROM AMMONIACAL SOLUTION.*

	Experiments performed by				
	Gooch and Medway.	Exner.	E. F. Smith.	E. F. Smith.	A. Fischer.
Electrode	Rotating crucible as cathode	Dish and rotating spiral	Dish and rotating spiral	Dish and rotating spiral	Dish and rotating disk
Electrolyte contained	20 cc. conc. NH_4OH and 1 gm. $(NH_4)_2SO_4$	1.5 gm. $(NH_4)_2SO_4$ and 20 to 25 cc. conc. NH_4OH	1.2 gm. $(NH_4)_2SO_4$ and 20 to 25 cc. conc. NH_4OH	1.2 gm. $(NH_4)_2SO_4$ and 3 gm. conc. NH_4OH	1.5 gm. $(NH_4)_2SO_4$ and 25 cc. conc. NH_4OH
Volume	45 cc.	125 cc.	125 cc.	125 cc.	125 cc.
Quantity of metal	0.1 to 0.17 gm. as nickel-ammonium sulphate	0.25 to 0.5 gm. as sulphate	0.25 to 0.5 gm. as sulphate	1 gm. as sulphate	0.18 gm. as sulphate
Temperature	Cold at the start	Hot at the start	Hot at the start	Hot at the start	75° to 80°
Potential of bath	8 volts	12 to 10 volts	5.5 volts	6.5 volts	10 volts
Current density ND_{100}	5 to 13 amperes	4 to 5 amperes	4 amperes	5.2 amperes	5 amperes
Revolutions	600 to 800	600 to 800	600 to 800	600 to 800	600 to 800
Time	30 to 25 minutes	15 to 17 minutes	15 to 20 minutes	25 minutes	20 minutes

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* General references on the rapid electrolysis of various nickel and cobalt solutions: Gooch and Medway, Am. J. Sci., [4], **15,** 320 (1903). Exner. J. Am. Chem. Soc., **25,** 896 (1903). A. Fischer and Boddaert, Z. Elektrochem., **10,** 945 (1904). E. F. Smith, J. Am. Chem. Soc., **26,** 1595 (1904). E. F. Smith and Kollock, *ibid.*, **27,** 1255 (1905). A. Fischer, Z. Elektrochem., **13,** 469 (1907).

Deposition of Nickel from Oxalate Solution.

Nickel, when deposited from a solution of the double oxalate, is always contaminated with carbon. Foerster regarded the formation of carbon compounds on the cathode as due, in this case, to the migration of colloidal substances to the cathode and supported this assumption by suggesting the possibility of oxalic acid being transformed into glycollic acid * with the accompanying formation of resin-like substances. The investigations of A. Mailhe,† Henseling ‡ and others indicate that the carbon deposition is more in the nature of a purely chemical reaction, in which the nickel probably acts as a catalyzer. To explain the phenomenon a number of experiments have been performed in the author's laboratory.

In most cases the analyst is not so much concerned in the determination of nickel in a solution of a pure nickel salt as in the determination and separation of nickel from other elements. A separation of nickel from chromium, aluminium and manganese is not accomplished electrolytically by the above-described ammonia method but is effected by the electrolysis of an oxalate solution. In such cases, other metals, such as copper, are deposited with the nickel so that it is necessary to redissolve the precipitate and free it from impurities including carbon. In the purified solution, the nickel may be determined by the ammonia method. For reasons such as this, the oxalate method of electrolyzing nickel solutions cannot well be discarded.

For carrying out the method the electrolyte is prepared in much the same way as in the determination of iron. About 25 cc. of the nickel solution (chloride or sulphate, but not the nitrate) are treated with 4 to 5 gms. of ammonium oxalate, which is dissolved by heating the liquid, and, after diluting to 100 to 120 cc., the electrolysis is carried out with a current of $ND_{100} = 1$ ampere. The deposition of 0.3 gm. nickel requires about 3 hours. The end of the reaction is determined and the treatment of the deposit before weighing is carried out as described on page 186.

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* Avery and Dales, Ber., **32,** 2237 (1899) obtained glycollic acid by the electrolysis of a nearly boiling oxalic-acid solution with a current of 10 amperes and 10 volts for 2.5 hours. These conditions are altogether different from those which prevail in the metal determination.

† Chem.-Ztg., **31,** 1083 (1907). ‡ Dissertation, Karlsruhe, 1906.

The following table gives some of the results obtained with stirred electrolytes.

RAPID DEPOSITION OF NICKEL FROM OXALATE SOLUTION.

	Experiments performed by A. Fischer and Boddaert in the laboratory at Aachen.	
Electrode	Dish and rotating disk	Dish and rotating disk
Electrolyte contained	15 gms. ammonium oxalate	80 cc. of a cold, saturated solution of ammonium oxalate
Volume	125 cc.	125 cc.
Quantity of metal	0.2 to 0.33 gm.	0.2 to 0.33 gm.
Temperature	60° to 95°	22° to 60°
Potential of the bath	6 to 5 volts	7 to 6.2 volts
Current strength	7.5 to 8 amp.	8 amp.
Revolutions	600 to 800	600 to 800
Time	50 min.	40 min.

With regard to the carbon content of the deposits obtained by the rapid method, what was said on page 190 holds true here also.

Cobalt.

At. Wt. = 58.97. Elec. Equiv. = 0.306 mg. for Co^{++} ions.
Elec. Potential = + 0.232 volt.

The methods given for the determination of nickel apply without any change for the determination of cobalt. In the oxalate method, the effect of this element is not so marked but there is still some deposition of carbon upon the cathode.

It is quite common to determine nickel and cobalt together by electrolysis and determine the nickel, however, independently as the salt of dimethyl glyoxime.

The electrolytic determination of cobalt, however, is likely to give results which are somewhat too high, probably on account of oxidation of the deposit, or too low, owing to formation of a little peroxide at the anode. Often the precipitated cobalt has a brown or black appearance. Bright deposits can be obtained by adding sodium hypophosphite to the bath, but the results are then too high because of the deposition of cobalt phosphide.

Perkin * states that the most satisfactory results are obtained when the electrolyte contains primary sodium phosphate and phosphoric acid.

Procedure.—To the neutral solution of the cobalt salt containing about 0.5 gm. of the metal in 80 cc. of water, add 2 cc. of a 5 per cent solution of phosphoric acid and 20–25 cc. of a 10 per cent solution of primary sodium phosphate (NaH_2PO_4) in water. Stir well while adding the sodium phosphate solution from a burette.

Start the electrolysis cold with a current of $ND_{100} = 0.2$ to 0.3 volt. After about an hour, increase the current to 0.8–1.2 ampere and heat the solution to 50 to 60°. If, in the meantime, a brown deposit of cobalt peroxide appears on the anode, bring it back into solution by adding about 0.1 gm. of hydroxylamine sulphate or chloride.

When, as a result of the removal of the cobalt, the bath has become colorless, add a few drops of dilute ammonium hydroxide to neutralize the mineral acid formed during the electrolysis. In this way the last traces of cobalt are precipitated.

To make sure that all the cobalt has been deposited test a little of the solution with ammonium hydroxide and sulphide. A still more sensitive test is the reaction with ammonium thiocyanate, amyl alcohol and ether (*cf.* Treadwell-Hall, Analytical Chemistry, Vol. I).

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* Electrochemical Analysis, 1905.

GROUP IV.

Metals which may be deposited on the cathode or may be obtained as oxide upon the anode.

Lead.

At. Wt. = 207.2. Elec. Equiv. = 1.073 for Pb^{++} ions. Elec. Potential = + 0.148 volt. Overvoltage of H_2 = 0.35–0.64 volt

Lead may be deposited as metal upon the cathode by electrolyzing solutions of the complex oxalate, the acetate, the hydroxide, dissolved in caustic alkali, or the phosphate dissolved in alkali hydroxide or in phosphoric acid, sp. gr. 1.7. Two difficulties are encountered: In many cases a little peroxide is likely to form on the anode and the deposited lead is very susceptible to slight oxidation. None of the many methods which have been proposed for the quantitative deposition of the metal upon the cathode is quite as satisfactory as the deposition of lead peroxide, PbO_2, upon the anode from a nitric acid solution. The acid concentration may be made so high that no copper will deposit upon the cathode or it may be regulated so that copper is deposited upon the cathode while lead peroxide is being formed on the anode.

Two explanations have been suggested to account for the formation of the lead peroxide, neither of which is entirely satisfactory. According to Liebenow, the bivalent lead ions are oxidized to negatively charged $PbO_2^{=}$ anions, which are discharged at the anode. Another explanation is that lead tetranitrate is formed by anodic oxidation and from this PbO_2 is formed by hydrolysis. It is not easy to determine whether the mechanism of the reaction is correctly explained by either of these assumptions. All we know is that the oxidation takes place at the anode and that the product is insoluble in nitric acid. Rather than attempting to assign hypothetical stages to this process, it seems simplest to express the reaction as follows:

$$Pb^{++} + 2H_2O + 2 \oplus \rightarrow \mathbf{PbO_2} + 4H^+.$$

To obtain a peroxide deposit adherent to the electrode and in a form suitable for weighing, Classen recommends the use of an anode with a dull, unpolished surface and uses either a platinum dish, the inside surface of which has been roughened by the sand blast, or a gauze electrode. In either case the precipitate has a relatively large surface upon which it can deposit.

The proper conditions for the deposition of lead vary according to the time desired to spend upon the analysis; if it is not a question of speed, the electrolysis may well be allowed to proceed overnight and at ordinary temperatures. If it is desired to hasten the process, the solution should be heated. The strength of the current and the amount of nitric acid are regulated accordingly.

If the analysis is to be made at room temperature, 10 per cent by volume * of nitric acid (sp. gr. 1.35 to 1.38) and a current density of $ND_{100}=0.05$ ampere are suitable. If the work is carried out at 60° to 65°, it is advisable to add 20 per cent by volume of the nitric acid and to use a current of $ND_{100}=1.5$ amperes.* In the latter case as much as 0.7 gm. of lead peroxide will be deposited in less than an hour; the precipitation of 1.5 gms. PbO_2 requires about 3 hours.

The lead peroxide is obtained in the form of a brownish-black coating upon the anode. A test is made to see if the analysis is finished by mixing about 20 cc. of water with the electrolyte and waiting 10 or 15 minutes to see if any fresh deposit is formed upon the newly exposed platinum surface. If the deposition is complete, the peroxide is washed, without interrupting the current, using nothing but water, and the anode is dried at a temperature of 220°.

As regards the exact chemical composition of the lead peroxide thus obtained, and especially as regards its water content and the proper temperature to be used in drying the deposit, conflicting statements have been made by different authors. Formerly, the lead peroxide was dried at 180°. Hollard and others have found, however, that the peroxide retains a little water when dried at this temperature, and even when dried at 220° it is not to be regarded as perfectly anhydrous. To compensate the error, Holland recommends that the weight of the lead in

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* This means 10 cc. of acid in 100 cc. of solution.

† For practice about 1 gm. of lead nitrate should be used.

the precipitate be computed by multiplying the weight of peroxide by the factor 0.853 instead of using the theoretical factor 0.8661.*

The experiments of A. Vossen in the Aachen laboratory confirm the fact that the lead peroxide is not perfectly anhydrous when dried for an hour at 220°. In determining small quantities of lead up to about 0.1 gm. PbO_2, the factor 0.8658, which is practically the theoretical value, gave correct results. For larger quantities of lead peroxide up to 0.3 gm., the factor 0. 865, and for quantities over 0.3 gm. the factor 0.8635, was found.

The oven drying at a high temperature and the use of an empirical factor may be avoided by cautiously heating the peroxide with the Bunsen flame, whereby it is changed into yellow PbO; from this the lead content can be found by multiplying by the theoretical factor, 0.9282.

The lead monoxide may be dissolved readily from the electrode, by means of dilute nitric acid. The lead peroxide is best dissolved from the platinum by placing the electrode in hot, dilute nitric acid and adding a little of reducing agent, such as oxalic acid, sugar or alcohol.

In the presence of phosphoric acid it is impossible to precipitate lead quantitatively as peroxide and when sufficient phosphoric acid is present, small quantities of lead may be deposited quantitatively as metal upon the cathode.†

The peroxide deposition is also incomplete in the presence of mercury, arsenic and selenium.

As will be shown in the part of this book which is devoted to the separation of the metals from one another, the determination of lead as peroxide serves to effect at the same time a separation of this element from other metals; it may be

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* Hollard uses the factor 0.853 for quantities of peroxide weighing less than 1 gm; this value is obtained as the mean of a great many experiments. For quantities of lead peroxide weighing between 1 gm. and 1.5 gms., Hollard found the factor 0.857 to give correct results. These factors refer to deposits dried at 200°. The high weight of the peroxide is not due to the presence of other oxides of lead. F. Lux found the theoretical content of PbO_2 by washing the deposit with water and then dissolving it in a mixture of dilute nitric acid and a known quantity of oxalic acid, finally titrating the excess of the latter with potassium-permanganate solution.

† A. L. Linn., J. Am. Chem. Soc., **24,** 435 (1902).

RAPID DEPOSITION OF LEAD PEROXIDE IN NITRIC-ACID SOLUTION.*

	Experiments performed by				
	Exner.	A. Fischer and Boddaert at Aachen.	R.O.Smith.	H.J.S.Sand.	A. Fischer at Aachen.
Electrode	Dish and rotating spiral	Dish and rotating disk	Dish and rotating spiral	Sand's electrodes	Dish and rotating disk
Electrolyte contained	20 cc. HNO_3 (sp. gr. 1.4)	....	25 cc. HNO_3 (sp. gr. 1.4)	15 cc. HNO_3 (sp. gr. 1.4)	20 cc. HNO_3 (sp. gr. 1.4)
Volume	125 cc.	125 cc.	125 cc.	85 cc.	125 cc.
Quantity of metal	0.26–1.1 gm. as nitrate	0.47 gm. as nitrate	0.06–0.58 gm. as nitrate	0.13–0.14 gm. as nitrate	0.29 gm. as nitrate
Temperature	Hot	95°	95°	60°	60° to 65°
Potential	4.5 volts	3.6 to 3.8 volts	3.6 to 3.8 volts	2.2 to 2.4 volts	1.9 to 2.2 volts
ND_{100}	10 amp.	10 to 11 amp.	10 to 11 amp.	....	....
Revolutions	600	800	800	800	800
Time in minutes	10 to 13	15	15	7 to 10	24

mentioned here, however, that in the presence of silver or bismuth the lead peroxide will be contaminated with a little of these metals. Chlorine, selenium, mercury, phosphorus and arsenic compounds must not be present in the solution analyzed. In the presence of very little manganese, the method gives satisfactory results, but it is then necessary to use a considerable excess of nitric acid (about 30 cc.) to carry out the analysis in a hot solution (70°), and to use a fairly strong current (up to 2 amperes) so that the deposition will take place quickly with but slight reduction of the nitric acid to ammonia.†

* General references concerning the rapid electrodeposition of lead and the separation of this metal in different solutions: Exner, J. Am. Chem. Soc., **25,** 896 (1903). A. Fischer and Boddaert, Z. Elektrochem, **10,** 945 (1904). R. O. Smith, Thesis, U. Pa., 1905. H. J. S. Sand, J. Chem. Soc., London, **91,** 373 (1907).

† B. Neumann, Chem.-Ztg., **20,** 381 (1896).

The fact that lead cannot be deposited as metal from a solution distinctly acid with nitric acid can be explained readily. To prevent deposition of lead as metal on the cathode, the potential of the cathode must be kept constantly below the discharge potential of lead ions. This is accomplished by providing ions which are more readily discharged than are the lead ions. In acid solutions, the hydrogen ions from nitric acid fulfil this requirement and their discharge is easier if the concentration of the acid is fairly high; hence the addition of an excess of nitric acid.* Luckow and others have discovered that the lead-peroxide deposit is particularly good when copper ions are present in the solution and this is explained by the fact that copper ions are discharged even more easily than hydrogen ions. Thus, some authorities recommend the addition of a little copper nitrate to the solution of lead nitrate.

Concerning the determination of lead in lead sulphate, consult page 231.

Manganese.

At. Wt. = 54.93. Elec. Equiv. = 0.285 mg. for Mn^{++} ions. Elec. Potential = + 1.075 volt.

It is practically out of the question to attempt to deposit manganese as metal upon the cathode, except perhaps in the form of an amalgam. It is more difficult to obtain satisfactory deposits of manganese dioxide upon the anode than in the case of lead. With lead, for example, a large excess of nitric acid can be employed, but with manganese the oxidation is likely to go too far, when much nitric acid is present, and a soluble permanganate results. Many methods have been proposed, but very few have given entire satisfaction. Moreover, the chief problem in the analytical chemistry of manganese is the separation of this element from others and the electrolytic method is suitable for such separations only in special cases.

Manganese sulphate and manganese nitrate are suitable for the electrolysis but manganese chloride is not. The solution, containing 0.2 to 0.25 gm. of manganese, is treated with 1.5 to 2 gms. of chrome alum and 10 gms. of sodium acetate, diluted to about 125 cc. and electrolyzed at 80° in a dish with sand-blasted inner

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* Concerning the decomposition of nitric acid itself, see p. 118.

surface using a current density of $ND_{100} = 0.6$ to 1 ampere and voltage of 2.8 to 4 volts; in this case, the dish serves as anode. The electrolysis requires about an hour and a quarter. After an hour or so has elapsed, some water is added to raise the surface of the liquid and it is noted whether any further deposit is formed (*cf.* p. 194).

A safer way is to test a portion of the solution with lead peroxide (free from manganese!) and nitric acid; a mere trace of manganese will show the permanganate color.

After breaking the circuit, the liquid is poured out of the dish, the deposit is washed repeatedly with water, and is changed finally into mangano-manganic oxide, Mn_3O_4, by ignition over the blast lamp. When the transformation is complete the platinum will be covered with a uniform reddish-brown deposit. After igniting and cooling it is well to rinse again with hot water, in order to remove traces of impurity deposited with the manganese dioxide by the current. After this final washing, the dish is ignited again and cooled in a desiccator.

In this determination the use of a platinum dish as anode is necessary because it will not do to ignite a platinum gauze electrode in the flame of the blast lamp; changes are likely to result in the composition of the oxide and losses due to the formation of fine powder. Engel found that after the ignition of his platinum dishes the weight was diminished about one milligram. He concluded that the loss took place during the electrolysis and not during the solution of the deposit (in sulphuric acid and hydrogen peroxide). Judging from the experience of other chemists, however, it seems probable that the loss was due to volatilization of some constituent of the dish during the heating over the blast lamp; it is a common experience to find a platinum crucible that will steadily lose weight on being heated over the blast lamp while another crucible under similar treatment does not show such loss. In the case of the electrolytic determination of manganese, therefore, the weight of the platinum dish should be determined after the deposit has been removed, rather than before starting the electrolysis. J. Köster * recommends the use of platinum-iridium ware; which does not experience more than 0.2 mgm. loss by heating over the blast lamp.

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* Z. Elektrochem., **10,** 553 (1904).

As regards the original deposit upon the anode, numerous experiments have shown beyond doubt that manganese dioxide is never deposited entirely as such. According to the conditions of the experiment, the black deposit contains varying quantities of water as well as of oxygen and must be regarded as consisting of a mixture of manganese dioxide and lower oxides in a hydrated condition; the only way to obtain a constant weight is to convert it into an oxide of more constant composition by igniting it.

Although the composition of the deposit is not of prime importance, the nature of the deposit is, nevertheless, of considerable moment; it must adhere so firmly to the platinum that it is not loosened during the washing and it must not be so brittle that it will scale off during the igniting. These necessary properties are obtained in Engel's method by the addition of chrome alum to the electrolyte containing the manganous salt and sodium acetate. The favorable effect of chrome alum upon the nature of the manganese deposit, is explained by Engel * as follows:

If one has in mind the disturbing effect that the evolution of hydrogen has upon the nature of the cathode deposit (*cf.* p. 80), it seems reasonable that the anode deposit would be loosened in a similar manner by evolution of oxygen. The favorable effect of the chromic salt, therefore, may be due to the fact that it is oxidized at the anode and thus prevents the evolution of oxygen gas. As a matter of fact, chromate is formed during the electrolysis, but, on the other hand, the fact that a deposit, which scales off, is formed in the absence of chrome alum, when the electrolysis is carried out at a potential below the decomposition-potential of water, is contrary to such an assumption. The mechanical effect of free oxygen, therefore, cannot be the cause of the bad adherence of the manganese peroxide to the anode. It appears more likely that a moderate evolution of oxygen is necessary to give the deposit a porous, pulverulent nature in virtue of which it will adhere so firmly to the anode that it will not be detached during the washing and will not spring away from the platinum during the ignition. In fact Engel assumes that the oxygen exerts a chemical effect. He believes that the desirable properties of the manganese-oxide deposit are due to the admixture of the

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* Z. Elektrochem., **2**, 413 (1895); **3**, 286, 305 (1896).

brittle peroxide with a pulverulent oxide. The mass thus formed is of such a nature that it will not scale off during the heating and has the property of adhering firmly to the platinum.

The part played by the oxygen, which Engel regards as a reducing effect (just as hydrogen peroxide may cause a reduction), is to reduce a part of the peroxide, deposited by the strong current, to oxide while the chrome alum takes care of any excess of oxygen and thus prevents it from exerting a harmful effect upon the nature of the anode deposit. If, however, the current strength is not sufficient to form the necessary oxygen to act upon the manganese peroxide, then the chromic salt itself serves to reduce a part of the peroxide and supports the action of the oxygen. Thus the chrome alum plays the part of a regulator: if the evolution of oxygen is too strong, it unites with a part of the oxygen to form chromate, and if the oxygen evolution is not strong enough, it serves to reduce a part of the peroxide. This reduction takes place as experiments have shown, in a solution containing ammonium acetate, chrome alum and manganese peroxide, only when the temperature reaches 80°; hence the necessity of heating the electrolyte to this temperature.

RAPID DEPOSITION OF MANGANESE PEROXIDE IN ACETATE SOLUTION.*

	Experiments performed by J. Köster at Aachen.
Electrode	Dish and rotating disk
Electrolyte contained	10 gms. of ammonium acetate 2 to 3 gms. of chrome alum 10 cc. of alcohol
Volume	110 to 130 cc.
Quantity of metal	0.3 gm. as manganous ammonium sulphate
Temperature	75° to 80°
Potential of the bath	7 volts
Current strength	4 to 4.5 amperes
Revolutions	600 to 700
Time	20 to 25 minutes

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* References on the rapid electrolytic estimation of manganese. Exner, J. Am. Chem. Soc., **25**, 896 (1903). Köster, Z. Elektrochem., **10**, 553 (1904).

The assumption by Engel of the reducing effect of the oxygen is not absolutely necessary, for the reducing action of the chrome alum is of itself sufficient to account for the same effect.

Köster, in the author's laboratory, has worked out the conditions for the rapid deposition of manganese peroxide.

Deposition of Manganese from Formic-acid Solution.

G. P. Scholl,* in studying the behavior of manganese salts in the presence of formate and free formic acid, found that the best results were obtained when formic acid alone was added. Since formic acid is a poor conductor of the current, it is necessary to use a current of unusually high voltage in order to get the requisite current strength. The difficulty is less serious, however, if a sieve electrode is used instead of the disk or spiral. The electrode used by Scholl had the same shape as the platinum dish which is used as anode but it is a little smaller. It is perforated like a sieve and has about 60 sq. cm. of surface (Fig. 22, p. 57). The solution, containing 0.1 to 0.2 gm. of manganese as sulphate, is treated with 5 cc. of formic acid (sp. gr. 1.09) and electrolyzed at the laboratory temperature with a current density of $ND_{100} =$ 0.8 to 1.0 ampere and at a final potential of about 7 volts; the time required is from 3 to 5 hours. Deposits yielding as much as 0.288 gm. of Mn_3O_4 after ignition are found to adhere well to the electrode. This is not possible by the acetate method (p. 166). Scholl noticed no decrease in the weight of the platinum dish.

Uranium.

At. Wt. = 238.2. Elec. Equiv. = 1.235 mg. for UO_2^{++} ions.

Uranium is deposited upon the cathode in the form of oxide from solutions of the acetate, sulphate or nitrate. The deposit is yellow at first and consists of uranyl hydroxide, but during the progress of the electrolysis it assumes a darker hue. When the solution has become colorless, a little of it is tested with potassium ferrocyanide or with ammonium sulphide.

The current is turned off, the deposit is washed first with water containing some acetic acid, then with hot water, and the oxide is converted by ignition into urano-uranic oxide, U_3O_8. If, during

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* J. Am. Chem. Soc., **25**, 1045 (1903).

the washing, a little of the deposit is washed off the dish, it may be collected upon a washed filter, placed in the dish and ignited.

L. Kollock and E. F. Smith * recommend the following conditions: To the solution containing 0.1 to 0.23 gm. of U_3O_8 in the form of uranyl acetate, 0.2 cc. of 29 per cent acetic acid is added, and after diluting to 125 cc. the solution is heated to 70° and electrolyzed. The current density may lie between $ND_{100} = 0.28$ and 0.065 ampere and the corresponding potential is 16.25 to 4.25 volts. The duration of the analysis is between 5 and 6 hours in either case.

A uranyl-nitrate solution containing 0.12 gm. of U_3O_8 in 125 cc. was electrolyzed at 75° with a current density of $ND_{100} = 0.019$ to 0.038 ampere at 2.25 to 4.6 volts; the electrolysis required between 5.5 and 7.75 hours.

For uranyl-sulphate solutions, containing 0.13 to 0.14 gm. of U_3O_8 in 125 cc., the conditions recommended are: 75°, $ND_{100} =$ 0.019 to 0.038 ampere, 2 to 2.25 volts, 5 to 7 hours.

Inasmuch as the separation of uranium from certain other metals offers considerable difficulty by other methods of analysis, the electrolytic method often proves serviceable.

Thallium.

At. Wt. = 204.0. Elec. Equiv. = 1.056 mg. for Tl^{++} ions.

The metal thallium resembles lead closely in its chemical behavior and like the latter can be deposited as metal upon the cathode; on coming in contact with the air, however, it is oxidized so rapidly that the deposit cannot be weighed accurately. G. Neumann,† while working at Aachen, devised an indirect method for determining thallium; an ammonium oxalate solution of the metal was electrolyzed out of contact with the air and the volume of hydrogen set free on dissolving the deposit in hydrochloric acid was determined.

Determination of Thallium as Oxide.

The conditions under which thallium may be deposited as Tl_2O_3 upon the anode were established by J. E. Heiberg.‡ From 0.2 to 1.0 gm. of thallous sulphate (a compound into which it is

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* J. Am. Chem. Soc., **23,** 607 (1901).

† Ber., **21,** 356 (1888).

‡ Z. anorg. Chem., **35,** 347 (1903).

easy to convert other thallous as well as thallic compounds) is dissolved in 80 to 100 cc. of water in a roughened platinum dish. The solution, after being treated with 3 to 6 cc. of normal sulphuric acid and 5 to 10 cc. of acetone, is electrolyzed at a potential of 1.7 to 2.3 volts, using the dish as anode. Toward the end of the electrolysis, the potential may be raised to 2.5 volts, provided there is not a strong evolution of oxygen, which would tend to loosen the deposit. The current strength in the poorly conducting solution is only 0.02 to 0.05 ampere. The temperature must lie between 50° and 55° and the water lost by evaporation must be replaced.

Potassium iodide precipitates pale yellow thallous iodide from very dilute thallium solutions and the precipitate is very insoluble in an excess of potassium-iodide solution. When, therefore, 0.5 cc. of the solution does not give more than a trace of opalescence on being treated with 5 cc. of 10 per cent potassium-iodide solution, the electrolysis may be regarded as finished. The dish is then emptied quickly, rinsed successively with water, alcohol and ether, and dried for 20 minutes at 160° to 165°. The brown coating consists of thallium sesquioxide, Tl_2O_3. From 7 to 10 hours are required for the deposition of 0.5 gm. of this oxide, corrresponding to 0.55 gm. of sulphate.

The conductivity of the solution can be increased by adding to the bath one or two grams of alkali sulphate but the deposit must be thoroughly washed or the results will be too high.

The prescribed acidity suffices to prevent the precipitation of hydroxide during the electrolysis but it is not sufficient to prevent any deposition of metallic thallium upon the cathode. This does no harm, however, as the deposit redissolves during the progress of the electrolysis and it is better to work with the above-mentioned quantity of acid rather than to attempt to prevent any deposition of metal by increasing the acidity, because in the latter case the deposition of oxide on the anode is likely to be incomplete.

It would be possible to prevent deposition of metallic thallium by keeping the voltage of the current below the decomposition potential of thallium, but this would result in making the current so weak that it would take too long to carry out the determination.

The acetone exerts a favorable effect upon the physical nature of the deposit but it is not yet quite clear why it does. Since the acetone is gradually decomposed by the action of the electric current, it is necessary to add enough at the start so that some of it will remain to the end of the process. The author has found that 10 cc. of acetone are sufficient for an experiment lasting 17 hours.

The evolution of oxygen caused by too high an electromotive force is also noticed when the electrolysis is carried out at high temperatures but the temperature most favorable for the determination has been found to lie between 50° and 55°. At this temperature there is considerable evaporation during the electrolysis and there is danger of the upper parts of the deposit becoming so dry that upon the addition of water the thin layer of oxide will be loosened from the platinum. To prevent this, it is advisable to allow water to constantly drop into the solution instead of adding it in larger quantities intermittently. Under the conditions given above, a beautiful brown coating of oxide which adheres well to the platinum is obtained.

In drying the deposit, care should be taken not to let it come in contact with a free flame, as this may introduce a positive error in the weight obtained (due to SO_3, etc.).

Thallium oxide, not being a peroxide, dissolves in hydrochloric acid without evolution of chlorine, and thus this acid may be used for dissolving the deposit from the platinum.

The deposition of thallium oxide will undoubtedly be hastened by stirring the electrolyte and using a stronger current.

Chromium.

At. Wt. = 52.0. Elec. Equiv. = 0.18 mg. for Cr^{+++} ions.

Electrolysis may serve in two ways for the quantitative determination of chromium: chromic ions may be converted into chromate ions by oxidation at the anode, after which it is necessary to determine the latter by one of the usual methods of quantitative analysis; or, the chromium may be converted into mercury amalgam by using a mercury cathode. Both methods are of value only in effecting certain separations.

Oxidation of Chromic Salt to Chromate.

Ammonium-chromium oxalate is converted into ammonium chromate by the action of the electric current. The method will be explained more fully in Part III of this book.

The oxidation may be accelerated by maintaining the following conditions.

RAPID OXIDATION OF CHROMIC SALT TO CHROMATE.*

	Experiments performed by A. Fischer at Aachen.
Electrode	Dish and rotating disk
Electrolyte contained	15 gms. of ammonium oxalate
Volume	120 cc.
Quantity of metal	0.14 gm. as chloride or sulphate
Temperature	80°
Potential	5 to 7 volts
Current strength	5.8 to 5.4 amperes
Revolutions	600 per minute
Time	90 minutes

Determination of Chromium as Chrome Amalgam.

R. E. Myers † used as electrolyzing vessel the beaker (Fig. 49) first proposed by E. F. Smith.‡ It is about 8.5 cm. tall and 3.5 cm. in diameter with a platinum wire fused into the bottom, or into the walls near the bottom. This wire is covered on the inside of the beaker with a layer of mercury, and is bent under the bottom of the beaker in such a way that when it is placed upon a copper disk, which is connected with the negative pole of a source of electricity, the mercury will serve as cathode. A strip of platinum foil, or a platinum wire wound into a spiral, may be used as anode.

About 70 gms. of mercury are placed in the beaker and the total weight of glass and mercury is determined. To make sure that the weighing takes place under precisely the same conditions as at the end of the experiment, it is washed successively with water, alcohol and ether in the same way that the amalgam is to be washed. This is done by filling the dish about one third full of water, and whirling it round with the beaker inclined so that all of the walls are rinsed. The same operation is repeated with alcohol and finally with ether. After the odor of ether has disappeared, the outside of the beaker is wiped with a cloth, and,

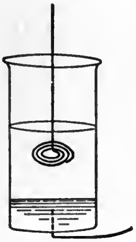

FIG. 49.

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* General references to the literature on the rapid electrolytic deposition of chromium in different solutions: E. F. Smith and Kollock, J. Am. Chem. Soc., **27**, 1255 (1904). A. Fischer, Chem.-Ztg., **31**, 25 (1907).

† J. Am. Chem. Soc., **26**, 1124 (1904). ‡ *Ibid.*, **25**, 887 (1903).

after standing fifteen minutes in a desiccator, the beaker and its contents are weighed.

The solution of chromic sulphate containing 0.1 to 0.2 gm. of chromium is poured into the weighed beaker and, after acidifying with 3 or 4 drops of concentrated sulphuric acid, it is electrolyzed with an initial potential of 7 to 7.5 volts, corresponding to a current of 0.3 to 0.4 ampere. On account of the increase of acid in the bath as a result of the electrolysis, the potential falls gradually to 5.5 or 6 volts and the current increases to 0.55 or 0.7 ampere. The electrolysis requires about 14 hours and can be carried out conveniently overnight.

The end of the process can be determined by making a little of the solution alkaline with caustic potash, adding hydrogen peroxide and acidifying with sulphuric acid. If a trace of chromium is present, the blue color of perchromic acid is obtained.

At the end, the mercury is washed with water without breaking the circuit until the pointer of the ammeter points nearly to the zero mark. The washing is finished in the way described on the previous page except that each liquid is added several times.

Chrome-amalgam is decomposed by water, setting free black, pulverulent chromium; for this reason the washing must be done as quickly as possible. The decomposition of the amalgam takes place more readily in proportion to the quantity of chromium in it and for this reason it is not advisable to deposit more than 0.2 gm. of chromium with 70 gms. of mercury. Such a quantity of mercury should therefore be used for but a single analysis

Molybdenum.

At. Wt. = 96.0. Elec. Equiv. = 0.166 mg. for hexavalent Mo.

Molybdenum belongs to the class of metals which, up to the present time, have only been obtained as oxide upon the cathode.*

According to L. G. Kollock and E. F. Smith,† the molybdenum in sodium molybdate, a salt into which it is easy to convert molybdenum (*cf.* p. 208), may be determined in the following manner:

The aqueous solution of the salt, containing 0.13 to 0.26 gm. of MoO_3, is acidified with 0.1 to 0.2 cc. of concentrated sulphuric

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*R. E. Myers used a mercury cathode and determined the molybdenum as amalgam, J. Am. Chem. Soc., **26**, 1124 (1904).

† J. Am. Chem. Soc., **23**, 669 (1901).

acid, diluted to 125 cc., heated to about 75° and electrolyzed with a current of $ND_{100} = 0.02$ to 0.04 ampere at about 2 volts potential. The solution assumes a deep blue color which gradually disappears.

The electrolysis requires from 2.5 to 7 hours, according to the quantity of molybdenum present, and the black, lustrous, firmly adherent coating upon the cathode consists of hydrated molybdenum sesquioxide, $Mo_2O_3.x\,H_2O$. The precipitation is complete when a little of the solution, after the addition of hydrochloric acid, ammonium thiocyanate and a little zinc, no longer shows the red color of molybdenum thiocyanate.* The deposited oxide is washed without breaking the circuit.

The black hydrated sesquioxide cannot be dried to constant weight. The moist deposit, therefore, is dissolved in dilute nitric acid, the solution evaporated to dryness and heated on an iron plate until the nitric acid is all expelled. If the residue should be colored blue by reduction, it is heated again with nitric acid. The residual white molybdic acid H_2MoO_4 is weighed.

A. Chilesotti and A. Rozzi † have found that the molybdenum precipitate obtained in this way may contain alkali and that the alkali content is made larger on increasing the quantity of alkali present in the solution and is lessened by increasing the quantity of free sulphuric acid. If the content of alkali salt (*e.g.*, K_2SO_4) does not exceed 0.75 per cent, then the error may be compensated by the addition of 0.4 to 0.5 per cent of free sulphuric acid to the electrolyte. With higher alkali content, as obtained by the fusion of a molybdenum ore with sodium carbonate (*cf.* p. 208), it is necessary, these authors claim, to dissolve the deposited oxide, after washing it in the usual way, in nitric acid and, after removing the excess of the latter by evaporation, to dissolve the residual molybdic acid in ammonia. The resulting solution is treated with enough sulphuric acid so that finally 0.4 to 0.5 per cent of free acid is present, and this solution is again electrolyzed. The deposition of the molybdenum from the ammonium-molybdate solution is quantitative if the free sulphuric-acid content lies between 0.5 and 0.05 per cent.

The method is suitable for the separation of molybdenum from the alkalies.

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* The color disappears upon the addition of phosphoric acid (difference from iron).

† Z. Elektrochem., **11,** 879 (1905).

Exner obtained a rapid electrolytic determination of molybdenum under the following conditions.

RAPID ELECTROLYTIC DEPOSITION OF MOLYBDENUM SESQUIOXIDE.

	Experiment performed by F. Exner.
Electrode	Dish and rotating spiral
Electrolyte contained	2 cc. H_2SO_4 (1 : 10) and 1 gm. K_2SO_4
Volume	120 cc.
Quantity of metal	0.23 gm. as MoO_3
Temperature	Hot
Potential	16 volts
Current strength	5 amp.
Revolutions	300 to 400
Time	20 min.

Analysis of Molybdenite.

To determine electrolytically the quantity of molybdenum present in the mineral molybdenite, 0.14 to 0.28 of the fine powder is fused with a mixture of sodium carbonate and sodium nitrate, the melt is extracted with water and filtered. The resulting aqueous solution is acidified with acetic acid, the carbon dioxide is all expelled by boiling, and, after diluting to 125 cc., the acetic-acid solution is electrolyzed at 85° with a current of $ND_{100} = 0.07$ at 4.4 volts. The electrolysis requires longer in an acetic-acid solution than in one of sulphuric acid.

After the solution has been freed from molybdenum, the sulphuric acid is determined by precipitation with barium chloride.

If it is not desired to determine the sulphur as well as the molybdenum, it is better to acidify the aqueous extract of the melt with sulphuric acid rather than with acetic acid.

Vanadium.

P. Truchot* has proposed a method for the electrolytic determination of vanadium whereby this element is obtained as hydrated oxide upon the electrode. The method succeeds only when the quantity of vanadium present is not more than 0.25 gm. per liter.

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* Annal. chim. anal. appl., **7**, 165.

GROUP V.

This group includes the most positive metals of the voltage series which cannot be deposited, even from alkaline solutions, except in the form of amalgams. With the exception of aluminium and beryllium, all the elements of this group are the so-called alkaline-earths and alkalies. In connection with this group the determination of various anions will also be discussed.

Aluminium.

If a solution of aluminium-ammonium oxalate, containing ammonium oxalate in excess, is submitted to the action of the electric current, the ammonium oxalate is changed into carbonate and the aluminium separates as hydroxide. When the oxalate is decomposed, the solution is heated until there is only a faint odor of ammonia, the hydroxide filtered off, washed with water and converted by ignition into Al_2O_3.

This behavior of aluminium is utilized only in the case of certain separations.

Barium, Strontium, Calcium.

These metals can be deposited electrolytically from their aqueous solutions only in the form of amalgams. Inasmuch as the amalgams of the light metals are much more readily decomposed by water than are the amalgams of the heavy metals (*cf.* p. 206) they cannot be determined quantitatively by weighing such amalgams. A. Coehn and W. Kettembeil * have attempted to use the amalgam method as a basis for separating the three alkaline earth metals from one another and have found that it is possible to effect such a separation because the voltages at which the individual amalgams are formed lie far enough from one another to enable one metal to be deposited completely before the next begins to deposit. Thus the potential difference between barium and strontium amounts to 0.2 volt, between strontium and calcium to 0.25 volt and between barium and calcium to 0.45 volt. The determination of the metal after it has been deposited in the mer-

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* Z. anorg. Chem., **38**, 198 (1903).

cury is effected by titrating the hydroxide which is formed by the action of water upon the amalgam. For more complete details, see the chapter on The Separation of the Alkali and Alkaline Earth Metals from Magnesium and from the Heavy Metals, page 218.

Determination of the Halogens.

The method originated by Vortmann * depends upon the principle that the halogens are set free from solutions of halogen salts by the electric current, and while in the nascent state combine with a silver anode to form insoluble silver halide. The increase in weight of the anode gives directly the quantity of halogen which has separated. The completion of the analysis is determined by applying one of the usual tests for halogen or by replacing the anode with the silver halide upon it by a second weighed silver anode and seeing whether there is any change in weight with the fresh electrode.

In Vortmann's method the following apparatus is used for the determination of iodine. The anode is a disk of pure silver having the shape of a 6-cm. watch glass; a stout platinum wire is fastened to the center. The cathode consists of a copper disk, 5 cm. in diameter; it is likewise fastened to a platinum wire and has a radial section cut out of it to give space for the wire of the silver anode, which is placed below the cathode. It is advisable to insulate the wire of the copper cathode by means of rubber tubing, or by sealing it in glass tubing. As electrolyzing vessel, a crystallizing dish of 100 to 150 cc. capacity may be used; during the electrolysis the dish is covered by a watch glass which has been cut into two equal pieces.

Enough of the iodide to correspond to about 0.1 to 0.25 gm. of iodine is dissolved in water, 6 (or 10) cc. of a 10-per-cent caustic-soda solution is added and the alkaline electrolyte is diluted to 100 (or 150) cc. The silver anode is placed about 0.5 cm. from the bottom of the dish and the copper cathode about 2 cm. above the anode. The potential of the current should lie between 1.94 and 2 volts and its strength should be from 0.03 to 0.07 ampere. The electrolyte is not heated. As soon as the yellow silver iodide assumes a brownish-violet tint in places, the solution is tested by

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* Monatsh. Chem., **15**, 280 (1894); **16**, 674 (1895).

taking a few drops, acidifying with sulphuric acid, and adding potassium nitrite; an iodide will give free iodine in this test and the color is intensified by shaking with carbon disulphide.

When the electrolysis is finished, the current must be stopped at once if sulphate, nitrate, acetate or tartrate is present, as otherwise traces of silver will be dissolved from the anode and carried to the cathode. The silver iodide is washed with water, dried for 15 to 30 minutes at 100° to 110° and then ignited. For this purpose the anode is placed in an iron dish and suspended about 0.5 cm. from the bottom. The dish is covered with the two halves of a watch glass and heated until the silver iodide has assumed a bright red color, or until it begins to melt. As a rule, black specks of silver peroxide are noticed on the silver iodide layer and these result at places where gas bubbles prevented the formation of silver iodide during the electrolysis. If this is the case, the heating is continued only until the black points have become white. The electrode is then cooled in a desiccator and weighed. A silver anode of 6 cm. diameter can take up as much as 0.5 gm. of iodine.

If less than 0.02 gm. of iodine is to be determined by this method, the solution of the iodide is treated before the electrolysis with only 3 cc. of caustic soda and with 2 or 3 gms. of Rochelle salt. The purpose of the latter is to prevent the liquid from becoming turbid by some of the silver-iodide deposit being loosened from the anode.

To regenerate the silver anode after the analysis is finished, it is placed as cathode in a platinum dish containing dilute caustic-soda solution and the dilute alkali is electrolyzed with a current of 2 volts. A light layer of spongy silver is formed upon the disk and is easily rubbed off (*cf.* p. 214).

Separation of the Halogens by Electro-Analysis.

By using the silver anodes recommended by Vortmann, and by taking advantage of the principle of electrolytic separation by the gradation of the electromotive force, H. Specketer * was the first to succeed in separating iodine, bromine, and chlorine from one another and in determining the first two of these elements upon the silver anode. Specketer ascertained, first of all, the decomposition potentials for potassium iodide, potassium bromide and potassium

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* Z. anorg. Chem., **21**, 273 (1899).

chloride in a normal solution of sulphuric acid and found that if, during the electrolysis of a mixture of the three halogen salts, the potential was not allowed to rise above 0.13 volt, the iodine was deposited with sufficient accuracy upon the silver anode without any admixture of bromine or chlorine.

To separate the bromine from chlorine, a potential of 0.35 volt must be employed; if this voltage is not exceeded, the bromine deposits upon the silver anode free from chlorine.

The electrolytic determination of chlorine in this way offers considerable difficulty and the method certainly has no advantage over the volumetric method for determining chlorine.

The principal conditions, then, for carrying out a satisfactory separation of the halogens are, first, to maintain a definite degree of acidity in the electrolyte; second, a constant potential of the bath; and third, to keep the solution out of contact with oxygen. This last requirement, the necessity for which is explained a little later on, is satisfied by passing hydrogen gas through the solution.

Apparatus. The source of current used by Specketer was a Gülcher thermopile which was short circuited with a resistance wire bearing a sliding contact (*cf.* p. 132). If storage cells are used, this wire is connected across the binding posts *AB*, at which the current is usually taken for the electrolysis. The current is now taken from two points *A* and *b* between which the voltmeter *V* shows the desired potential difference. A sensitive ammeter, *Amp.*, is used for measuring the strength of the current.

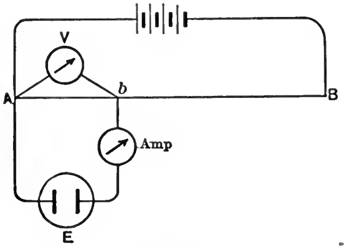

FIG. 50.

As electrolyzing vessel a narrow cylinder is used which is tall enough to prevent losses by spattering when hydrogen is passed through the solution. The hydrogen is taken from a Kipp generator and enters the solution near the bottom of the cylinder, through a glass tube drawn out to a capillary at the end. The top of the cylinder contains a cork stopper with perforations through which the gas delivery tube passes, as well as the electrode wires; the cork fits loosely in the cylinder to permit the escape of hydrogen gas. As cathode, platinum foil is used, and as anode a piece of gauze made from thin silver wire. It is necessary to use *pure* silver because impurities, such as copper, will be dissolved during the electrolysis and pass to the anode.

Separation of Iodine from Bromine and Chlorine.

The halogen salts are dissolved in 100 cc. of normal sulphuric acid and electrolyzed, while passing hydrogen through the cell, at a potential of 0.13 volt, until there is no further evolution of hydrogen at the cathode and the ammeter no longer shows any deflection. If a sensitive ammeter is not at hand, the end of the electrolysis is determined by testing for iodine by means of bromine water and starch. Toward the end of the process it is necessary to wash down the sides of the cylinder.

When all the iodine has been deposited, the current is turned off, the anode rinsed in the usual way and dried at 120°. If, besides the iodine, only one other halogen is present, it is simplest to determine the bromine or chlorine by titration. If, however, both bromine and chlorine are present, the bromine is also deposited by the current.

Separation of Bromine from Chlorine.

The electrolysis is carried out in exactly the same way as before except that now the current is kept at 0.35 volt. Since the solution has been diluted by washing the anode during the preceding analysis, it is necessary to restore the acidity to that of a normal solution by the addition of stronger sulphuric acid of known acid strength. As the test for traces of bromine in the presence of chloride by means of chlorine water and carbon disulphide is not very delicate, it is better to determine the end of the electrolysis with the aid of a sensitive galvanometer.

After the removal of the bromine, the chlorine remaining in solution is always determined by titration because it is impossible to determine chlorine upon a silver anode without some silver passing into solution.

Instead of treating the silver anode as described on page 211, to free it from halogen, it may be reduced by using it as cathode in the electrolysis of an approximately normal solution of sulphuric acid; another simple method is the use of zinc and dilute sulphuric acid.

The principal points to be observed in the above-described method for separating the halogens are: (1) a constant current with which the proper voltage can be maintained; (2) a solution of approximately normal acidity; (3) exclusion of atmospheric oxygen.

The necessity of the first condition is apparent, for in order to effect a separation of iodine from bromine it is necessary to use a current at a voltage high enough to discharge iodine ions, but not high enough to discharge bromine ions. It is only possible to maintain the conditions by the arrangement described on page 212, when the original current remains constant during the analysis.

The second condition must be fulfilled because the prescribed voltages were determined experimentally in solutions containing the halogen salts in normal sulphuric acid, and because the decomposition potentials are different in solutions of different acidity.

Finally, the exclusion of oxygen is extremely important. If a silver anode is dipped into a sulphuric-acid solution together with a platinum cathode and the two electrodes are connected outside the solution, then, without the application of any outside electromotive force, hydrogen is evolved (with solution of the silver) and when this hydrogen combines with dissolved oxygen in the solution, an electromotive force of 1.08 volts is produced; or, in other words, a voltage results which is more than sufficient to deposit bromine and chlorine as well as iodine. It is, therefore, absolutely necessary to direct a stream of hydrogen against the anode, from the capillary at the end of the glass tubing mentioned above, in order to avoid the depolarizing effect of oxygen.

Electrolytic Determination of Halogens and other Anions Combined with the Volumetric Determination of the Corresponding Cations.

The above-described determinations of the halogens depend upon the combination of the halogen with silver, in alkaline solution according to Vortmann's method or in acid solution according to Speketer's method. No attention was paid to the determination of the cations which were originally combined with the halogen. By using the Vortmann's silver anode and E. F. Smith's mercury cathode (p. 205), J. H. Hildebrand * has succeeded in decomposing the neutral solution of an alkali halide in such a

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* J. Am. Chem. Soc., 29, 447 (1907).

way that the halogen is caused to unite with the silver while the metal forms an amalgam with the mercury; on decomposing the amalgam with water, a solution of alkali hydroxide is obtained and can be titrated against a standardized solution of acid.

If such an analysis is carried out with the silver anode and its halogen deposit in the same electrolyzing dish that contains the alkali amalgam, then, even during the electrolysis, some alkali hydroxide is formed as a result of the action of water upon the amalgam, and when the current, after the halogen salt has been completely decomposed, acts upon this solution of alkali hydroxide, some silver oxide is formed at the anode whereby its weight is gradually increased. It is, therefore, necessary to know just when the last of the halogen is deposited and to stop the electrolysis then.

To overcome this difficulty, Hildebrand made use of the principle which is involved in the technical preparation of caustic soda; the alkali halide is electrolyzed and the amalgam decomposed in different compartments. The electrolyzing vessel (Fig. 51) consists of a crystallizing dish 11 cm. in diameter and 5 cm. deep in which a glass cylinder 4.5 cm. high rests upon a thin glass rod bent into a triangle. The glass cylinder is obtained by cutting off the bottom of a beaker. It is held firmly in place, by wedg-

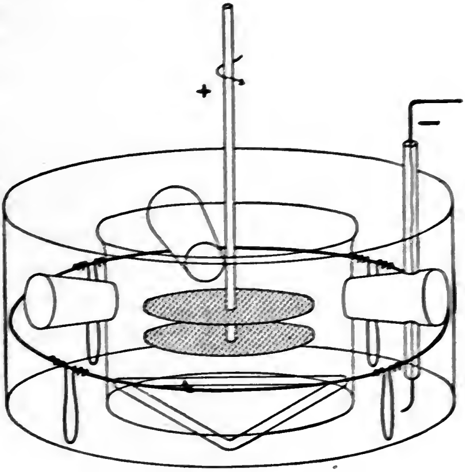

Fig. 51.

ing three corks between it and the sides of the crystallizing dish, so that it does not float when mercury is added. Enough mercury is poured into the dish to make its surface about 3 mm. above the bottom of the inner cylinder and thus liquid poured upon the mercury is kept perfectly isolated in the two compartments. The inner space is for the salt solution, into which the silver anode dips. The end of a short platinum wire dips into the mercury near the walls of the dish and it is connected with the negative pole in the following manner: a piece of platinum wire is melted into the bottom of a narrow glass tube so that it extends about 1 cm. within and without the tube; mercury is poured into the tube and into this dips a copper wire leading to the negative binding post. All the mercury in the bottom of the dish serves as the cathode.

A little water and a few cubic centimeters of a saturated salt solution are poured upon the mercury in the outer compartment. When the current is turned on, the silver anode in the middle takes up the halogen from the solution in the inner space while the alkali metal combines with the mercury at the bottom to form an amalgam. This amalgam distributes itself throughout the entire mercury and when it comes in contact with the water in the outer compartment, it is decomposed with the formation of alkali hydroxide. Thus the mercury on the outside becomes impoverished of its amalgam and, as a result, that present in the middle of the dish constantly diffuses toward the outside. When all of the halogen salt within the inner compartment has been decomposed, all of the hydroxide will be found in the outer space and only pure water will surround the anode. To hasten the decomposition of the amalgam, a nickel wire bent into a ring is placed inside the dish about 1 cm. above the surface of the mercury; the wire rests upon four wire supports as shown in the drawing. If enough dilute salt solution has been poured upon the mercury to cover this wire, a galvanic element is now obtained, consisting of alkali metal — salt-solution — nickel, and this serves to hasten the decomposition of the amalgam so that at the end of the electrolysis only pure water remains in the inner space. The salt is added merely to lessen the resistance in this galvanic cell.

The anode recommended by Hildebrand consists of two disks of platinum gauze having about 300 meshes to the square centimeter. The disks are about 5 cm. in diameter and the ends of the wire are fused together at the periphery, by means of the blast, in order to make the disks a little stouter. The two disks, each weighing about 16 gms. and each having about 75 sq. cm. of surface, are fastened about 5 mm. apart upon a platinum wire which is about 1 mm. thick and 10 cm. long; the upper end of the wire is bent into a loop so that it may be suspended from the beam of the balance.

The platinum disks are plated with from 3 to 4 gms. of silver which is deposited upon them from a cyanide solution (*cf.* p. 133), with a current of 1 or 2 amperes and a rotating anode. With this quantity of silver many halogen determinations may be made, dissolving the silver halide after each analysis by letting the electrode remain in potassium-cyanide solution for a short time.

Procedure. There are several reasons why it is advisable to keep the anode revolving: the silver compounds adhere better to the electrode and the motion of the electrolyte is imparted to the mercury at the bottom of the dish so that the amalgam in the middle of the dish is more quickly transported to the outer space. The stirring has less result upon the duration of the analysis, for as the electrolysis proceeds the composition of the electrolyte approaches that of pure water; the resistance then increases and the current sinks so that it requires a long time for the decomposition of the last traces of the salt.

The solution of about 0.1 gm. of the salt to be analyzed is poured into the inner compartment and the anode is fixed in place so that the lower disk is about 5 mm. above the surface of the mercury; it is made to revolve at a rate of 250 to 300 times per minute. If necessary, enough water is added so that the upper disk is covered by liquid. If only little halogen salt is present, however, it suffices in most cases to keep only the lower disk covered with solution.

For the analysis of potassium chloride and of potassium bromide, Hildebrand started with a current of 5 volts and 0.65 ampere; the electrolysis was continued until the strength of the current fell to 0.01 ampere and this required 30 minutes with 0.1 gm. potassium bromide.

Potassium ferrocyanide was electrolyzed with an initial voltage of 3 to 4 volts and an initial current of 0.15 to 0.2 ampere. Potassium ferricyanide gave good results with a current of 0.2 to 0.4 ampere at 2 to 4.5 volts.

In the analysis of sodium carbonate it is best to have both disks covered with electrolyte and a somewhat roughened silver surface is desirable. The roughening is accomplished, after the electrode has been plated in a cyanide solution with the anode rotating, by allowing the electrolysis to continue for a short time with a stationary electrolyte. The analysis of the carbonate is carried out slowly, with an initial potential of 3.5 to 4 volts and a current of only 0.15 ampere. The analysis requires from 60 to 90 minutes. After weighing the deposit of silver carbonate, the best way to prepare the electrode for future use is to ignite it gently.

In the analysis of normal sodium phosphate, the potential of the current must not exceed 4 volts, if a good deposit is desired. The current should not be more than 0.3 to 0.4 ampere at the start.

Owing to the poor conductivity of this salt and the low voltage employed in the analysis, the time required is 75 to 120 minutes. The duration of the experiment may be shortened to about an hour if a fresh electrode is used for the deposition of the last traces of phosphoric acid.

Since, in all these cases, the solution in the interior compartment is nearly pure water at the last, it is hardly necessary to wash the electrode with water; rinsing with alcohol and then with ether should suffice.

When the decomposition of the solution is complete, the entire contents of the crystallizing dish are transferred to a beaker, the dish rinsed, and the alkaline solution titrated with tenth-normal sulphuric acid, using methyl orange as indicator.

McCutcheon and Lukens, in studying the determination of halogens by means of the Hildebrand decomposition vessel, devised the following method of separation.*

Separation of Alkali and Alkaline Earth Metals from the Heavy Metals.

In general, it has been found that when metal chlorides are decomposed in Hildebrand's apparatus, the amalgams of lithium, sodium, potassium, calcium, strontium and barium diffuse into the outer compartment and there, after being decomposed by the water, the resulting hydroxides may be determined by titration;

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* The separations to be described really belong in Part III but will be understood more readily if described here.

whereas the amalgams of magnesium, cadmium, tin, antimony, iron, aluminium, chromium, manganese, zinc, nickel, cobalt, titanium, uranium, vanadium, zirconium, thorium, lanthanum, cerium, neodymium and praseodymium remain in the inner compartment and are decomposed by water forming insoluble hydroxides. By this classification the general way of separating metals of the two groups is indicated. The behavior of calcium when magnesium is also present is, however, quite different from that of the other members of the group. In this case the calcium amalgam behaves as if it belonged to the second group, *i.e.*, it is deposited together with the magnesium in the middle compartment as insoluble hydroxide.

Although this makes it impossible to separate calcium and magnesium under the ordinary conditions of the analysis, yet advantage can be taken of this behavior when it is desired to separate metals such as potassium, sodium, lithium and especially barium and strontium from calcium; it is only necessary to add magnesium chloride, in case it is not already present.

To illustrate the usefulness of the method the separations described by H. S. Lukens and E. F. Smith will be given.

Barium chloride, in solutions containing about 0.228 gm. of Ba, was decomposed quantitatively in 50 to 60 minutes, by a current of 0.3 ampere at 3.5 to 4 volts. The anode made 300 revolutions per minute and contained all the chlorine in the form of chloride.

The details of the metal determination will be given later.

Strontium bromide, in a solution containing 0.727 gm. of Sr, was electrolyzed under the same conditions with the same success. In this particular case the bromine was not determined.

Separation of Potassium or Sodium from Calcium and Magnesium. Solutions containing 0.022 gm. Ca, 0.0210 gm. Mg as chloride, in one experiment with 0.0474 gm. Na and in another with 0.0582 gm. K, likewise as chloride, were electrolyzed with a current of 0.25 ampere at 3.5 volts in 50 minutes; all the sodium, or potassium, was obtained by titrating the solution in the outer compartment. In these separations, no weight is placed upon the determination of the halogen.

Barium or Strontium from Calcium and Magnesium. The solution contained in one case 0.0222 g. Ca, 0.021 gm. Mg and 0.0455 Ba as chloride; in another case twice as much Ba, 0.091 gm.;

in a third case 0.0563 gm. of Sr as bromide instead of the barium chloride. The current used was 0.3 ampere at 3.5 to 4 volts. To effect the deposition of the last traces of barium or strontium, it was found necessary toward the last to add a few drops of hydrochloric acid to the solution. Calcium and magnesium were found in the inner compartment in the form of an insoluble hydroxide precipitate which could be titrated (see below).

Barium or Strontium from Magnesium alone. The solutions contained 0.0358 gm. Mg and either 0.0455 gm. Ba or 0.0221 gm. Sr. The conditions were the same as when calcium was present with the magnesium.

Metals of the Alkali or Alkaline-earth Group from Iron. The metals were present as chloride, in quantities designated below, and the current was 3 to 5 volts and 0.3 ampere. The experiments required not more than 50 minutes in any case. The iron began to deposit as hydroxide almost immediately:

Barium from *Iron:* 0.0455 gm. Ba, 0.0276 gm. Fe.
Strontium from *Iron:* 0.0565 gm. Sr, 0.0276 gm. Fe.
Potassium from *Iron:* 0.0580 gm. K, 0.0276 gm. Fe.
Sodium from *Iron:* 0.0474 gm. Na, 0.0276 gm. Fe.

Metals of the Alkali and Alkaline-earth Groups from Aluminium. The solutions contained the metals as chloride and the conditions were the same as before:

Barium from *Aluminium:* 0.0455 gm. Ba, 0.0199 gm. Al.
Strontium from *Aluminium:* 0.0221 gm. Sr, 0.0199 gm. Al.
Potassium from *Aluminium:* 0.0580 gm. K, 0.0199 gm. Al.
Sodium from *Aluminium:* 0.0474 gm. Na, 0.0199 gm. Al.

In all the above cases only the metal obtained as hydroxide in the outer compartment was determined by titration. For the determination of the calcium, whose hydroxide is the least soluble and whose amalgam is the most difficult to decompose, T. P. McCutcheon proceeded as follows:

The liquid in the interior compartment was removed, with the aid of a pipette or siphon, and the inner walls as well as the mercury surface were thoroughly washed with water. Then the entire contents of the crystallizing dish were transferred to a wide beaker and the mercury was thoroughly stirred with a glass rod, the end of which was covered with a piece of rubber tubing; this stirring served to hasten the complete decomposition of the calcium amalgam. An excess of tenth-normal acid was added and the excess finally titrated with tenth-normal alkali solution, using methyl orange as indicator.

The same author accomplished a *separation of calcium from magnesium* by using a current of higher voltage. A solution containing 0.1 gm. $MgCl_2$ and 0.0771 gm. $CaCl_2$ was electrolyzed with an initial current of 0.3 ampere at 9 volts; the current dropped to 0.2 ampere toward the last. Decomposition was complete in 3 hours so that the calcium could be determined in the outer compartment by the method given above. A few drops of hydrochloric acid were added from time to time to the inner solution, in order to hasten the electrolysis.

McCutcheon also carried out the following separations:

Sodium from *Uranium.* Used 0.1 gm. of uranyl chloride and 0.1172 gm. NaCl; 3 volts, 0.3 ampere; time, 3 hours. The current at the end had fallen to 0.02 ampere and the potential had increased to 5 volts.

Potassium from *Uranium.* Used 0.1 gm. UO_2Cl_2, 0.1467 gm. KCl; initial potential 3 volts, final potential 5 volts; 0.5 ampere at the start and 0.01 ampere at the last; time, 2 hours.

Lithium from *Uranium.* Used 0.1 gm. UO_2Cl_2, 0.0846 gm. LiCl; potential 5 volts; current strength 0.30 to 0.02 ampere; time, 2 hours.

Barium from *Uranium.* Used 0.1 gm. UO_2Cl_2, 0.104 gm. $BaCl_2$; potential 5 volts, current strength 0.15 to 0.01 ampere. A little hydrochloric acid was added, as mentioned above; time, 1 hour.

Strontium from *Uranium.* Used 0.1 gm. UO_2Cl_2, 0.1456 gm. $SrBr_2$; potential 5 volts, current strength 0.4 to 0.02 ampere; time, 2 hours.

Under similar conditions, separations of barium from thorium, cerium, lanthanum, and neodymium were carried out successfully.

Potassium, Ammonium (Nitrogen).

The usual gravimetric method for determining potassium and ammonium is to form the potassium or ammonium chloroplatinate and weigh it upon a tared filter, or in a Gooch crucible, after drying at 110°. The weighing of the filter after such drying is always more or less inaccurate and it is better to dissolve the chloroplatinate in hot water, determine the platinum electrolytically and from this compute the potassium or ammonium content. The electrolysis is carried out as described on page 140.

O. Schumm * has used this method to advantage in the determination of the potassium in blood.

Determination of Nitric Acid in Nitrates.

In connection with Luckow's observation that a sulphuric-acid solution of pure alkali nitrate, on being electrolyzed with platinum electrodes, is not transformed completely into ammonia although a quantitative transformation takes place if copper sulphate is also present in the solution, G. Vortmann † was led to determine the conditions under which the quantitative determination of nitric acid in nitrates could be made. Under these conditions, the copper is deposited upon the cathode and the nitric acid is reduced to ammonia so that eventually all the nitrogen is present as ammonium sulphate, provided a sufficient quantity of free sulphuric acid was present at the start. The liquid is subjected to distillation after adding a large excess of caustic soda and the distillate is caught in a measured volume of standardized sulphuric-acid solution. The excess of the latter is finally determined by titration with caustic-soda solution, and from this the quantity of nitric acid is computed.

In the course of time, the method has experienced some modification. K. Ulsch ‡ found that the reduction of the nitric acid to ammonia took place if a spiral of copper wire was used as the cathode, which was ignited just before starting the analysis and plunged into cold water. The addition of copper sulphate to the electrolyte is then unnecessary. Moreover, Ulsch found that if a measured quantity of standardized sulphuric acid was added to the solution of the nitrate, then after the electrolysis the acidity of the solution could be determined by titration and thus the quantity of ammonia formed could be at once computed and the distillation avoided. It is necessary to bear in mind that only half of the sulphuric acid neutralized during the experiment is combined with ammonium for the other half is combined with potassium (in case potassium nitrate was analyzed). It is also assumed that the solution of the nitrate was neutral at the

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* Z. anal. Chem., **40,** 385 (1901).

† Ber., **23,** 2798 (1890).

‡ Z. Elektrochem., **3,** 546 (1897).

start. Such a simplification of the process was suggested by Vortmann and later used by L. H. Ingham.* The last-named author shortened the operation by stirring the electrolyte. W. H. Easton sought to determine the most favorable experimental conditions with stationary electrolytes.

Up to the present time, however, the method has nearly always been tested with pure potassium nitrate; further experiments are desirable to see whether the method is applicable to all sorts of products such as those which have to be analyzed in agricultural experiments stations. Above all it would be desirable to know what effect the usual impurities, such as chloride, etc., have upon the results. On account of the uncertainty which is still attached to the method there will be given here only a statement of the working conditions which Easton found to be the most favorable.

From 0.1 to 0.5 gm. of potassium nitrate and an equal quantity of copper sulphate are dissolved in water, 30 cc. of sulphuric acid (sp. gr. 1.062) are added, and, after diluting to 150 cc., the electrolysis is carried out with a platinum cathode using a current of $ND_{100} = 1$ ampere at the ordinary temperature. After 2.5 hours all the copper will have been deposited on the cathode, in an adherent form, and all the nitric acid transformed into ammonium sulphate. The solution is poured out of the beaker, evaporated with the washings, and distilled with an excess of caustic soda. The excess of sulphuric acid in the receiver is determined by titration with caustic alkali, using methyl orange as indicator. †

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* J. Am. Chem. Soc., **26**, 1251 (1904).

† In the determination of the nitrogen in organic substances, G. Budde and C. Schou (Z. anal. Chem., **38**, 344 (1899)) have attempted to decompose the substance in concentrated sulphuric acid with the aid of the electric current, without adding any of the ordinary substances recommended for the Kjeldahl method. This process, however, has not proved universally applicable.

Preparation of Standard Sulphuric Acid Solution.

When a neutral solution of copper sulphate is electrolyzed, the changes that take place may be represented by the following equations:

$$\text{cathode,}\quad 2Cu^{++} + 4\ominus \rightarrow 2Cu;$$
$$\text{anode,}\quad 2H_2O + 4\oplus \rightarrow 4H^+ + O_2\uparrow.$$

After all the copper is deposited, hydrogen ions are discharged at the cathode just as fast as they are formed at the anode.

$$4H^+ + 4\ominus \rightarrow 2H_2\uparrow \qquad 2H_2O + 4\oplus \rightarrow 4H^+ + O_2\uparrow.$$

The acidity of the solution, therefore, can be computed either from the weight of copper sulphate decomposed or from the weight of copper deposited. From 1.249 gm. of $CuSO_4 \cdot 5H_2O$ or for 0.3179 gm. of deposited copper, acid equivalent to 100 cc. of tenth-normal solution is obtained. The solution may be used for accurately standardizing a solution of alkali.

In carrying out the electrolysis a spongy deposit of copper is likely to be obtained with a stationary electrolyte if the current density is over $ND_{100} = 0.4$ ampere. More current may be used if the anode is rotated, the solution is kept warm, and a gauze cathode is used.

PART III.

SEPARATION OF METALS.

COPPER.

Separation of Copper from Silver.

In Nitric-acid Solution. The separation depends upon the fact that silver can be deposited at a certain low voltage at which copper is not deposited. It is of great importance to keep the voltage within certain limits throughout the electrolysis. The method of Küster and v. Steinwehr was described on page 131.

If the copper solution has become too dilute by the washing of the silver deposit, it is concentrated by evaporation and the copper is deposited in the nitric acid solution as described on page 124.

In Potassium-cyanide Solution, according to E. F. Smith and L. K. Frankel.* When the solution contains 0.1 to 0.2 gm. of silver and about 0.2 gm. copper, it suffices to add 2 gms. of pure potassium cyanide; if more copper is present, *e.g.*, 0.5 gm., twice as much potassium cyanide is added. The solution is diluted to about 125 cc. and electrolyzed at 65° to 75° with a current density of $ND_{100} = 0.03$ to 0.07 ampere at 1 to 1.4 volts. According to the quantity of silver, the separation requires from 4 to 8 hours. The determination of the copper will be discussed on page 226.

The above two separations are based upon two different principles. In the first method, the silver is deposited at a voltage so low that no copper is deposited from a nitric-acid solution; in the second method, both metals are converted into complex salts of which one is more stable than the other. In the first case it is necessary to keep the voltage within certain limits, if the copper is to remain in solution; and in the second case it is necessary that the cuprocyanide ion shall retain its strongly complex character until all the silver is deposited, or, in other words, the secondary dissociation of the complex cuprocyanide ion must be prevented as far as possible. Strictly speaking, both methods depend upon

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* E. F. Smith, Electrochemical Analysis.

the fact that different electromotive forces are necessary to deposit the two elements, for this, as was stated on page 80, is the general principle upon which all electrolytic separations are based.

From what has been said above, as well as on page 51, the necessity of a large excess of potassium cyanide to form the cuprocyanide complex is apparent. Since potassium cyanide is itself decomposed by the action of the electric current, there is another reason for adding an excess of this salt. O. Brunck * has shown that it is sufficient to add for 100 cc. of liquid 2 gms. of potassium cyanide more than the quantity necessary to form the complex salt. Under these conditions it is possible to separate even small quantities of silver from large quantities of copper, because it is possible to use voltages far above the decomposition potential of copper from normal cupric ions. Thus Brunck obtained very accurate silver determinations in 2 or 3 hours under the following conditions of working. The nitric-acid solution, which may contain from 0.24 to 0.05 gm. of silver and from 0.08 to 0.43 gm. of copper, was neutralized with caustic-potash solution; 3 or 4 gms. of potassium cyanide and 0.5 gm. of solid potassium hydroxide were added, and after diluting to 100 cc. the solution was electrolyzed at the laboratory temperature using a platinum gauze electrode and a current at 2.5 to 4 volts. The current density under these conditions was $ND_{100} =$ 0.45 to 0.25 ampere.

If the quantity of copper is large in proportion to the quantity of silver, it is advisable to keep the current density down to 0.25 ampere or to use a correspondingly larger quantity of potassium cyanide, to prevent the dissociation of the complex cuprocyanide ion. The small quantity of solid potassium hydroxide is added to prevent the formation of paracyanogen which separates out at the anode when stronger currents are employed; the cyanogen, as fast as it is set free by the action of the current, unites with potassium hydroxide to form potassium isocyanate. If, toward the end of the electrolysis, a little copper should deposit, on account of the presence of insufficient potassium cyanide, this is shown by the reddish tint which the silver deposit assumes. It is necessary, then, to stop the current for a few minutes, when the copper will at once go back into solution, and to continue the electrolysis for a short time after adding a little more potassium cyanide.

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* Ber., **34,** 1607 (1901).

When the deposition of the silver is complete, both electrodes are raised from the solution, without breaking the circuit, and quickly plunged into a beaker containing distilled water, after which the current is turned off.

It is not advisable to attempt the electrolytic deposition of copper from the solution containing considerable potassium cyanide; it is better to evaporate the solution under the hood with sulphuric acid, until all the potassium cyanide is decomposed, and then to determine the copper as described on page 124.

Rapid Separation of Copper from Silver.

In a potassium-cyanide solution of the two metals, Julia Langness * succeeded in effecting a separation in 15 to 20 minutes. The solution, which may contain about 0.12 gm. of silver and an equal quantity of copper in 125 cc., was treated with 2 gms. of potassium cyanide, heated, and electrolyzed in a platinum dish with a spiral or sieve anode (Figs. 15 and 22) making about 600 revolutions per minute; the current was 0.4 to 0.1 ampere at 2.5 volts.

In the solution freed from silver, the potassium cyanide was destroyed as described above and the copper determined according to page 116 or page 124.

In Boiling Acetic-acid Solution, Sand (p. 42) found it possible to deposit silver in the presence of copper by keeping the cathode potential at 0.3 volt (by means of the auxiliary electrode, p. 40), or by simply keeping the potential between the electrodes below 1.25 volts. This voltage must not be exceeded even in the short time required to take away the beaker and wash the deposit.

The solution containing about 0.5 gm. of silver and 0.1 to 0.25 gm. of copper was treated with 4 or 5 cc. of concentrated nitric acid (or 4 cc. of concentrated sulphuric acid) and 25 gms. of sodium acetate and the boiling-hot solution electrolyzed with an initial potential difference between the electrodes of 1 volt (corresponding to 2.8 amperes). After 7 minutes, when the potential had risen to 1.2 volts and the current strength had sunk to 0.5 to 0.8 ampere, all the silver had been deposited.

In working with the auxiliary electrode the solution contained about 0.27 gm. of silver, 0.59 gm. of copper, 4 cc. of concentrated nitric acid and 25 gms. of sodium acetate. The cathode potential

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* J. Am. Chem. Soc., **29,** 471 (1907).

was kept at 0.3 volt; the current strength was 2.7 amperes at the start and 0.4 ampere at the finish.

The copper is best determined, after evaporation with either sulphuric or nitric acid, according to page 116 or page 124.

Separation of Copper from Cadmium.

Three methods have been used successfully for accomplishing this separation. 1. The deposition of copper from a nitric-acid solution. 2. The deposition of copper from a sulphuric-acid solution. 3. The deposition of cadmium from a potassium-cyanide solution.

1. *Deposition of Copper from Nitric-acid Solution.*

According to E. F. Smith and Wallace,* the solution containing the two metals in 100 cc. is acidified with 2 cc. of nitric acid (sp. gr. 1.4) heated to 50° and the copper deposited with a current of 2.5 volts and $ND_{100} = 0.1$ ampere. The electrolysis under these conditions requires about 3 hours.

2. *Deposition of Copper from Sulphuric-acid Solution.*

Heidenreich, who tested the method proposed by Freudenberg, found that the separation succeeds best when the potential difference between the electrodes does not exceed 1.85 volts. The neutral solution of the two sulphates is treated with 15 cc. of sulphuric acid (sp. gr. 1.09) and the copper is deposited with a current at 1.7 to 1.8 volts and $ND_{100} = 0.07$ to 0.05 ampere, at the laboratory temperature. Since the complete deposition of the copper with such a weak current requires a long time, it is necessary to let the current run overnight (*cf.* p. 229).

3. *Deposition of Cadmium from Potassium-cyanide Solution.*

The two methods already described for separating copper from cadmium have been based upon the fact that the decomposition potential of copper cations is less than that of cadmium cations; thus the copper ions are discharged before the cadmium ions.

Cadmium may be deposited before the copper in a solution of the complex cyanides, owing to the different degree of stability of these salts. By the addition of potassium cyanide, both copper and cadmium are transformed into complex anions but the $Cd(CN)_4^{=}$ anion is less stable than the $Cu_2(CN)_8^{\equiv\equiv}$ anion.

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* J. Am. Chem. Soc., **19,** 870 (1897).

The difference in behavior is shown by the fact that cadmium is precipitated by hydrogen sulphide from a potassium-cyanide solution, whereas under the same conditions copper is not, because there are practically no copper cations in the solution. The primary and secondary dissociation of potassium-cadmium cyanide is expressed by the following equilibrium expressions, of which the first takes place almost completely and the second to a slight extent.

$$K_2[Cd(CN)_4] \rightleftarrows 2\,K^+ + [Cd(CN)_4]^=$$
$$[Cd(CN)_4]^= \rightleftarrows Cd^{++} + 4\,(CN)^-.$$

The presence of cadmium cations in the solution permits the electrolytic deposition of the cadmium, inasmuch as the decomposition potential of cadmium ions is less than that of hydrogen from an alkaline solution.

If the solution is not already neutral, it is made so by the addition of caustic-potash solution, and potassium cyanide is added in sufficient quantity to dissolve the cyanides of copper and cadmium which are first precipitated. After adding an excess of 3 or 4 gms. potassium cyanide, the solution is diluted and electrolyzed with a current whose potential is not allowed to exceed 2.6 to 2.7 volts.

To determine the copper, the solution should be freed from cyanide and the electrolysis carried out in a sulphate or nitrate solution (*cf.* p. 227).

Rapid Separation of Copper from Cadmium.

According to D. S. Ashbrook,* a deposit of 0.27 gm. of copper, free from cadmium, can be obtained in 20 minutes if a solution of the two metals, containing 1 cc. of nitric acid (sp. gr. 1.43), is electrolyzed, using a platinum dish as cathode, and a spiral making 300 to 400 revolutions per minute as anode, with a current of $ND_{100} = 3$ amperes at 4 to 5 volts.

P. Denso † proceeds in the following manner. From a solution of the sulphates, containing about 0.13 gm. of copper and 0.1 gm. of cadmium, enough sulphuric acid is added to make the acidity correspond to a double-normal solution, and the copper is deposited at a potential of not over 2 volts. This maximum potential is obtained by connecting the cell directly to the poles of a single accumulator cell. As cathode, a gauze electrode serves

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* J. Am. Chem. Soc., **26,** 1285 (1904).

† Z. Elektrochem., **9,** 469 (1903).

(p. 59), and as anode, Denso recommends a platinized platinum wire wound into a spiral; this anode is fastened to the clapper of an electric bell (the bell is removed) and the rapid motion of the clapper back and forth serves to stir the solution. Unquestionably the same effect could be attained by rotating the anode or otherwise stirring the electrolyte. The precipitation of the copper requires about one hour.

In the solution freed from copper, which is concentrated by evaporation if the washings have made it too dilute, the cadmium is deposited in a stationary electrolyte with a current of 0.57 ampere at 2.6 volts. A single accumulator cell is naturally insufficient in this case. Each electrolysis requires about an hour.

Separation of Copper from Mercury.

As electrolyte for this separation, only a potassium-cyanide solution is to be considered. The solution, which may contain about 0.12 gm. of mercury and an equal quantity of copper, is treated with 2 or 3 gms. of pure potassium cyanide, diluted to 125 cc. and electrolyzed at about 65° with a current of 1.5 volts and 0.06 to 0.08 ampere. E. F. Smith and Spencer found that the duration of the experiment was so shortened by heating the electrolyte that only 2.5 to 3 hours were required to deposit the above quantity of mercury. With regard to heating the solution, however, the danger of losing mercury by volatilization, as mentioned on page 127, must be borne in mind.

Rapid Separation of Copper and Mercury.

H. J. S. Sand,* by the use of his rotating gauze electrode and the auxiliary electrode, succeeded in depositing mercury in 6 minutes from a nitric-acid solution containing copper. The cathode potential was kept at 0.14 volt and the anode made about 600 revolutions per minute.

Separation of Copper from Lead.

According to what was stated on page 194 concerning the deposition of lead as peroxide in nitric-acid solution, and on page 124 concerning the deposition of copper in a nitric-acid solution, it is obvious that it is possible to precipitate the two elements simultaneously by the electrolysis of a nitric-acid solution, the

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* See p. 42.

lead as peroxide upon the anode and the copper as metal upon the cathode. To prevent the deposition of lead upon the cathode it is necessary to provide an excess of nitric acid and, unless the electrolysis is carried out long enough to reduce the excess of nitric acid, there is danger of some of the copper not being deposited. The author considers it safer, therefore, to deposit the lead peroxide from a solution so acid that none of the copper will deposit and then, after neutralizing the excess of acid with ammonia, to determine the copper by itself.

The solution containing 20 cc. of nitric acid (sp. gr. 1.35) is diluted to only 75 cc., heated to 60° and electrolyzed with a current of $ND_{100} = 1.5$ to 1.7 ampere, using a roughened platinum dish as anode. As cathode a perforated, roughened platinum disk, or a gauze electrode of suitable shape, is used and its weight is determined. After about an hour, the whole or greater part of the lead (if 0.5 gm. was in the solution) will be deposited upon the dish as peroxide, while the disk will show little or no copper. The current is broken and the solution transferred to a second weighed platinum dish. The deposited peroxide is washed with water and the washings added to the main solution. The deposit is treated as described on page 194.

To determine the copper, the solution is neutralized with ammonia until the dark blue color is obtained and then 5 cc. of nitric acid are added. The platinum dish is made the cathode and, in order to obtain any remaining lead, the above-mentioned disk or gauze electrode is now used as anode. It makes no difference whether copper was deposited on it or not during the previous electrolysis, for any copper on this electrode, which is now the anode, will dissolve and be deposited upon the dish. When the solution has become perfectly cold, it is diluted to about 120 or 140 cc. and electrolyzed with a current of 1 to 1.2 ampere. To deposit 0.25 gm. of copper and any residual lead, 3 or 4 hours are required.

This method permits a rapid and accurate quantitative separation of the two metals irrespective of the relative amounts present.

If a precipitate of lead sulphate is present in the solution of the two metals (*e.g.*, on account of the oxidation of sulphide ores with nitric acid) the analysis often requires more time, as the precipitate dissolves in hot nitric acid more or less slowly, depending upon its physical nature. Formerly, the author recommended adding a slight excess of ammonia and heating the solution, whereby the dense lead sulphate was transformed into less dense lead hydroxide. The ammoniacal liquid was poured, little by little, into the platinum dish containing about 20 cc. of hot nitric acid (sp. gr. 1.35) while stirring constantly with the electrode. The lead sulphate, which formed again upon coming in contact with the acid, either redissolved immediately, or, if much was present, it dissolved after heating the acid for a short time. The vessel in which the neutralization with ammonia took place was first washed with a little nitric acid and then with pure water, the washings being added to the main solution, kept for the copper determination.

H. J. S. Sand has found, however, that it is unnecessary to bring the lead sulphate into solution, and that the electrolysis may be carried out in the presence of a lead-sulphate precipitate provided the electrolyte is stirred. The process is carried out in the following manner.

Rapid Separation of Copper and Lead.

By using his gauze electrodes, the inner of which acted as anode and made 300 to 600 revolutions per minute, Sand obtained a very accurate separation of 0.14 gm. of lead and 0.25 gm. of Cu in a solution containing some of the lead in the form of a sulphate precipitate. The solution was treated with 1 cc. of concentrated nitric acid, heated, and electrolyzed for 5 minutes with a current of 2 amperes. During this time the lead sulphate gradually dissolved and the lead peroxide deposited upon the anode. The current was then strengthened to 10 amperes and thereby all the copper was deposited. Although the lead peroxide did not adhere very firmly, there was no loss during the washing.

It is noteworthy in such a case that in spite of the slight acidity of the solution no lead is deposited upon the cathode if the quantity of copper present is so large that all the lead is deposited as peroxide upon the anode before the precipitation of the copper begins (*cf.* p. 197 and Analysis of Commercial Zinc, p. 303).

If more lead than copper is present in the solution, there is not enough nitric acid in Sand's method to prevent the deposition of metallic lead upon the cathode. In such cases more nitric acid must be added.

A. Fischer, while working at Aachen, has succeeded in depositing 0.15 gm. of lead and 0.27 gm. of copper in 15 to 20 minutes according to the following experimental conditions. The solution in the platinum dish, which served as anode, amounted to 120 cc. and contained 20 cc. of nitric acid (sp. gr. 1.3). The temperature was 95°, the current strength 6 to 7 amperes, the potential 3.8 to 3.9 volts. The disk cathode made 800 to 1000 revolutions per minute.

For the rapid determination of the copper, the greater part of the nitric acid was neutralized with ammónia and the analysis carried out as described on page 129.

Separation of Copper from Arsenic.

If a copper solution containing arsenic is electrolyzed by one of the usual methods, toward the end of the electrolysis black specks will appear upon the pink copper deposit; if considerable arsenic is present the entire copper deposit becomes covered with a black film. Since nearly all copper ores, copper alloys and commercial copper contain some arsenic, it is evident that the electrolysis of a copper solution in the presence of arsenic is a matter of considerable importance. Of the various methods which have been proposed for keeping the arsenic in solution, the following three methods have proved to be the best.

1. *In Sulphuric-acid Solution.* Freudenberg * found that the separation could be effected in a solution containing 10 to 20 cc. dilute sulphuric acid, if the difference of potential between the electrodes was not allowed to exceed 1.9 volts. In this way as much as 0.3 gm. of copper can be separated overnight from an equal amount of arsenic and it makes no difference whether the latter element is present in the trivalent or quinquevalent condition; the copper deposit is free from arsenic.

2. *In Nitric-acid Solution.* If the copper is present in a nitric-acid solution, as is frequently the case (analysis of alloys, black copper, etc.), a copper deposit free from arsenic can be obtained in such a solution if about 5 cc. of nitric acid are present in 100 cc. of solution and the electrolysis is carried out at 50° to 60° with a maximum potential of 1.9 volts. At ordinary temperatures the electrolysis requires longer, and it is best to let the current run overnight.

As long as the arsenic is present in the quinquevalent condition, it is not deposited by the current because only $AsO_4^{\equiv}$ anions are present. When the arsenic acid is partly reduced to arsenious

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* Z. physik. Chem., **12**, 117 (1893).

acid by the action of the current, then more or less trivalent As cations are present in the solution and the possibility exists for arsenic to be deposited at the cathode. To prevent the reduction, A. Hollard and L. Bertiaux * add a little ferric sulphate to the solution (*cf.* Analysis of Commercial Copper).

3. *In Ammoniacal Solution.* Apparently Le Roy W. McCay † was the first to observe that it was possible to obtain a copper deposit free from arsenic by the electrolysis of an ammoniacal solution. According to E. F. Smith the solution containing about 0.2 gm. of copper is treated with 20 cc. of ammonia (sp. gr. 0.91) and 2.5 gms. of ammonium nitrate. After diluting to about 125 cc., it is electrolyzed at 50° to 60° with a current of $ND_{100} = 0.5$ ampere at 3.5 volts. At the end of about 3 hours, the copper is completely deposited and contains no arsenic.

The fact that such a strong current does not cause the deposition of any arsenic, irrespective of whether the arsenic is present as arsenite or arsenate, is due to the fact that arsenic cations cannot exist as such in an alkaline solution; quinquevalent arsenic is always present as AsO_4^{---} anions, except perhaps in very concentrated hydrochloric-acid solution, and trivalent arsenic yields a small quantity of the trivalent arsenic cation, As^{+++}, only in an acid solution; in an alkaline solution trivalent arsenic can only dissociate into the AsO_3^{---} anion.

Freudenberg treats the nitric-acid solution of copper and arsenic with ammonia until an excess of about 30 cc. of 10 per cent ammonia is present and the electrolysis is carried out with a current at 1.9 volts until the solution is completely decolorized, which requires from 6 to 8 hours.

Rapid Separation of Copper from Arsenic.

D. S. Ashbrook, using Exner's electrodes, *i.e.*, a platinum dish as cathode and a platinum spiral making 300 to 400 revolutions per minute as anode, succeeded in separating 0.27 gm. of copper from an equal amount of arsenic by electrolyzing, for 20 minutes, a solution to which 1 cc. of concentrated nitric acid (sp. gr. 1.43) had been added. The volume of the solution was about 125 cc. and the current density was $ND_{100} = 5$ amperes at 4 to 5 volts.

The conditions for the rapid electrolysis in an ammoniacal solu-

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* Bull. soc. chim., [3], **31,** 900 (1904).

† Chem.-Ztg., **14,** 509 (1890).

tion were the following. The electrolyte contained the above quantities of copper and arsenic in 125 cc., 25 cc. of ammonia (sp. gr. 0.91) and 2.5 gms. of ammonium nitrate. The deposition of the copper was completed in 15 minutes by using a current of ND_{100} = 5 amperes at 7 volts.

Separation of Copper from Aluminium, Magnesium, Barium, Strontium, Calcium and the Alkali Metals.

1. *In Nitric-acid Solution.* The conditions outlined on page 124 serve for the separation of copper in the presence of salts of the above metals.

2. *In Sulphuric-acid Solution.* On account of the difficult solubility of the sulphates of barium, strontium and calcium, the electrolytic separation of copper from these elements does not need to be considered. The deposition of the copper in the presence of aluminium, magnesium and the alkali metals takes place under the conditions described on page 116, as in their absence.

Rapid Separation of Copper from Aluminium, Magnesium, Alkaline Earths and Alkali Metals.

1. *In Nitric-acid Solution.* According to Ashbrook,* who only attempted the separation of copper from aluminium and from magnesium, it is possible to deposit 0.27 gm. of pure copper in the presence of about the same quantity of aluminium or magnesium, if the solution is treated with 1 cc. of concentrated nitric acid, diluted to 125 cc. and electrolyzed for 20 minutes with a current of ND_{100} = 3 amperes at 4 to 5 volts. The spiral anode (*cf.* p. 54) is given a velocity of 300 to 400 revolutions per minute.

2. *In Sulphuric-acid Solution.* If, instead of the nitric acid, 0.1 cc. of concentrated sulphuric acid is added, the electrolysis of the above quantity of copper in the presence of magnesium and aluminium requires 10 minutes with a current of ND_{100} = 4 or 5 amperes.†

Separation of Copper from Bismuth.

These two metals stand close to one another in the potential series and thus it is obviously impossible to effect a separation in

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* J. Am. Chem. Soc., **26**, 1285 (1904).

† The voltage was given as from 1 to 4.8 volts in the original article, and in E. F. Smith's book it is given as 14 to 8 volts. There is evidently some mistake in each case.

an acid solution. Even in solutions of the complex salts, the separation is associated with difficulties. In electro-analysis the only question that has received attention is the prevention of the deposition of bismuth when present in small quantities in copper solutions (from ores or crude copper). For this purpose A. Hollard and L. Bertiaux have devised a simple method which consists in adding a little finely powdered lead sulphate to the substance (copper, alloy, or ore) while dissolving it in nitric acid. The adherent deposit of lead peroxide on the anode causes bismuth peroxide to deposit and adhere there, so that no metallic bismuth reaches the cathode.

It is not advisable to let the heavy lead sulphate remain in contact with the copper deposit while the latter is being formed and for this reason it is better to carry out the electrolysis with a stirred electrolyte. (For more specific details, see Analysis of Commercial Copper.)

If small quantities of antimony are present in the solution, they will also adhere as oxide to the lead-peroxide precipitate.

Separation of Copper from Chromium.

The conditions described for the separation of copper from aluminium hold here both for stationary and for moving electrolytes (*cf.* p. 235).

For the rapid separation in sulphuric-acid solution, Ashbrook recommends starting the analysis with 3 amperes and gradually increasing the current to 5 amperes. In a rapid separation from nitric-acid solution, the results are a little too high if the current is more than 3 amperes.

Separation of Copper from Antimony.

Although small quantities of antimony remain in solution during the deposition of copper from ammoniacal solution (p. 129), for the separation of larger quantities of antimony from copper a different method must be chosen. E. F. Smith and D. L. Wallace * add to the solution containing 0.1 gm. of each metal, or even twice as much antimony in the quinquevalent condition, 8 gms. of tartaric acid and 30 cc. of ammonia (sp. gr. 0.91). The resulting

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* Z. anorg. Chem., **4**, 273 (1893); see also S. C. Schmucker, Z. anorg. Chem., **5**, 199 (1894).

solution is heated to 50° and electrolyzed at a volume of 150 cc. with a current of $ND_{100} = 0.08$ to 0.1 ampere at 1.8 to 2 volts.

The solution, after being freed from copper, is converted into sulpho salt and the antimony determined according to page 158.*

Concerning the deposition of pure copper in the presence of antimony, consult the article on Commercial Copper, in Part IV.

Separation of Copper from Iron.

In a nitric-acid solution the deposition of copper, free from iron, is effected under the conditions described on page 124. If larger quantities of iron are in solution, the ferric nitrate exerts a solvent effect upon the deposited copper; at all events the time required is longer. Inasmuch as large quantities of nitric acid hinder the deposition of copper, Hollard and Bertiaux recommend the reduction of the excess nitric acid by the addition of a saturated solution of sulphurous acid; an excess of this reagent must be avoided as otherwise copper sulphide may be precipitated.†

For the determination of the iron, the solution after the electrolysis is evaporated with concentrated sulphuric acid until the nitric acid is all expelled, the free sulphuric acid is neutralized with ammonia, 8 gms. of ammonium oxalate are added, and the iron is determined electrolytically as described on page 183.

The separation of copper from iron takes place more satisfactorily in a sulphuric-acid solution, because the ferric salt is reduced to ferrous salt during the electrolysis and the above-mentioned solvent effect is lost.‡

The iron determination is carried out as described above, after concentrating the solution by evaporation.

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* Another method for separating copper and antimony is described by Puschin and Trechzinsky, Z. Elektrochem., **14**, 47 (1907).

† For the determination of copper in materials rich in iron, see page 293.

‡ This is true only when the work is carried out at ordinary temperatures. If the deposition of the copper takes place with a potential of 2 volts (p. 119) and at a temperature of 75°, then 0.15 gm. of iron in 100 cc. of solution can prevent the quantitative deposition of the copper, because at this temperature the ferric salt formed at the anode diffuses quickly to the cathode and is reduced to ferrous salt by the current more readily than cupric ions are discharged. At ordinary temperatures, however, the presence of even 0.6 gm. iron in 100 cc. does not hinder the deposition of 0.15 gm. copper, because in this case the diffusion takes place more slowly. (F. Foerster, Z. angew. Chem., **19**, 1895 (1906)).

In ammoniacal solution copper can be separated from large quantities of iron by the method of G. Vortmann.* The iron is oxidized to the ferric condition by nitric acid, ammonium sulphate is added and the iron precipitated by an excess of ammonia. Without filtering off the precipitated ferric hydroxide, the copper is determined with a current of $ND_{100} = 0.1$ to 0.06 ampere. It is advisable in this case, as in all analyses carried out in the presence of a substance in suspension, to use a cylindrical or conical cathode rather than a platinum dish; because the long contact of the precipitate with the deposit may give rise to inaccuracies.† It is well to carry out the work with a stirred electrolyte.

The method given in previous editions of this book, which consisted in using an ammonium-oxalate solution with oxalic, tartaric or acetic acid, has no advantages over the methods already described.

Rapid Separation of Copper from Iron.

According to D. S. Ashbrook, the same conditions are necessary as in the separation of copper from aluminium in nitric- or sulphuric-acid solution (*cf.* p. 235).

To prevent the impeding action of nitric acid, A. Fischer recommends the addition of 0.5 to 1 gm. of hydrazine sulphate toward the end of the electrolysis. Fischer used a platinum dish as cathode and a disk making 1000 to 1200 revolutions per minute as anode. The solution contained 1 cc. of concentrated nitric acid and was electrolyzed at 95° at a volume of 125 cc. with a current of 3.5 to 4 amperes at 6.3 to 8.5 volts. Under these conditions, about 0.27 gm. of copper can be separated from 0.2 gm. of iron in 20 to 25 minutes.

In Potassium-cyanide Solution. The separation of copper from iron in ammoniacal solution depends upon the removal of the ferric ions by precipitation, but the separation in a potassium-cyanide solution depends upon the removal of ferrous and ferric ions by converting them into the extremely stable ferrocyanide and ferricyanide ions. In either case no iron cations are present in the solution. The cuprocyanide anion is less stable than the complex iron anions, and undergoes a secondary dissociation to

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* Monatsh. Chem., **14,** 552 (1893).

† B. Neumann first called attention to this source of error and A. Thiel has confirmed it, Z. Elektrochem., **14,** 205 (1908); *cf.* p. 186.

some extent, forming a few copper cations, and the extent to which this secondary dissociation takes place is greater in proportion as less potassium cyanide is added (*cf.* p. 228). Moreover, the potassium cyanide is decomposed by the current and thus the tendency for the complex cuprocyanide to dissociate becomes increased while, at the same time, the more stable ferrocyanide or ferricyanide anions are not decomposed by the current used. If, furthermore, only a little potassium cyanide is used the salt does not attack the anode * causing deposition of platinum, together with the copper, upon the cathode. Such an attack by the potassium cyanide is also prevented by the addition of ammonia.

On the basis of these facts, A. L. Flanigen † successfully accomplished the separation of copper from iron under the following conditions. To the solution containing about 0.2 gm. copper, 1.5 gms. of pure potassium cyanide and 10 cc. of ammonia (sp. gr. 0.93) were added, and after heating to 65° the copper was deposited with a current of ND_{100} = 8 to 10 amperes at 10 volts. The anode made about 400 revolutions per minute and the analysis required 10 minutes. It makes no difference whether the iron content is greater or less than the copper content.

If it is desired to determine the iron electrolytically, this method is a tedious one because it is necessary to destroy the complex anions, by evaporating with sulphuric acid, before going on with the analysis.

Separation of Copper from Manganese.

The simultaneous deposition of copper upon the cathode and manganese dioxide upon the anode gives uncertain results; for one reason because the conditions necessary for the deposition of the manganese (*cf.* p. 197) give rise to poor deposits of copper, and for another reason because the presence of mineral acids, which favor the formation of good copper deposits, tend to prevent the complete deposition of manganese dioxide. It is necessary, therefore, to deposit the copper as described on page 116, and then, in case it is desired to determine manganese electrolytically, transform the solution into one suitable for such a determination.

Separation of Copper from Magnesium.

See Separation of Copper from Aluminium, etc., on page 235.

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* F. Spitzer, Z. Elektrochem., **11,** 407 (1905).

† J. Am. Chem. Soc., **29,** 455 (1907).

Separation of Copper from Cobalt and Nickel.

This separation, which is of importance in the analysis of such alloys as German silver, (Cu, Ni, Zn), can take place with stationary electrolytes either in sulphuric- or nitric-acid solutions; by the rapid method good results are obtained only in nitric-acid solution.

Deposition of the Copper from Sulphuric-acid or from Nitric-acid Solution. The solution, containing about 0.25 gm. of copper and 0.2 gm. of nickel or cobalt, is treated with 3 cc. of concentrated-sulphuric acid, or with 5 cc. of concentrated nitric acid, diluted to 150 cc. and the copper deposited, without heating the solution, with a current of 1 ampere. The analysis requires about 3 hours (*cf.* p. 116 *et seq.*).

In the solution freed from copper, the nickel or cobalt can be deposited by the method described on page 185.

According to P. Denso,* copper can be separated from cobalt and nickel by keeping the voltage within certain limits. The solution, containing 0.13 gm. copper and 0.1 gm. nickel in the form of sulphates, is made 0.2 normal with acid and a current is used of which the potential cannot rise above 2 volts, *e.g.*, the current from a single accumulator cell. Denso recommends the use of a platinized rotating anode. The deposition of the copper is complete at the end of 2 hours and 45 minutes.

The nickel or cobalt can be determined in the solution, freed from copper, after adding an excess of ammonia; or the solution is nearly neutralized with sodium carbonate, and the barely acid solution electrolyzed with a current of 4 volts (two storage cells in series). Platinizing and rotating the anode are desirable.

Rapid Separation of Copper from Nickel.

This method gives good results only in the presence of nitric acid. F. F. Exner † carries out the separation in the following manner. The solution, containing about 0.25 gm. of each metal in 125 cc., is treated with 0.24 cc. of concentrated nitric acid and 3 gms. of ammonium nitrate. The electrolysis is carried out with a platinum dish and rotating spiral anode (about 600 revolutions per minute) with a current of $ND_{100} = 4$ amperes at 5 volts. The deposition of the copper requires about 15 minutes. The stated

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* Z. Elektrochem., **9**, 469 (1903). † J. Am. Chem. Soc., **25**, 905 (1903).

quantity of nitric acid has been found most favorable. The solution is heated nearly to boiling before beginning the electrolysis and it is kept hot by the heating effect of the current.

A. Fischer, in the author's laboratory, confirmed the data of Exner but found it better to give the anode a speed of 1000 revolutions per minute.

Analysis of a Nickel Coin.

Exner carried out a complete analysis of a coin containing copper, nickel and a little iron in 2 hours and 30 minutes by the following method.

The coin, weighing 4.925 gms., was dissolved in 20 cc. of concentrated nitric acid diluted with an equal volume of water, the solution exactly neutralized with ammonia and diluted up to the mark in a 250-cc. calibrated flask. One-tenth of the solution was treated with 3 gms. of ammonium sulphate, diluted to 125 cc., and electrolyzed hot (see above) with a current of $ND_{100} = 5$ amperes at 5.5 volts. The copper was deposited in 20 minutes.

The nickel was next precipitated by caustic soda and bromine water, the precipitated nickelic hydroxide (and ferric hydroxide) filtered off and dissolved in 2 cc. of concentrated sulphuric acid and water. The resulting solution was diluted to 125 cc., after the addition of 30 cc. of strong ammonia, and electrolyzed hot with a current of $ND_{100} = 6$ amperes at 5 volts. The nickel was deposited in 20 minutes.

The solution still contained ferric hydroxide in suspension. It was filtered off, dried, ignited and weighed.

In the above case the ammonium nitrate, formed by the neutralization of the nitric acid, serves to make the nearly neutral solution a better conductor.

Separation of Copper from Molybdenum and from Tungsten.

The deposition of copper in the presence of one of the above metals can be effected in a potassium-cyanide solution. About 1.5 gms. of potassium cyanide are dissolved in 150 cc. of the solution and the electrolysis is carried out at 60° with a current of $ND_{100} = 0.28$ ampere at 4 volts. After 5 or 6 hours, all the copper is deposited.

Separation of Copper from Palladium and from Platinum.

If 1.5 gms. of potassium cyanide and 5 gms. of ammonium carbonate are added to 125 cc. of solution, and the electrolysis is carried out at 70° with a current of $ND_{100} = 0.2$ ampere at 2 to 2.5 volts, the copper will be deposited in 5 or 6 hours.

Rapid Separation of Copper from Platinum.

J. Langness * succeeded in depositing 0.13 gm. of copper free from platinum in 35 minutes under the following conditions. The solution contained 3 gms. of potassium cyanide and 10 cc. of ammonia (*cf.* p. 239) and was electrolyzed hot with a current of 3 to 3.5 amperes at 5 volts potential.

Separation of Copper from Selenium (E. F. Smith)†.

In Sulphuric- or Nitric-acid Solution. To the solution containing about 0.08 gm. copper and 0.25 gm. sodium selenate in 150 cc., 1 cc. of concentrated sulphuric, or nitric acid is added and after heating to 65° the copper is deposited with a current of $ND_{100} =$ 0.05 to 1 ampere at 2.25 volts.

In Potassium-cyanide Solution. The solution, containing 1 gm. of potassium cyanide in 150 cc., is electrolyzed with a current of $ND_{100} = 0.2$ ampere at 4 volts. In both cases the electrolysis requires about 5 hours.

Separation of Copper from Tellurium.

In Nitric-acid Solution. (D. L. Wallace.) To 100 cc. of solution containing about 0.15 gm. copper and 0.11 gm. tellurium, 0.5 cc. of concentrated nitric acid is added and the solution electrolyzed with $ND_{100} = 0.1$ ampere at 2.06 volts. The deposition of the copper requires 5 hours.

In Sulphuric-acid Solution. E. F. Smith ‡ deposited the copper in 6 hours under the following conditions. Used 0.074 gm. copper, 0.2 gm. sodium tellurate, 1 cc. concentrated sulphuric acid; volume 150 cc.: temperature 65°; $ND_{100} =$ 0.05 to 0.1 ampere; 2 to 2.25 volts.

Separation of Copper from Tungsten.

See Separation from Molybdenum on page 241.

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* J. Am. Chem. Soc., **29**, 471 (1907).

† *Ibid.*, **25**, 895 (1903).

‡ *Ibid.*, **25**, 895 (1903).

Separation of Copper from Uranium.

In Nitric-acid Solution. Copper is deposited in 3 hours under the following conditions. Volume 150 cc. with 0.5 cc. concentrated sulphuric acid; temperature 60°; $ND_{100} = 0.14$ to 0.27 ampere; 2 to 2.4 volts.

In Sulphuric-acid Solution. Volume 150 cc.; 2 cc. concentrated sulphuric acid; temperature 55°; $ND_{100} = 0.16$ ampere; 2 volts; time, 4 hours.

Rapid Separation of Copper from Uranium.

In nitric- or sulphuric-acid solution, the separation is effected in the same way as in the separation of copper from aluminium (Ashbrook, see p. 235).

Separation of Copper from Zinc.

In Nitric-acid Solution. M. Heidenreich * has tested the conditions proposed by E. F. Smith and Wallace and found good results as follows. Volume 120 cc.; 4 cc. nitric acid (sp. gr. 1.3); potential of the bath not more than 1.4 volts; time, 18 to 20 hours.

In Sulphuric-acid Solution, the separation can be carried out under the conditions given for the separation of copper from aluminium, or from nickel (pp. 235, 240).

The separation in an oxalic-acid solution has no advantages over these methods.

Rapid Separation of Copper from Zinc.

In Nitric-acid Solution. Exner states that the conditions may be made the same as in the separation of copper from nickel (p. 206), with the difference that the potential is 9 volts.

In Sulphuric-acid Solution. D. S. Ashbrook † obtained a satisfactory separation under the following conditions. Used 0.29 gm. Cu, 0.25 gm. Zn; volume 125 cc.; 1 cc. concentrated H_2SO_4; $ND_{100} = 3$ amperes, gradually raised to 5 amperes; 5 volts; time, 10 minutes. A platinum dish was used as cathode and the spiral anode made 600 revolutions per minute.

Separation of Copper from Tin.

A solution containing these two metals is seldom obtained in the course of an ordinary analysis; as a rule the tin is converted

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* Ber., **28,** 1585 (1895).

† J. Am. Chem. Soc., **26,** 1287 (1904).

into insoluble metastannic acid by the action of nitric acid upon the alloy or ore, while the copper dissolves as nitrate. In this case it is unnecessary to filter the solution. If the electrolysis is to be carried out with a stationary electrolyte, a platinum cone or gauze cathode is used, as mentioned on page 123.

It is a well-known fact that the insoluble metastannic acid invariably contains traces of copper. To free the precipitate from this copper, the cathode is removed from the electrolyte (it may be laid upon a watch glass without washing), the metastannic acid is stirred up into the liquid which is heated and allowed to settle; the cathode is then replaced and the rest of the copper deposited.

In the technical analysis of bronze, a sufficiently pure metastannic acid is obtained by treating the alloy with 50 cc. of nitric acid (sp. gr. 1.2), evaporating just to dryness (without baking the residue) and treating with successive portions of 10 cc. concentrated nitric acid in 50 cc. of water. Finally the solution is heated to boiling and the precipitate allowed to settle (*cf.* Analysis of Bronze).

For the deposition of copper in the presence of metastannic acid, the use of a gauze cathode and rotating anode is advisable and in this way there is little danger of the deposited copper being contaminated with inclusions of metastannic acid.

SILVER.

Separation of Silver from Aluminium.

If the silver is deposited from a nitric-acid solution as described on page 131, the aluminium remains in solution.

Rapid Separation of Silver from Aluminium.

Ashbrook, using a rotating spiral anode (*cf.* p. 229), was able to obtain a quantitative deposition of the silver, but the metal adhered badly to the cathode and was hard to wash without loss. The conditions were: volume = 125 cc.; 1 cc. HNO_3 (sp. gr. 1.43); ND_{100} = 3 amperes, at 3.5 volts; time = 15 minutes.

Under the same conditions, silver may be separated from lead, chromium, iron, cadmium, cobalt, magnesium, manganese, nickel and zinc.

Separation of Silver from Antimony.

The methods based on the use of graded potentials as devised by H. Freudenberg * have been tested and modified by A. Fischer.†

Deposition of Silver in Nitric-Tartaric-acid Solution.

The presence of the tartaric acid, which is necessary to keep the antimony in solution, has a favorable effect; it lessens the resistance of the bath and the discharge potential of the silver from such a solution lies about 0.3 volt higher than from a solution containing only nitric acid. Thus, for depositing the last traces of the silver, it is perfectly safe to increase the potential up to 1.45 volts. The solution containing from 0.24 to 0.29 gm. of silver and 0.18 to 0.34 gm. of quinquevalent antimony is treated with 5 gms. of tartaric acid and 2 cc. of nitric acid (sp. gr. 1.4), diluted to 160 cc. and heated to 50° or 60°. The electrolysis is first carried out for 3 hours at a potential of 1.35 volts corresponding to 0.12 ampere; then, when most of the silver has been deposited, the potential is increased to 1.4 to 1.45 volts. At the end of 8 or 9 hours the deposition of the silver is complete and no antimony will be found with the silver because under the above conditions antimony is not reduced to the trivalent condition until the potential of the current reaches between 1.5 and 1.6 volts. The current strength then falls to 0.02 ampere. The tartaric acid, owing to its reducing action, prevents the deposition of silver peroxide upon the anode and thus the addition of alcohol is unnecessary for this purpose. If the electrolysis is conducted at the laboratory temperature, the analysis requires nearly 18 hours. The deposit must be washed while the current is passing.

To prepare the electrolyte for the antimony determination, it is merely necessary to concentrate by evaporating and, after neutralizing with sodium hydroxide, to treat with 80 cc. of a saturated solution of sodium sulphide. A little potassium cyanide is added (*cf.* p. 159) and the electrolysis carried out at 60° to 70° with 1 to 1.5 amperes and 1.3 to 1.6 volts.

Deposition of the Silver from Potassium-Cyanide Solution.

The antimony must be present in the quinquevalent condition and the reason for this will be made clear. In a solution of potas-

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* Z. phys. Chem., **12,** 109 (1893). † Ber., **36,** 3345 (1903).

sium-silver cyanide containing about 0.3 per cent silver and some tartaric acid, the deposition of silver begins with an electromotive force lying between 1.9 and 2 volts. This must be raised to 2.6 volts at the last in order to precipitate the last traces of silver, within a reasonable length of time. In such a solution the deposition of antimony in the quinquevalent condition does not begin until the potential of the current reaches 2.6 volts, but it takes place between 2 and 2.1 volts if the antimony is present in the trivalent condition. It is thus impossible to carry out the separation if trivalent antimony is present.

The solution must contain 0.5 to 1 gm. of tartaric acid and 3 to 5 gms. of potassium cyanide in 150 to 180 cc. It is heated to 40° or 50° and electrolyzed with a current whose potential reaches 2.5 volts but must not rise above 2.6 volts. The current strength is 0.18 ampere at the start and falls toward the end of the reaction to about 0.04 ampere. The analysis requires about 8 hours (19 to 20 hours at the ordinary temperature). The washing of the deposit can be accomplished after the circuit is broken if it is done quickly.

In the solution concentrated by evaporation, the antimony can be determined as described above after the addition of a little more cyanide.

As regards the choice between the above two methods, the latter, on account of the limited solubility of the antimonate, is to be recommended when less antimony than silver is present.

The potassium cyanide must be pure and free from cyanate, being dissolved freshly before each analysis. An impure cyanide will cause the formation of an ill-looking, yellowish-green silver deposit and its weight will be too high.

Separation of Silver from Arsenic.

The separation of silver in potassium-cyanide solution succeeds under the conditions described for the separation of silver from antimony and the arsenic must be present in the quinquevalent condition.

Separation of Silver from Lead.

It has been shown (p. 131) that slight acidity and a low-potential current are necessary for the formation of a good silver deposit and that the best deposits of lead peroxide are obtained in a strongly acid solution with a high voltage (p. 194). Arth and Nicolas * take advantage of this contrasted behavior for the determination of small quantities of silver in the presence of much lead. Since the volume of the solution is relatively large, on account of taking a large sample for the analysis, the electrolysis is conducted in a beaker with gauze electrodes (p. 59). According to the silver content, from 2.5 to 100 gms. of the lead alloy are dissolved in nitric acid and the excess of acid is removed by evaporating to dryness, because in carrying out the electrolysis it is necessary to regulate closely the quantity of acid present. The dry residue is dissolved in water and the volume of the solution is adjusted about as follows: 130 cc. for 2.5 gms. of alloy, 300 cc. for 5 to 20 gms., 500 cc. for 40 to 100 gms. One per cent by volume of concentrated sulphuric acid is added and 6 cc. of 95 per cent alcohol. If less acid were added, some lead is likely to precipitate with the silver upon the cathode. The solution is heated to 55° or 60° and electrolyzed with a maximum potential of 1.1 volts. A current of higher voltage than this may give rise to spongy deposits. At the laboratory temperature the electrolysis would require a long time but at 60°, 7 hours is usually enough. If the volume of the solution is large, the current must be allowed to flow a little longer and the solution stirred often to hasten the migration of the silver to the cathode.

The authors have published numerous results to show the value of the method. The quantity of silver present in the alloys tested varied from 0.011 gm. Ag and 2.5 gms. Pb to 0.001 gm. Ag and 100 gms. Pb. For the determination of still smaller quantities of silver, an even larger weight of alloy may be taken and a larger volume of solution used but the percentage of acid present should be kept the same. In the more concentrated solutions, a deposit of lead peroxide is often noticed on the anode but this has no effect upon the silver determination. If the gain in weight at the cathode is too small to determine with certainty, the same cathode may be used in the analysis of another portion of the alloy.

Small quantities of copper or bismuth, often present in commercial lead, do not cause any difficulty as they are not deposited at the low voltage used.

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* Bull. soc. chim., [3], **29**, 633 (1903).

Rapid Separation of Silver from Lead.

The difficulty of determining large quantities of silver in the presence of lead lies in the danger of some silver peroxide being deposited upon the anode with the lead peroxide. Silver peroxide, however, is very unstable in a sulphuric-acid solution at the boiling temperature and Sand makes use of this fact in his method for depositing lead in the presence of silver (*cf.* p. 42). The solution he used contained, in about 85 cc., 0.28 gm. of lead and 0.27 gm. of silver; it was treated with 10 to 15 cc. of concentrated nitric acid and was kept boiling during the ten minutes required for the electrolysis. As outer electrode (anode) for receiving the lead-peroxide deposit, the gauze electrode shown on page 66 was used and the inner electrode (cathode) made 300 to 600 revolutions per minute. The potential of the current was 1.6 to 1.7 volts and the current strength was 3 to 4 amperes.

Before attempting to deposit the silver in the solution freed from lead, it is necessary to dissolve the small deposit of silver that has formed upon the cathode while the lead peroxide was being precipitated. The solution is then transformed into an acetate solution and the silver determined.

Separation of Silver from Bismuth.

Bismuth is near copper in the potential series of the metals. Thus H. Freudenberg * succeeded, in his analyses based upon graded potentials, in effecting a separation of silver and bismuth in much the same manner as in the case of silver and copper. The best conditions for the separation of silver and copper, however, are those of Küster and v. Steinwehr (p. 225), and these should be followed here.

Rapid Separation of Silver from Bismuth.

This can be effected in the same way as in Sand's method for separating silver from copper (p. 227).

Separation of Silver from Platinum.

According to L. G. Kollock,† a solution containing 0.2 gm. of each metal and 1.25 gms. of pure potassium cyanide in about 125 cc. may be electrolyzed at 70° with a current of ND_{100} =

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* Z. phys. Chem., **12,** 108 (1893).

† J. Am. Chem. Soc., **21,** 911 (1899).

0.04 ampere at 2.5 volts. In about 3 hours all the silver will be deposited.

For the rapid separation, the electrolysis may be carried out in the manner described for separating silver from copper (p. 227). About 0.12 gm. silver is deposited in 20 minutes with a current of 3 volts in an electrolyte containing 1.5 gms. potassium cyanide. The current strength is 0.25 ampere at the start but falls to 0.05 ampere (Julia Langness).

Separation of Silver from Selenium.

Inasmuch as silver selenite requires for its solution more nitric acid than should be present in a solution from which a satisfactory deposit of silver is to be obtained, J. Meyer,* who determined the atomic weight of selenium in this way, used a potassium-cyanide solution as electrolyte. The silver selenite is dissolved in 100 cc. water, some potassium cyanide is added, and, after heating to 60° or 70°, the solution is electrolyzed with a potential of 2.25 volts at the start. Toward the last the electromotive force should be increased to 3.65 volts. The above temperature is maintained throughout the 6 hours required for the complete deposition of the silver. The voltage may be regulated with the thermopile or by means of the arrangement described on page 212. A platinum dish and disk anode are suitable electrodes.

No method is known for the electrolytic determination of selenium. The potassium-cyanide solution from which the silver has been deposited is made slightly acid with hydrochloric acid, 1 or 2 gms. of hydrazine sulphate † are added and the solution is heated upon the water bath until the precipitated selenium is changed into the black modification, and the supernatant solution is clear. The selenium is filtered upon an asbestos filter (Gooch crucible), washed, and dried at 100° to 110° before weighing.

Separation of Silver from Zinc.

After E. F. Smith and Spencer had found that this separation was accomplished much more quickly in a hot solution containing potassium cyanide than in a similar solution at the ordinary temperature, Smith and Wallace ‡ studied the conditions more closely but paid no attention to the voltage of the current used. In this

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* Z. anorgan. Chem., **31,** 391 (1902).

† P. Jannasch., Ber., **31,** 2393 (1898).

‡ Z. Elektrochem., **2,** 312 (1895).

respect the work was perfected by M. Heidenreich in the Aachen laboratory. Heidenreich found that the separation took place best at a temperature of 60° to 70° with an electromotive force of 1.9 to 2 volts. The solution should contain 0.2 to 0.25 gm. silver, 0.16 gm. zinc and 2 to 2.5 gms. of potassium cyanide. As electrodes a roughened platinum dish and disk anode may be used. The current strength may run from 0.05 to 0.02 ampere. The determination of the silver will require about 6½ hours.

If only 1 gm. of potassium cyanide is added to a solution containing about 0.1 gm. of each metal, the electrolysis may be carried out, according to L. G. Kollock,* in 3 hours with a current of ND_{100} = 0.32 to 0.38 ampere and a potential of 2.6 volts.

Rapid Separation of Silver from Zinc.

Julia Langness electrolyzed a solution containing 0.12 gm. silver and 2.5 gms. of potassium cyanide with a current of 0.35 ampere and potential of 3 volts at the start; toward the end the current strength dropped to 0.08 ampere. The silver was all deposited at the end of 20 minutes. The other conditions were the same as given for the separation of copper from silver (p. 227).

MERCURY.

Separation of Mercury from Aluminium.

The method is the same as that described for the deposition of mercury in nitric-acid solution (p. 135).

Separation of Mercury from Antimony, Arsenic and Tin.

In an ammoniacal tartrate solution the mercury may be deposited in the presence of one or all of these other metals. A solution containing about 0.1 gm. of each metal is treated with 8 gms. tartaric acid and 30 cc. of 10 per cent ammonia, diluted to 175 cc. and electrolyzed at 60° with a current of ND_{100} = 0.05 ampere at 1.7 volts. The mercury is deposited in 6 hours.

If only one metal other than mercury is present, the addition of 5 gms. of tartaric acid and 15 to 30 cc. of ammonia suffices (S. C. Schmucker).†

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* J. Am. Chem. Soc., **21,** 911 (1899).

† *Ibid.,* **15,** 204 (1893).

Separation of Mercury from Alkaline Earths, Magnesium and the Alkalies.

The same conditions hold as for the electrolysis of mercury from a nitric-acid solution.

Separation of Mercury from Cadmium, Cobalt, Nickel and Iron.

This separation also is conducted in a *nitric-acid solution* in the same manner as in the separation of mercury from aluminium.

In Potassium-cyanide Solution mercury can be separated from cadmium. To a solution containing about 0.12 gm. mercury and 0.22 gm. of cadmium, 2.5 gms. of potassium cyanide are added, and enough water to make the total volume 125 cc. The electrolysis is conducted with a current of ND_{100} = 0.18 ampere and potential 1.7 volts. At the laboratory temperature the time required is about 7 hours.

Separation of Mercury from Manganese.

In a sulphuric-acid solution the mercury is obtained as metal upon the cathode and the manganese as dioxide upon the anode (dish). The latter deposit, however, does not always adhere well, particularly when more than 0.06 gm. of manganese is present. Moreover, much mercury cannot be determined if a disk is used as cathode; it has a relatively small surface upon which but little mercury can be held without its dropping off. More mercury can be determined if a platinum gauze cathode is used.

According to B. Neumann, the solution is prepared for electrolysis by adding 10 drops of concentrated sulphuric acid. The current strength is ND_{100} = 0.4 to 0.6 ampere at 4 volts.

Separation of Mercury from Selenium.

E. F. Smith * effected this separation in a potassium-cyanide solution (*cf.* p. **136**) containing about 0.13 gm. of mercury, 0.25 gm. of sodium selenate and 1 gm. potassium cyanide. The volume of the solution was 150 cc., the temperature 60° † and the mercury was deposited in 6 hours by a current of 0.03 ampere at 3 volts. Concerning the determination of the selenium, see page 249.

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* J. Am. Chem. Soc., **25**, 894 (1903).

† Regarding the possibility of some loss of mercury, see page 135.

Separation of Mercury from Tellurium.

Smith succeeded in accomplishing this separation in a potassium-cyanide solution (see the preceding paragraph), but not in a nitric-acid solution. The conditions were: about 0.13 gm. of mercury, 0.25 gm. of sodium tellurate, 3 cc. of sulphuric acid (sp. gr. 1.43), total volume 150 cc., temperature 60°,* $ND_{100} = 0.04$ to 0.05 ampere, potential 2 to 2.25 volts, time 5 hours.

Separation of Mercury from Zinc.

According to Kollock the following conditions proved satisfactory: To a solution containing 0.12 gm. of mercury as mercuric chloride and 0.1 gm. of zinc as zinc sulphate, 2 gms. of potassium cyanide were added, and the solution having a volume of 125 cc. was electrolyzed at 50° with a current of $ND_{100} = 0.03$ ampere and a potential difference of 2.9 volts. The mercury was completely precipitated in 4 hours.

Separation of Mercury from Bismuth.

This can be accomplished, according to Sand, by the method recommended for the separation of mercury from copper (p. 230).

GOLD.

Separation of Gold from Platinum.

The solution of the two metals is treated with 1.5 gms. of potassium cyanide, diluted to about 350 cc. and the gold deposited at 70° with a current of $ND_{100} = 0.01$ ampere at 2.7 volts. In 3 hours about 0.15 gm. of gold may be deposited in the presence of 0.1 gm. of platinum. (L. G. Kollock.)†

Rapid Separation of Gold from Platinum.

Julia Langness ‡ effected a successful separation under the following conditions. The solution of the chlorides, containing 0.05 to 0.1 gm. of gold and 0.04 to 0.1 gm. of platinum, was treated with 2 gms. potassium cyanide, diluted to 125 cc. and electrolyzed at the boiling temperature with 2.5 amperes at 6 volts. The spiral anode made 500 to 600 revolutions per minute and the analysis required from 15 to 20 minutes.

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* *Cf.* footnote, p. 251.

† J. Am. Chem. Soc., **21,** 923 (1899).

‡ *Ibid.*, **29,** 470 (1907).

Separation of Gold from Palladium.

The gold is deposited under similar conditions as when platinum is present. Potassium cyanide 2 gms., volume 150 cc., temperature 65°, $ND_{100} = 0.03$ to 0.04 ampere, 2.5 volts. For the deposition of 0.13 gm. of gold, 5 hours are required.

Rapid Separation of Gold from Palladium.

The conditions are similar to the rapid method for separating gold from platinum. Potassium cyanide 1 gm., potential 6 volts, and current strength 2 amperes. The gold is deposited in 10 to 30 minutes.

PLATINUM.

Separation of Platinum from Iridium.

As stated on page 141, a dense deposit of platinum may be obtained with the aid of a current of $ND_{100} = 0.05$ ampere at 1.2 volts potential. Under these conditions, all the iridium will remain in solution.

ANTIMONY.

Separation of Antimony from Tin.

The quantitative separation of antimony from tin offers considerable difficulty according to the usual methods of gravimetric analysis but the electrolytic separation is simple as well as accurate. The quantitative deposition of the antimony takes place in a concentrated solution of pure sodium monosulphide to which a certain amount of pure sodium hydroxide has been added.

Sufficiently pure commercial sodium monosulphide (free from antimony and iron) can now be purchased. The sodium hydroxide must likewise be pure and the product prepared from metallic sodium is to be recommended. Although the addition of sodium hydroxide is unnecessary in the absence of tin (*cf.* p. 157), in this case it is required to react with any sodium-hydrogen sulphide that may be present. This salt tends to prolong the time required for the complete deposition of the antimony and also favors the deposition of some tin with the antimony. Some sodium-hydrogen sulphide, NaSH, may be present in the sodium monosulphide or it may be formed from the latter as the result of hydrolysis:

$$Na_2S + H_2O \rightleftarrows NaSH + NaOH.$$

In accordance with the mass-action principle, the addition of sodium hydroxide prevents the hydrolysis.

To reduce polysulphides, shown by a yellow-colored solution to be present, and to prevent their formation during the progress of the electrolysis, it is necessary to add some potassium cyanide (*cf.* p. 156). As a result of the absence of polysulphides, the reducing action at the cathode is more energetic than it would be otherwise, for a part of the current would be used for the reduction of the polysulphides. When polysulphides are absent there is danger of some of the current being used for the liberation of hydrogen at the cathode or for the deposition of some tin. Since in order to accomplish the complete deposition of the antimony the potential of the bath cannot be lowered below 0.8 volt, it is necessary to keep the temperature of the bath close to 30° which has been found experimentally to be the most favorable temperature. In this case the potential may be as high as 1.1 volts.

The experiments of A. Fischer * at Aachen have established the following conditions: The concentrated, aqueous solution of the salts, or the solid salts or sulphides, containing about 0.3 gm. antimony and from 0.3 to 0.5 gm. of tin, is treated with a solution of sodium monosulphide which is saturated with the salt at 30°, with 5 to 15 cc. of a 30 per cent potassium-cyanide † solution, and with a concentrated solution of about 2 gms. of sodium hydroxide. Then, if necessary, enough more of the sodium-sulphide solution is added to make the total volume 110 to 120 cc. The success of the separation depends largely upon the use of a properly prepared saturated sodium-sulphide solution. The current is adjusted to a potential of 1.0 to 1.1 volts and the current strength is then 0.35 to 0.64 ampere. The quantity of potassium-cyanide solution stated above is regulated according to the current strength, more being added with a strong current than with a weak one. The voltage and temperature (30°) are kept constant during the entire operation. After 7 or 8 hours the deposition of the antimony is complete and the current drops to between 0.24 and 0.57

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* Dissertation, Leipsic, 1904.

† Hollard and Bertiaux state that the addition of potassium cyanide prevents the deposition of copper. There is little danger of copper being present, however, because the solubility of copper sulphide in alkaline-sulphide solutions is due to the presence of sodium-hydrogen sulphide or of sodium polysulphide and these compounds are absent in the solution used here.

ampere. The method of testing to see when the analysis is finished was described on page 158.*

In discussing the determination of antimony by itself (p. 157), it was stated that the presence of alkali hydroxide caused the results to be a little too high. Experiments by Dr. Scheen at Aachen have shown that there is little harm caused if not more than about 2 gms. of pure sodium hydroxide are used. For the most accurate results, however, it is advisable to dissolve the deposit in alkali polysulphide solution, to add the requisite amount of potassium cyanide, and to repeat the electrolysis.

Determination of Tin after the Removal of Antimony.

It was indicated on page 160 that the deposition of tin from the solution of its thio salt has no advantages over the electrolysis of an oxalate solution. This is especially true in the case at hand. The complete deposition of tin is possible only in a solution of ammonium sulphide and does not succeed in the presence of sodium sulphide. Moreover, the presence of potassium cyanide increases the difficulty of preparing a suitable electrolyte, because the cyanide must be removed, or a spongy tin deposit will be obtained.

The simplest way to prepare the electrolyte for the tin determination is to acidify with acetic acid, heat until all the hydrogen sulphide and hydrogen cyanide have been expelled and filter off the precipitated tin sulphide. After the precipitate has been washed free from the greater part of the salts in solution, the filter paper, with precipitate, is spread out on the bottom of a small dish and the sulphide dissolved by heating with water and 20 gms. of oxalic acid. The solution is transferred to the electrolyzing vessel, treated with 10 gms. of ammonium oxalate and the electrolysis is conducted as described on page 160. Since a large quantity of oxalic acid is already present, it is not usually necessary to add any more during the electrolysis (*cf.* p. 160).

Separation of Antimony from Arsenic.

The fact that it is not practicable to determine arsenic electrolytically was mentioned on page 162. In many cases, however,

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* To test the antimony deposit for tin, it is merely necessary to allow a little hydrochloric acid to flow over the deposit and to pour this acid into a solution of mercuric chloride; a turbidity will result if tin is present in the deposit.

arsenic is deposited upon the cathode in the electrolytic determination of other metals and, to prevent such contamination, special precautions have to be taken in each individual case. This is especially true with regard to the electrolytic determination of antimony, and here, as in other cases, a marked difference is observed in the behavior of arsenic, dependent upon whether it is present in the trivalent or quinquevalent condition. In an *alkaline* solution arsenious acid is oxidized to arsenic acid by the action of the electric current. If, however, a solution containing both antimony and arsenious acid is electrolyzed, a mixture of antimony and arsenic is deposited. The action is different if the arsenic is present in the solution as *arsenic* acid; in the presence of free alkali, the antimony alone is precipitated from a *concentrated sodium-sulphide* solution.

To separate these two elements, therefore, any arsenic present as arsenious acid must be oxidized to arsenic acid. Nitric acid or aqua regia should be added to the solution, the acid completely expelled by evaporating to dryness on a water bath and the residue treated with 80 cc. of a solution of sodium sulphide, saturated at 30°. The potassium cyanide and sodium hydroxide are added and the electrolysis is conducted as in the separation of antimony from tin (*cf.* p. 254).

To determine the arsenic, the antimony-free solution is acidified with dilute sulphuric acid, heated on the water bath to expel the hydrogen sulphide and hydrogen cyanide, filtered, and the precipitate dissolved in hydrochloric acid with the addition of potassium chlorate. This solution is treated with ammonia in excess, and the arsenic acid precipitated as magnesium-ammonium arsenate with magnesium mixture.

The precipitate may be dried, at 110°, on a tared filter and weighed as magnesium ammonium arsenate, or it may be converted into magnesium pyroarsenate by careful ignition in a porcelain crucible.

Separation of Antimony, Tin and Arsenic.

Since arsenic cannot be separated from tin electrolytically, it is necessary to determine the arsenic by the ordinary analytical methods before attempting to determine the tin by electrolysis. One of the best methods for separating arsenic from tin is the distillation of the arsenic trichloride from a solution containing a reducing agent. The arsenic may be expelled first, and in this way separated from both antimony and tin; or the antimony may be determined electrolytically and the distillation accomplished after the removal of the antimony. The second method requires that the arsenic should be in the quinquevalent conditions (see preceding page) and thus, in most cases, a preliminary oxidation is necessary. In the subsequent removal of the arsenic by distillation, it is necessary to convert the arsenic wholly into the trivalent condition. When the first method is employed, *i.e.*, when the arsenic is distilled from a solution containing both tin and antimony, it is immaterial what the condition of the arsenic is at the start, as enough reducing agent is added in all cases to effect the complete reduction. Moreover, a further advantage of this method lies in the fact that if hydrogen sulphide is used as the reducing agent, as recommended by Piloty and Stock, no foreign solid need be added to the solution. Formerly ferrous chloride was used to reduce the arsenate. It was then necessary to precipitate the tin, or the antimony and tin, with hydrogen sulphide and to transform the precipitated sulphides into the soluble thio salts before going on with the electrolysis.

The method for distilling arsenic trichloride is discussed in many textbooks of quantitative analysis and will not be considered in detail here.* The solution remaining in the flask after the distillation is boiled to expel hydrogen sulphide, neutralized with sodium hydroxide, and treated with sodium monosulphide solution, potassium cyanide and sodium hydroxide as described on page 254.

If the arsenic, antimony and tin are present at the start in the form of sulphides, they are dissolved by warming with concentrated hydrochloric acid and potassium chlorate; the excess of chlorine is expelled, and the solution rinsed into the distillation flask with concentrated hydrochloric acid.

Separation of Antimony from Bismuth.

These two metals may be separated in much the same way as copper and antimony (p. 236). S. C. Schmucker† treats the solution with 5 gms. of tartaric acid and 15 cc. of ammonia. After diluting to 175 cc. the solution is electrolyzed at 50° with a current of $ND_{100} = 0.022$ ampere at 1.8 volts. After 6 hours all the bismuth is deposited.

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* *Cf.* Treadwell-Hall, "Quantitative Analysis."

† J. Am. Chem. Soc., **15**, 203 (1903).

ZINC.

Separation of Zinc from Manganese.

The zinc is deposited from a solution containing free oxalic acid (p. 172), which prevents the deposition of any manganese dioxide upon the anode.

E. J. Riederer * deposits the zinc in a lactic-acid solution under the following conditions. As cathode a silvered platinum dish is used and to obtain an even deposit it is necessary to keep the solution well stirred; a rotating anode is placed 0.5 cm. from the cathode. The electrolyte contains about 0.11 gm. of zinc as sulphate in 230 cc. (nitrates of chlorides should not be present) 5 gms. of ammonium lactate, 0.75 gm. of lactic acid and 2 gms. of ammonium sulphate. The temperature should lie between 15° and 28°. The current density, $ND_{100} = 0.2$ to 0.24 ampere and the potential, about 3.8 volts. The deposition of the zinc requires from 4 to 5½ hours. The manganese content may lie between 0.03 and 0.35 gm. During the electrolysis the color of permanganate formed is darker in proportion to the quantity of manganese present. The electrolysis would take too long if carried out below 15°, and above 28° a crystalline or spongy deposit of zinc will be obtained; this is also true if the current density is over 0.3 ampere.

In formic-acid solution, G. P. Scholl † carries out the deposition of zinc in the presence of manganese as follows: To the solution, containing about 0.1 gm. of zinc as sulphate, 10 cc. of formic acid (sp. gr. 1.06) and 5 cc. of ammonium-formate solution (obtained by neutralizing formic acid of the above strength with strong ammonia) are added and the electrolysis is conducted with a current of $ND_{100} = 1$ ampere and a potential of 5.4 volts. A roughened platinum dish is used as cathode with the sieve anode shown on page 57. The electrolysis requires about 11 hours.

Separation of Zinc from Aluminium.

The separation is accomplished by depositing the zinc from an oxalate solution. Too high a temperature must be avoided for the reasons stated on page 269.

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* J. Am. Chem. Soc., **21**, 789 (1899).

† *Ibid.*, **25**, 1055 (1903).

Separation of Zinc from Lead.

The lead is deposited in nitric-acid solution as peroxide (p. 194), and then, after neutralizing with caustic-potash solution, the zinc is determined according to page 184.

Separation of Zinc from Bismuth.

When bismuth is deposited from a nitric-acid solution, the zinc remains dissolved and can be determined subsequently as described on page 169.

CADMIUM.

Separation of Cadmium from Aluminium, Alkaline Earths, Magnesium and the Alkalies.

The separation can be effected in a sulphuric-acid solution by the methods described on page 174 *et seq.* It is best to filter off any insoluble sulphates of the alkaline earths.

Rapid Separation of Cadmium from Aluminium.

In a sulphuric-acid solution, Ashbrook separated 0.27 gm. of cadmium in 10 minutes from an equal quantity of aluminium under the following conditions: Volume 125 cc. with 2 cc. of concentrated sulphuric acid; solution heated to boiling before electrolyzing; current $ND_{100} = 5$ amperes at 5 volts. The deposits were somewhat spongy but could be weighed without loss. A platinum dish was used as cathode and the spiral anode revolved about 600 times in a minute.

Separation of Cadmium from Antimony.

According to Schmucker, these two elements may be separated in a strongly ammoniacal solution, as in the separation of copper from antimony on page 236.

Separation of Cadmium from Arsenic.

In Ammoniacal Tartrate Solution. According to Schmucker, this separation is the same as the separation of cadmium from antimony.

In Potassium-cyanide Solution. H. Freudenberg * obtained deposits of cadmium free from arsenic, by using only a slight excess of potassium cyanide, having the arsenic in the quinquevalent condition, and not letting the potential rise above 2.6 to 2.7 volts.

The separation depends upon the fact that there is a greater tendency to form cadmium cations than trivalent arsenic cations (*cf.* p. 233).

Separation of Cadmium from Bismuth.

Sand, by controlling the cathode potential with the aid of his auxiliary electrode, was able to effect a quantitative separation. This is due to the fact that cadmium is not deposited until the potential of the auxiliary electrode † is more than 1 volt and under this voltage the bismuth can be deposited.

The solution, containing about 0.38 gm. of bismuth and the same quantity of cadmium, was treated with 2.5 cc. of concentrated nitric acid, and 18 gms. of tartaric acid, heated to 80° and the potential of the auxiliary electrode adjusted to 0.43 volt. The potential between the electrodes was then about 1.7 volts and the initial current 3 amperes. The potential of the auxiliary electrode was gradually allowed to rise to 0.53 volt. At the end of 10 minutes all the bismuth was deposited and the current had sunk to 0.2 ampere.

To deposit the cadmium, the solution was made alkaline with 17 gms. of sodium hydroxide and the cold solution electrolyzed with a current of 2 amperes at a potential of 2.7 volts. This determination required 18 minutes.

Separation of Cadmium from Cobalt.

In Sulphuric-acid Solution, H. Freudenberg‡ succeeded in depositing the cadmium under the following conditions. The solution contained 0.2 gm. cadmium, 3 to 4 cc. of concentrated solution of ammonium sulphate, and 2 to 3 cc. of dilute sulphuric acid. The maximum potential between the electrodes was 2.8 to 2.9 volts.

In a Potassium-cyanide Solution, the same author deposited the

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* Z. phys. Chem., **12**, 122 (1893).

† This expression is used here and at other places on account of its simplicity. It is not an accurate statement; *cf.* p. 42.

‡ Z. phys. Chem., **12**, 122 (1893).

cadmium in the presence of an excess of potassium cyanide with a potential of 2.6 to 2.7 volts.*

Separation of Cadmium from Iron.

In Sulphuric-acid Solution, the conditions are the same as in separation of cadmium from cobalt.

In Potassium-cyanide Solution. According to W. Stortenbeker,† the sulphates of the two metals are dissolved in 100 cc. of water slightly acidified with a few drops of dilute sulphuric acid, and to this solution 2 to 3 gms. of potassium cyanide are added. The mixture is then warmed until perfectly clear, and if it takes too long for the solution to assume the yellow color of potassium ferrocyanide, a few drops of a solution of potassium hydroxide are added. The solution is diluted to 200 cc. and electrolyzed with a current of ND_{100} = 0.05 to 0.10 ampere, at the room temperature. Cadmium will be deposited. It is well to electrolyze overnight but the analysis may be hastened by increasing the current to 0.4 ampere.

If the solution contains considerable ferric salt, a small quantity of ferric hydroxide remains undissolved in the potassium-cyanide solution. Although this precipitate does little harm, it is better to reduce the ferric salt, before adding the potassium cyanide, by the addition of sodium sulphite to the solution slightly acid with sulphuric acid.

Rapid Separation of Cadmium from Iron.

The same method may be used as described for the separation of cadmium in sulphuric-acid solution (Ashbrook, *cf.* p. 259).

In Potassium-cyanide Solution, A. L. Davison ‡ succeeded in depositing, in 25 minutes, about 0.26 gm. of cadmium in the presence of 0.25 gm. of iron. The electrolyte was prepared, as described above, by the addition of 12 gms. of potassium cyanide and 2 gms. of sodium hydroxide, and, after heating to boiling, it was electrolyzed with a current of $ND_{100} = 5$ amperes at 5 volts. A platinum dish was used as cathode and a spiral anode was made to revolve 700 times per minute.

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* The rapid separation has met with difficulties. See D. S. Ashbrook, J. Am. Chem. Soc., **26**, 1288 (1904); A. L. Davison, *Ibid.*, **27**, 1286 (1905).

† Z. Elektrochem., **4**, 409 (1898).

‡ J. Am. Chem. Soc., **27**, 1286 (1905).

Separation of Cadmium from Lead.

See Separation of Lead from Other Metals, page 284.

Separation of Cadmium from Manganese.

According to E. F. Smith the simultaneous deposition of cadmium upon the cathode and of manganese dioxide upon the anode may be effected under the following conditions. The solution is acidified with 2 to 3 cc. of sulphuric acid (sp. gr. 1.09), diluted to 125 cc. and electrolyzed at 65° with a current of $ND_{100} = 0.08$ ampere at 2.6 volts. A roughened platinum dish is used as the anode.

Separation of Cadmium from Mercury.

In Sulphuric-acid Solution. To 125 cc. of the solution, 3 cc. of concentrated sulphuric acid are added and the electrolysis is carried out at 65° with a current of $ND_{100} = 0.5$ ampere at 3.5 volts. The deposit is washed before breaking the circuit.

After concentrating the solution and washings the cadmium may be determined directly or after transformation into a potassium-cyanide solution (*cf.* p. 176).

In Potassium-cyanide Solution. Kollock * describes an experiment in which 2.5 gms. of potassium cyanide were added to a solution containing 0.1182 gm. of mercury as mercuric chloride and 0.2 gm. of cadmium as sulphate, and the solution having a volume of 125 cc. was electrolyzed at 65° with a current of $ND_{100} = 0.018$ ampere and a potential difference of 1.7 volts. The mercury was completely precipitated in 7 hours. At lower temperatures and with higher current density the cadmium is deposited with the mercury.

After the deposit of mercury had been removed, the cadmium was determined with a stronger current (*cf.* p. 176).

Separation of Cadmium from Nickel.

In Sulphuric-acid Solution, the separation is carried out as described for the separation of cadmium from manganese.

The rapid separation is the same as for the separation of cadmium from aluminium.

In Potassium-cyanide Solution. Owing to the slight stability of the complex potassium cadmium cyanide, the separation of

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* J. Am. Chem. Soc., **21**, 919 (1899).

cadmium from cobalt was accomplished without any difficulty (p. 228), but the separation of cadmium from nickel was first attempted in vain by E. F. Smith and L. K. Frankel as well as by H. Freudenberg.* This difference in the behavior of nickel and cobalt is explained by the well-known fact that the cobaltocyanide anion is readily changed by oxidation into the more stable cobalticyanide anion

$$2\,[Co(CN)_6]^{--} + H_2O + O = 2\,[Co(CN)_6]^{---} + 2\,OH^-.$$

The nickelocyanide does not experience the corresponding change but tends, rather, to break down into nickel cations and cyanogen anions.

$$K_2\,[Ni(CN_4)] \rightleftarrows 2\,K^+ + [Ni(CN)_4]^{--}$$
$$[Ni(CN)_4]^{--} \rightleftarrows Ni(CN)_2 + 2\,(CN)^-$$
$$Ni(CN)_2 \rightleftarrows Ni^{++} + 2\,(CN)^-.$$

Smith and Frankel attributed the fact that the cadmium deposit contained nickel to the presence of nickelous cations. These authors finally succeeded in effecting a separation by adding potassium hydroxide to the solution. The alkali tends to prevent the breaking down of the potassium nickelocyanide. The separation was carried out in the following manner.

To the solution, containing about 0.17 gm. of cadmium and 0.16 gm. of nickel, 3 gms. of potassium cyanide and 2 gms. of potassium hydroxide (or NaOH) were added and, after diluting to 175°, the solution was electrolyzed at 40° with a current of ND_{100} = 0.03 to 0.04 ampere at 2.25 to 3 volts.

To determine the nickel in the solution after it has been freed from cadmium, the cyanide may be decomposed by boiling with sulphuric acid under the hood and the nickel determined in ammoniacal solution as described on page 185.

Separation of Cadmium from Silver.

The silver can be deposited in *nitric-acid* solution by the method given on page 132, using a maximum potential of 1.35 to 1.38 volts.

The nitric-acid solution may then be changed into an acetic-acid solution by adding sufficient sodium acetate to combine with the nitric acid. From this solution, heated to 50°, the cadmium is

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* Z. phys. Chem., **12**, 122 (1893).

deposited by a current of $ND_{100} = 0.05$ to 0.06 ampere at 3.5 volts. The washing is done before the current is turned off.

The silver may also be deposited from a *potassium-cyanide* solution by adding 2 gms. of potassium cyanide to the solution containing about 0.15 gm. of each metal. The solution is diluted to 125° and electrolyzed at about 70° with a current of $ND_{100} = 0.02$ ampere at 2.1 volts.

The potassium-cyanide solution may be analyzed for cadmium as described on page 176.

Separation of Cadmium from Zinc.

In Sulphuric-acid Solution. The values for the decomposition potentials of these two metals (in normal solution: $CdSO_4 = 2.24$ volts, $ZnSO_4 = 2.54$ volts) is sufficient to permit an electrolytic separation of these two elements. Moreover, on account of the overvoltage of hydrogen toward cadmium, the electrolysis can be carried out in fairly acid solution and it is thus possible to separate cadmium from relatively large quantities of zinc. According to P. Denso,* the solution containing 0.1 gm. of each metal is made double-normal with respect to sulphuric acid (1 per cent H_2SO_4) and electrolyzed with gauze electrodes. The solution has a volume of about 100 cc. and the potential of the current should not exceed 2.6 volts,† corresponding to a current strength of 0.08 ampere. The deposition of this quantity of cadmium is complete at the laboratory temperature in 6 hours.

From a solution containing 8 gms. of zinc and about 0.2 gm. of cadmium, made normal with sulphuric acid, the cadmium was deposited quantitatively overnight with a current of 2.6 to 2.88 volts (0.22 ampere).

This separation in sulphuric-acid solution by the use of a graded potential is desirable, because copper, which is found frequently in the presence of cadmium and zinc, can be deposited from sulphuric-acid solution (*cf.* p. 116).

After the removal of the cadmium, the zinc may be deposited in alkaline solution after neutralization of the free acid (*cf.* p. 184).

In Acetic-acid Solution. The solution containing the two metals

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* Z. Elektrochem., **9**, 470 (1903).

† The potential of the bath must exceed somewhat the decomposition potential in order to overcome the Ohm's resistance of the electrolyte.

in about 100 cc. is treated with 3 gms. of sodium acetate and a few drops of acetic acid. The cadmium is deposited at about 70° with a current of $ND_{100} = 0.10$ ampere at 2.2 volts. The deposition of 0.2 gm. of metal requires 4 hours (A. Yver).*

In the laboratory of the Munich Polytechnic School the following modification of Yver's method is in use: To a sulphuric-acid solution of the two metals, sodium-hydroxide solution is added until a permanent precipitate is formed, the precipitate is dissolved by adding the smallest possible quantity of dilute sulphuric acid, the solution is diluted to about 70 cc., and the cadmium is precipitated with a current of $ND_{100} = 0.07$ ampere. When the greater part of this metal has been precipitated, the free sulphuric acid is neutralized with sodium hydroxide, 3 gms. of sodium acetate are added, the solution is warmed to about 45° and electrolyzed with a current of $ND_{100} = 0.3$ ampere and a potential difference of about 2.4 volts.

In Oxalate Solution. The experiments of S. Eliasberg † and of A. Waller ‡ in the Aachen laboratory have shown that the following conditions will give favorable results. In the solution of the chlorides at a volume of about 120 cc., 8 gms. of potassium oxalate and 2 gms. of ammonium oxalate are dissolved, the solution heated to 80° or 85° and the cadmium deposited with a current of 0.1 to 0.3 ampere, keeping the potential at 2.4 volts or less.

The deposit is washed while the current is passing and in this way the zinc solution becomes much diluted. It is concentrated by evaporation and the zinc determined, after making acid with tartaric acid, according to page 173.

IRON.

Separation of Iron from Nickel and Cobalt.

As mentioned on page 182, the iron deposits obtained from tartaric- or citric-acid solutions invariably contain carbon. For this reason, the methods based upon the electrolytic deposition of iron from such solutions will not be discussed here.

G. Vortmann§ has found that ferric hydroxide suspended in an ammoniacal solution is not acted upon by a current of 1.0 ampere

* Bull. soc. chim., **34,** 18 (1880).

† Z. anal. Chem., **24,** 548 (1885).

‡ Z. Elektrochem., **4,** 241 (1897).

§ Monatsh., **14,** 536 (1893).

or less and that from an ammoniacal solution such metals as cobalt, nickel and copper can be deposited quantitatively. To convert the iron into the condition in which it has no bad effect, the solution is oxidized by bromine water and after the excess of the reagent has been removed by heating the solution, 3 to 6 gms. of ammonium sulphate are added and the iron is precipitated by a liberal excess of ammonia.

The objection that the deposits may be injured by long contact with the ferric-hydroxide precipitate is removed if the wire-gauze electrode shown on page 59 is used as cathode instead of a platinum dish, and the stirrer is given a moderate velocity (*cf.* p. 238).

With a current density of $ND_{100} = 0.4$ to 0.8 ampere, as much as 0.1 gm. of nickel is deposited in 2 or 3 hours. As a rule the deposit will contain traces of iron, and for the most accurate results the metal should be dissolved in dilute sulphuric acid, with the addition of a little bromine, and the electrolysis repeated in this solution under the same conditions as before.

To determine when the electrolysis is complete, a little of the clear ammoniacal solution is tested with ammonium sulphide; if no brown coloration appears, all the cobalt or nickel has been deposited (*cf.* p. 188).

Separation of Iron from Zinc.

If a solution containing ammonium-iron oxalate and either ammonium-zinc oxalate or potassium-zinc oxalate is electrolyzed, then, when less than one third as much zinc as iron is present, the two metals deposit together upon the cathode. If the zinc content is higher, it is noticed that zinc during the progress of the electrolysis begins to dissolve with evolution of hydrogen and at the same time a precipitate of ferric hydroxide forms. The method, therefore, is limited in its application; it is carried out as described for the electrolytic determination of iron (p. 183).

After the total weight of iron and zinc has been determined, the deposit is dissolved in dilute sulphuric acid and the iron titrated in the platinum dish with potassium-permanganate solution.

G. Vortmann * deposits the zinc alone, by keeping the iron in solution as potassium ferrocyanide. If necessary the iron is reduced to the ferrous state by treatment with sulphurous acid,

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* Monatsh., **14**, 549 (1893).

then enough potassium cyanide is added to dissolve the precipitate that first forms, and caustic-soda solution is added.

A too great excess of potassium cyanide has an injurious effect upon the deposition of the zinc. The electrolysis is carried out in a copper- or silver- coated platinum dish with a current density of ND_{100} = 0.3 to 0.6 ampere. When a portion of the solution shows no turbidity on being heated with a few drops of ammonium-sulphide solution, all the zinc will have been deposited.

Separation of Iron from Manganese.

Most of the methods recommended for the electrolytic separation of iron and manganese have no practical value because they lead to the determination of the iron rather than to that of the manganese. Moreover the deposition of the iron from an oxalic-acid solution containing manganese gives rise to the precipitation of considerable ferric hydroxide with the manganese dioxide at the anode. Thus the attempt has been made to prevent the formation of a manganese-dioxide deposit, or to defer its formation as long as possible.

The first method proposed was to add a large excess of ammonium oxalate and to electrolyze at 70° (Classen). In the hot liquid there is a strong hydrolysis of ammonium oxalate so that free oxalic acid is formed. This exerts a reducing effect upon the manganese dioxide and prevents the formation of ammonium carbonate which causes the precipitation of ferric hydroxide. Good results are obtained, however, only when the manganese content of the solution is not too high.

A. Hollard and L. Bertiaux * carry out the electrolysis in an ammoniacal-citrate solution and add sulphurous acid as the reducing agent. The deposited iron contains carbon and sulphur (*cf.* p. 182).

J. Köster,† while working in the Aachen laboratory, successfully used phosphorous acid as the reducing agent. The solution of the double oxalates is prepared by the addition of about 10 gms. of ammonium oxalate (*cf.* p. 182), and the electrolysis is conducted in a roughened platinum dish at the ordinary temperature, with a current of ND_{100} = 1.5 to 2 amperes at 3 to 4 volts. As soon as a deposit of manganese dioxide begins to be noticed at the anode, a few cubic centimeters of a 10 per cent phosphorous acid solution

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* Bull. soc. chim., **29**, 926 (1903).

† Ber., **36**, 2716 (1903).

are added and this causes the dioxide to dissolve, imparting a pink color to the liquid. The addition of this reagent is repeated from time to time, but the quantity added is kept as small as possible as it tends to delay the deposition of the iron. After the manganese has been kept in solution for 2 hours, no attention is paid to the formation of deposit at the anode as the amount of iron remaining in solution is too small to be effected; thus no more phosphorous acid solution is added. As a rule the addition of 5 cc. of the reagent suffices for an entire analysis. The deposition of the iron requires about 6 hours. If, however, so much phosphorous acid was added that no manganese deposit is formed at the anode (*e.g.*, 15 cc. with 0.6 gm. of manganese) then the iron will not be deposited until 7 or 8 hours have elapsed.

After the iron is all down, the dish is washed without breaking the circuit and treated as described on page 184. Any manganese-dioxide precipitate adhering to the dish may be removed by a soft hair brush.

In the solution from which the iron has been removed, the manganese is determined as sulphide.

Simultaneous Deposition of Iron and Manganese Dioxide.

Using the roughened platinum dish as anode and the sieve shown on page 57 as cathode, G. P. Scholl * succeeded in electrolyzing a solution containing 0.1 gm. of manganese as sulphate and 0.1 gm. of iron as ferric-ammonium alum; the iron was deposited upon the sieve and the manganese dioxide upon the dish. To the solution, 5 cc. of formic acid (sp. gr. 1.06) and 10 cc. of ammonium-acetate solution (content not specified) were added and the solution was electrolyzed at the laboratory temperature with a current of $ND_{100} = 1.1$ amperes at 3.9 volts. After 5 hours the electrolysis was finished as shown by raising the level of the solution. The deposits were washed without breaking the circuit and the iron was dissolved in sulphuric acid and titrated with permanganate. The direct weighing of the deposit would not give as accurate results because of the presence of carbon. After dissolving in sulphuric acid, the hydrocarbons had to be boiled off and the ferric salt, formed during this operation, reduced by zinc. The manganese deposit was treated as described on page 198.

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* J. Am. Chem. Soc., **25**, 1054 (1903).

Separation of Iron from Aluminium.

When a solution containing the above metals and a great excess of ammonium oxalate is electrolyzed *in the cold*, iron is deposited on the negative electrode, while the aluminium remains in solution as long as the quantity of unchanged ammonium oxalate present in the solution is larger than the quantity of ammonium bicarbonate formed from it by the action of the current. The current must not be allowed to pass, therefore, longer than is requisite for the complete deposition of the iron. This is determined by withdrawing a little of the solution from time to time, by means of a small capillary tube, and testing with an excess of hydrochloric acid and potassium thiocyanate (*cf.* p. 183).

The process is as follows: The aqueous or weakly acid solution (neutralized with ammonia if necessary) of the sulphates (the chlorides are less suitable) is treated with about 8 gms. of ammonium oxalate.

If the temperature of the solution is not over 40°, it may be submitted to electrolysis at once, as it cools sufficiently while the current is passing. The current density is $ND_{100} = 0.5$ to 1.0 ampere and the potential of the current is 2.75 to 3.8 volts. About 0.1 gm. of iron will be deposited in 5 or 6 hours. Stronger currents and higher temperatures favor the precipitation of aluminium hydroxide.

If the quantity of aluminium present is not greater than that of the iron, the method gives good results. If a large excess of aluminium is present, or if the current is allowed to act for too long a time, a part of the aluminium is precipitated as hydroxide, and clings so closely to the negative electrode that it is removed with difficulty.

In such a case it is necessary, without stopping the current, to bring the aluminium hydroxide into solution by adding oxalic acid little by little to the solution until there is no more evolution of carbon dioxide and the aluminium precipitate has all dissolved. It is well to pour the oxalic-acid solution upon the watch glass which covers the dish and it can then slowly run into the electrolyte through a perforation in the center of the watch glass. The electrolysis must be continued until all the iron is deposited.

To determine the aluminium in the liquid poured off from the iron deposit, the ammonium oxalate still remaining is decomposed by the current and the solution finally heated in a porcelain dish to expel the excess of ammonia. The precipitate of aluminium hydroxide is filtered off and converted into Al_2O_3 by ignition in a crucible.*

Rapid Separation of Iron from Aluminium.

A. Fischer in the Aachen laboratory used for this separation a platinum dish as cathode and a disk anode making 600 revolutions per minute. About 0.2 gm. of iron was separated from the same quantity of aluminium in 35 minutes. The solution contained 7 gms. of ammonium oxalate in 125 cc. and was electrolyzed at 70° with a current of 7 amperes at 6 to 7 volts.

To dissolve small quantities of aluminium hydroxide adhering to the deposited iron, the dish, after the usual washing, was rinsed with a dilute solution of potassium hydroxide, and finally with water again.

Separation of Iron from Uranium.

The iron is deposited under the same condition as in the presence of aluminium (p. 269). In this case the formation of ammonium bicarbonate has the favorable effect of keeping the uranium in solution. The current, therefore, must not be made strong enough to heat the solution above 40°, as above this temperature the bicarbonate is decomposed and the ammonium uranate precipitated.

In the solution freed from iron, the oxalate is decomposed by continuing the electrolysis, and then the solution is heated to decompose the ammonium bicarbonate, whereupon the ammonium uranate precipitates. The precipitate is in such a finely divided condition that it is hard to filter; it is, therefore, dissolved by heating with nitric acid and ammonium uranate is reprecipitated by the addition of ammonia. It is ignited and weighed as U_3O_8.

Separation of Iron from Chromium.

A solution containing a chromic salt is converted into ammonium-chromium oxalate after an excess of ammonium oxalate has been added. If such a solution is subjected to electrolysis, all the chromium is converted into chromate. If iron is also present in the solution, it is deposited as metal upon the cathode, and the

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* The fact that iron in approximately neutral solution is readily taken up by the mercury cathode has been utilized by E. F. Smith for the quantitative determination of iron in the presence of aluminium.

deposit, in this case, is characterized by a particularly brilliant luster. The solution of the two metals is treated with 8 gms. of ammonium oxalate, diluted to about 120 cc., and the electrolysis is conducted at 65° with a current of ND_{100} = 1.5 to 2 amperes at 3 to 3.4 volts potential. The deposition of about 0.11 gm. iron requires from 4 to 5 hours.

After the iron is all deposited, the liquid is poured off, boiled to decompose the ammonium bicarbonate, and the chromium is reduced to chromic salt again by boiling with hydrochloric acid and alcohol. From the resulting green solution, chromic hydroxide is precipitated with ammonia, taking the usual precautions, and determined as Cr_2O_3.

Rapid Separation of Iron from Chromium.

The deposition of 0.2 gm. of iron in the presence of an equal quantity of chromium was accomplished by A. Fischer in 45 minutes under the following conditions. Volume of solution 100 to 120 cc., addition of 7.5 gms. of ammonium oxalate, temperature 75° to 80°, current strength 6.9 to 7.1 amperes, potential 5.6 to 7 volts. As cathode a roughened platinum dish is used and as anode the corrugated foil electrode (p. 61). This form of anode is chosen for the following reason. During the electrolysis there is considerable foaming and spattering of tiny drops of the electrolyte. If an ordinary disk anode is used and the dish is covered with the ordinary type of watch glass, then the bottom of the latter will become covered with the spattered solution from which ferric hydroxide is deposited and dissolved only with difficulty by oxalic acid. This objection is overcome by using the corrugated electrode and a watch glass of unusually deep curve. The anode is made to revolve only moderately fast and the surface of the liquid is kept in constant contact with the bottom of the watch glass, thus preventing the deposition of the ferric hydroxide upon it. After setting the anode in motion, therefore, enough water is added to the solution to make it touch the glass.

Separation of Iron, Aluminium and Chromium.

The method is the same as for the separation of iron from aluminium. The temperature there prescribed is sufficient for the oxidation of the chromium and must be maintained on account of the likelihood of some aluminium being present.

To determine the aluminium and chromium, the electrolysis is continued after the removal of the iron until the ammonium oxalate is wholly decomposed (*cf.* p. 209), the free ammonia is expelled by boiling, and the aluminium hydroxide is filtered off. In the filtrate, the chromium is determined as outlined on page 271.

Separation of Iron, Chromium and Uranium.*

The separation is accomplished by the precipitation of iron as metal from the double-oxalate solution, and the oxidation of chromium to chromic acid by the current; the uranium remains dissolved in the ammonium-bicarbonate solution (p. 270). To accomplish the quantitative separation of chromium from uranium, the electrolysis must be continued till the oxalic acid is completely oxidized. The solution is then boiled to decompose the ammonium bicarbonate, and allowed to stand 6 hours so that the precipitate will assume a condition suitable for filtration. The chromium is determined, as above, in the filtrate from the uranium (p. 271).

Separation of Iron from Beryllium.†

The separation of these two metals offers no difficulties whatever if the soluble double salts with ammonium oxalate are prepared, and if care is taken to have an excess of ammonium oxalate present as in the separation of iron from aluminium (p. 271). The beryllium hydroxide behaves toward ammonium bicarbonate as uranium hydroxide does; to keep it in solution strong currents and rise in temperature must be avoided.

The determination of beryllium in the solution freed from iron is very simple: after all the oxalate has been destroyed by the action of the electric current, the solution is boiled to decompose the ammonium carbonate and the heating is continued until the liquid smells only faintly of ammonia. The beryllium hydroxide is then filtered off, washed with hot water and converted into BeO by ignition in a platinum crucible.

In a sulphuric-acid solution, R. E. Myers ‡ has effected the separation of iron from beryllium with the aid of the mercury cathode (p. 205) under the following conditions. The solution

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* Classen, Ber., **14**, 2771 (1881); **17**, 2483 (1884).

† Classen, Ber., **14**, 2771 (1881).

‡ J. Am. Chem. Soc., **26**, 1134 (1904).

contained 0.02 to 0.2 gm. of iron and 0.008 to 0.16 gm. of beryllium oxide; it was acidified with 2 drops of concentrated sulphuric acid. The current strength was 0.4 to 0.6 ampere at the start and the potential 6.5 to 6.8 volts; toward the last the current was 1.2 to 0.8 ampere. Owing to the increase in the acidity during the electrolysis, the conductivity of the solution becomes better toward the last. The electrolysis required 14 hours.

Separation of Iron, Beryllium and Aluminium.*

The iron is deposited upon the cathode under precisely the same conditions as those just given. After the deposition of the iron is complete, the solution is poured into another platinum dish and the electrolysis continued until all the oxalate is decomposed, and the aluminium is precipitated as hydroxide.

Inasmuch as the precipitate may contain small quantities of beryllium hydroxide, it is advisable to dissolve it in as little oxalic acid as possible, to add about 3 gms. of ammonium oxalate and to electrolyze again until the aluminium is reprecipitated by the current.

Separation of Iron from Aluminium, Uranium, and Rare Earths with a Mercury Cathode and Rotating Anode.

By the combination of a mercury cathode of small dimensions and a rotating spiral anode, L. G. Kollock and E. F. Smith † effected this separation with a great economy of time. As electrolyzing vessel a test tube, 3.5 cm. wide and 7.5 cm. tall, was used. The bottom was flattened out and a platinum wire fused into it (*cf.* Fig. 49, p. 205). The anode was formed from a stout piece of platinum wire 1 mm. thick, the bottom of the wire was wound into a spiral of 1.5 cm. diameter and the upper end fastened to the binding post of the rotating axis. The quantity of mercury used was 40 to 50 gms. and sufficed for two determinations. Concerning the weighing, washing and drying of the mercury, see page 205. The iron determinations made by the above authors were under the following conditions. As salts, the sulphates or nitrates were used and the spiral anode made 520 to 900 revolutions per minute.

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* Classen, Ber., **14**, 2771 (1881).

† J. Am. Chem. Soc., **27**, 1255, 1527 (1905).

1. *Iron from Uranium.* Iron 0.18 gm.; uranyl sulphate 0.2 gm.; volume 7 cc.; sulphuric acid 2 drops (30 drops = 1 cc.); current strength at the start 2.5 amperes, at the last 5 amperes; potential, 7 volts at first, 5 volts toward the last; time 15 minutes.

2. *Iron from Aluminium.* Aluminium sulphate 0.2 gm.; current strength 2 and 5 amperes (see above); potential 9 and 7 volts; the other conditions as under 1.

3. *Iron from Thorium.* Thorium nitrate 0.2 to 0.3 gm.; current strength 3 and 4 amperes; potential 7 and 5 volts; the remaining conditions as under 1.

4. *Iron from Lanthanum.* Iron 0.12 gm.; lanthanum sulphate 0.15 to 0.25 gm.; volume 10 cc.; sulphuric acid 2 drops; current strength 2 and 4 amperes; potential 8 and 6 volts; time 15 minutes.

5. *Iron from Praseodymium.* Iron 0.12 gm.; praseodymium sulphate 0.25 to 0.3 gm.; volume 8 cc.; current strength 3 and 5 amperes; potential 9 and 6 volts; time 20 minutes; otherwise as under 4.

6. *Iron from Neodymium.* Neodymium sulphate 0.16 to 0.24 gm.; volume 7 to 8 cc.; current strength 3 and 5 amperes; potential 9 and 5 volts; time 20 minutes; otherwise as under 4.

7. *Iron from Cerium.* Cerium sulphate 0.12 to 0.36 gm.; volume 8 to 10 cc.; current strength 2 and 4 amperes; potential 9 and 6 volts; time 20 minutes; otherwise as under 4.

8. *Iron from Zirconium.* Zirconium sulphate 0.2 to 0.5 gm.; volume 7 to 10 cc.; current strength 2 and 5 amperes; potential 7 and 5 volts; time 20 to 25 minutes; otherwise as under 4.

In a similar manner, iron may be separated from titanium and from phosphoric acid.

Separation of Iron from Vanadium.

R. E. Myers * accomplished the electrolytic deposition of iron in the presence of vanadium by using a mercury cathode and a rotating anode (*cf.* p. 205), under the following conditions. Iron 0.1 to 0.2 gm.; vanadium 0.02 to 0.1 gm.; concentrated sulphuric acid 12 drops if considerable iron was present and 5 drops if only little iron was present; current strength 0.3 to 0.6 ampere; potential 7 volts. Larger quantities of vanadium, *e.g.*, 0.2 gm., tend to prevent the complete deposition of the iron; this diffi-

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* J. Am. Chem. Soc., **26,** 1134 (1904).

culty can be overcome by diluting the solution and electrolyzing the diluted solution in separate portions.

Separation of Iron from Lead.

The lead is deposited as peroxide upon the anode in the presence of nitric acid (*cf.* p. 194), the nitric acid is removed from the solution by evaporation with sulphuric acid, and the iron determined in an oxalate solution according to page 183.

NICKEL.

Separation of Nickel from Lead.

The electrolysis is carried out exactly as described for the determination of lead on page 194.

Separation of Nickel from Zinc.

From an ammoniacal solution containing nickel and zinc, the current, under ordinary conditions, causes the deposition of an alloy of these metals on the cathode. A. Hollard and L. Bertiaux * have found that at 90° and in the presence of sulphite only the nickel is deposited and the separation is quantitative. F. Foerster † explains why such a separation is possible on the basis of measurements made by F. Blankenberg on the discharge potentials of nickel and of zinc in ammoniacal solutions at different temperatures.

In Fig. 52, the discharge potentials are plotted as abscissas and the current densities, in amperes per 100 sq. cm. of electrode surface, are plotted as ordinates.

The curve for zinc at 18° shows that in an ammoniacal solution the current density can vary from about 0.04 (*a*) to about 0.45 (*b*) while the discharge potential changes only from 1.14 to 1.15 (*b*).

The curve for zinc at 50° shows that if the same solution is heated to 50° and the current density is changed from 0.04 (*c*) to 0.45 (*d*) the discharge potential will vary from 1.09 (*c*) to 1.12 (*d*) volts.

In general, it may be said that the discharge potential of zinc

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* Bull. soc. chim., **31,** 102 (1904).

† Z. Elektrochem., **13,** 563 (1907).

ions in ammoniacal solution varies but little as the solution is heated, or as the current density is changed.

The fact that the same is not true of an ammoniacal nickel solution is evident from a study of the other four curves. From the curve of nickel at 18°, it is seen that when the current density changes in a solution at this temperature from 0.05 (*e*) to 0.45 (*f*) the discharge potential of the nickel rises from 0.85 (*e*) to 0.98 (*f*) volt; it is apparent, moreover, that at the lower current density, $ND_{100} = 0.05$, there is a difference between the discharge potentials of zinc and of nickel amounting to $a - e = 0.29$ volt, whereas the difference in the discharge potentials of zinc and nickel with a higher current density, $ND_{100} = 0.45$ ampere, the difference is only $b - f = 0.17$ volt. This slight difference between the discharge potentials of the two metals at ordinary temperatures, and, as we have seen, the difference becomes less at higher current densities, is the reason why nickel and zinc cannot be separated from one another by an electrolysis of an ammoniacal solution at the laboratory temperature.

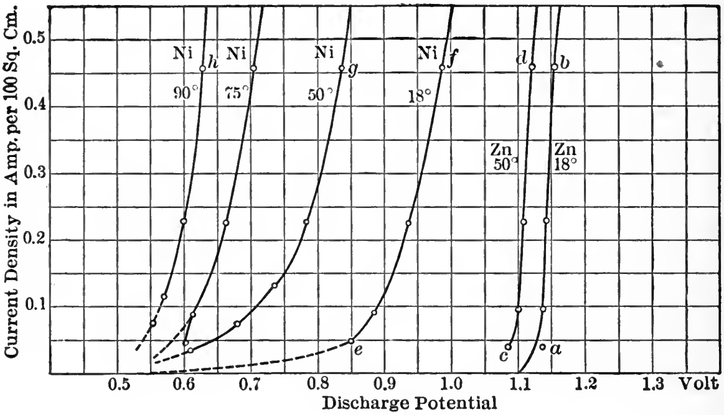

Fig. 52.

The relations are different, however, as the temperature of the bath is raised. The diagram shows that at 50° with current density of $ND_{100} = 0.45$ the potential difference between the zinc and the nickel is $d - g = 0.28$ and the difference increases as the temperature is raised. At 90° the potential of the nickel for $ND_{100} = 0.45$ ampere is only 0.63 volt (*h*) while that of zinc remains not far from the value at 50°; there is then a difference in the discharge potentials of $d - h =$ about 0.49 volt, or nearly three times the difference at 18° under otherwise similar conditions.

Thus, because the discharge potential of zinc remains about the same at different temperatures while that of nickel drops considerably as the temperature rises, the separation of nickel from zinc, which is impossible at 18°, can be accomplished at 90° (*cf.* p. 94).

If the separation of nickel and zinc were attempted at 90° without the addition of any sulphite, it would take a long time to deposit the last traces of nickel. The cause of the sulphite effect is explained differently by Foerster than by Hollard and Bertiaux. It is certain, however, that the delay in the deposition of the nickel is closely related to reactions taking place at the anode, and Hollard and Bertiaux succeeded in stopping this disturbing effect by adding sulphite.

Foerster carries out the electrolytic separation of nickel from zinc as follows: The solution of the sulphates (such as remains, for example, in the analysis of German silver after the electrolytic deposition of the copper according to p. 240) is neutralized with strong ammonia. If enough sulphuric acid was already present to form about 5 gms. of ammonium sulphate by the neutralization, no more is needed; otherwise enough ammonium sulphate is added to make about 5 gms. of the salt. Then 30 to 35 cc. of ammonia (sp. gr. 0.91) and 0.5 to 1 gm. of crystallized sodium sulphite are added, the solution diluted to 250 cc., and heated to 90° or 92°. The electrolysis is carried out with gauze electrodes using a current of 0.1 ampere; 0.15 gm. nickel will be deposited in about 2 hours. When a little of the solution shows no brown coloration with ammonium sulphide (or, better, no test for nickel with dimethyl glyoxime) the electrodes are raised, while directing a stream of water against them from the wash bottle, and the weight of nickel is determined (p. 186).

The determination of the zinc can be accomplished by electrolyzing the cold solution with a current of 0.3 to 0.5 ampere using a copper-plated gauze cathode. The electrode used in the nickel determination may be used here, after the nickel deposit has been given a slight coating with copper. The deposition of 0.16 gm. of zinc requires about 3 hours.

F. Foerster and W. Treadwell * in testing the above method found that the nickel deposits contained sulphur and the error increased with the quantity of sodium sulphite added. Thus with 0.11 gm. of nickel and 2 gms. of $Na_2SO_3.7 H_2O$, the error was from 2 to 2.6 per cent of the total amount of nickel. If the nickel deposit contains as much sulphur as this, it should be redissolved and deposited electrolytically without the addition of any sulphite (p. 187).

Rapid Separation of Nickel and Zinc.

The method just described can be used as a basis for a rapid separation provided an auxiliary electrode (p. 40) is used, as A. Fischer † has proved by experiments in the Aachen laboratory.

The solution containing about 0.15 of each metal as sulphate is treated with 5 gms. of ammonium sulphate, 1 to 3 gms. of sodium sulphite and 30 cc. of ammonia (sp. gr. 0.91), and diluted to 250 or 300 cc. The gauze electrodes shown on page 66 are used. The temperature of the electrolyte is kept between 90° and 92° from start to finish, and the current is regulated so that the potential difference between the mercurous sulphate — $2\ N.H_2SO_4$ electrode and the cathode is constant at 1.35 volts. To maintain this electromotive force, the current strength, which is 1 ampere at the start, must be reduced gradually until at the last it is only 0.1 ampere. (See pp. 39, 148 for details of the procedure.) Under these conditions the nickel is deposited in about 20 minutes.

In the solution freed from nickel, the unchanged sodium sulphite is oxidized by heating with hydrogen peroxide. Then the excess of ammonia is expelled by heating more strongly, and the heating is continued with the addition of sodium hydroxide until finally all the ammonia from the ammonium salts is expelled. In the alkaline solution, the zinc is determined according to page 184.

A. Fischer in testing the rapid method could find only traces of sulphur in the nickel deposit even under unfavorable conditions.

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* Z. Elektrochem., **14,** 89 (1908).

† Chem.-Ztg., **32,** 185 (1908).

Deposition of Zinc in the Presence of Nickel from Alkaline-tartrate Solution.

According to G. Vortmann * the solution of the two metals is treated with 4 to 6 gms. of Rochelle salt, made alkaline with concentrated sodium-hydroxide solution, and electrolyzed at the laboratory temperature with a current density of $ND_{100} = 0.3$ to 0.6 ampere. The deposition of the zinc is complete in from 2 to 4 hours according to the quantity present (0.02 to 0.1 gm.). There is no good way of testing the solution to see if all the zinc has been deposited. Either the cathode should be weighed and the electrolysis continued a little longer to see if any change in weight is experienced, or, as is not quite as satisfactory, a narrow strip of brass may be suspended over the edge of the cathode to see if any zinc is deposited upon it.

To determine the nickel, the solution is made slightly acid with sulphuric acid, treated with an excess of ammonia, and electrolyzed according to page 185.

Separation of Nickel from Chromium.

The separation is the same as that of iron from chromium. It is to be remembered that the nickel deposited from oxalate solution is contaminated with carbon (*cf.* p. 190), and, for this reason, should be dissolved in nitric acid and deposited in ammoniacal solution as described on page 185. The presence of the carbon is shown by the brown coloration of the nitric-acid solution obtained on dissolving the first deposit.

Rapid Separation of Nickel from Chromium.

According to the experiments of A. Fischer in the Aachen laboratory, the solution of the sulphates, containing about 0.18 gm. of nickel and 0.13 gm. of chromium, is treated with 10 gms. of ammonium oxalate, diluted to 120 cc. and electrolyzed at 50°, using a platinum dish as cathode and a disk making 600 revolutions per minute as anode; the current should be 7.5 amperes at 5.3 volts. During the progress of the electrolysis, the temperature rises, as a result of the heating effect of the relatively strong current, and is about 85° at the end of the electrolysis, which usually requires 50 minutes.

The nickel deposit, on account of its carbon content, is dissolved

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* Monatsh., **14**, 546 (1893).

in nitric acid, the solution changed to sulphate by evaporating with concentrated sulphuric acid, and, after diluting and neutralizing with ammonia, it is treated with 1.5 gms. of ammonium sulphate and 40 cc. ammonia (sp. gr. 0.91). The electrolysis of the hot solution (120 cc.) is conducted with a current of 5 amperes and 10 volts with the disk anode revolving about 800 times per minute. The deposition of the nickel requires about 30 minutes.

The chromium remaining in the solution after the first electrolysis is oxidized completely to chromate by electrolyzing the solution at 80°, with the addition of 5 gms. more of ammonium oxalate, and using a current of 5 amperes at 7 volts, while the anode is making about 600 revolutions per minute. The oxidation is complete at the end of 50 minutes. In case the solution contains no nitrate, the chromium can be determined iodometrically.

Separation of Nickel from Aluminium and Uranium.

The method is the same as that employed in the separation of iron from aluminium and uranium (p. 269 *et seq.*), but with a second deposition of the nickel (*cf.* p. 190).

COBALT.

Separation of Cobalt from Zinc.

From 4 to 6 gms. of Rochelle salt are dissolved in the solution of the two metals and a moderate excess of 10 to 20 per cent sodium-hydroxide solution is added. To prevent the deposition of Co_2O_3 at the anode, 1 or 2 gms. of potassium iodide are added: the latter acts as depolarizer and lowers the anode potential until the positive electricity at the anode finds it easier to oxidize the iodine ion to iodate rather than the cobaltous ion to cobaltic oxide. In spite of this precaution, however, it is always necessary to weigh the anode as some oxide usually deposits there. The solution is heated to 60° and electrolyzed with a current of $ND_{100} = 0.07$ to 0.1 ampere at 2 volts. At the end of the process, the cathode is weighed after the customary treatment; the anode is rinsed carefully with water, dried at 110° in an air-bath, and the weight of cobalt corresponding to the Co_2O_3 found is added to the weight of the metal on the cathode. This method was proposed by Vortmann* and proved satisfactory by the experiments of A. Waller† in the Aachen laboratory.

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* Z. Elektrochem., **1,** 6 (1894–95).

† *Ibid.*, **4,** 243 (1897).

To determine the zinc the solution freed from cobalt, together with the washings, is electrolyzed with a current of $ND_{100} = 0.3$ to 0.6 ampere. The electrolysis is conducted in a beaker and a gauze cathode, plated with copper or with silver, is used.

Separation of Cobalt from Aluminium, Chromium and Uranium.

The separation is accomplished as in the separation of iron from the last three metals (p. 270). The cobalt deposit from the oxalate solution will contain carbon and thus for accurate results it must be dissolved and the metal deposited from an ammoniacal solution (*cf.* p. 187).

Separation of Nickel from Cobalt.

The physical and chemical similarity between nickel and cobalt is so marked that it is extremely difficult to devise a satisfactory electrolytic separation and comparatively few attempts have been made in this direction. Still, on account of the importance of the matter, a few of the researches will be mentioned. The method recommended by D. Balachowsky * is complicated and the results obtained are not accurate enough to satisfy the demands of electro-analysis.

A. Coehn and M. Gläser † deposit the cobalt as cobaltic oxide, Co_2O_3. They found that in a slightly acid solution cobalt is deposited as oxide upon the anode while nickel is not; in a strongly acid solution there is no formation of oxide with either metal. They also found that it was possible to make the deposition of the cobaltic oxide quantitative provided means were taken to prevent any deposition of metallic cobalt upon the cathode. This tendency of depositing upon both cathode and anode is a property that cobalt shares with other metals such as silver, lead, bismuth and manganese.

There are several ways to prevent the deposition of the metal upon the cathode. An ion may be provided in the solution which is more readily discharged than the metal ion in question: thus in the case of cobalt or lead, such an ion is the hydrogen ion. The deposition of the cobalt may be prevented, therefore, by

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* Compt. rend., **131,** 1492 (1901).

† Z. anorg. Chem., **33,** 9 (1903)

adjusting the potential of the electric current so that hydrogen is barely liberated at the cathode. Under these conditions no cobalt is deposited because the discharge potential of cobaltous ions is 0.22 volt higher than the discharge potential of hydrogen ions. By using a platinized cathode (*cf.* p. 82), the liberation of hydrogen is made more easy. Unfortunately, however, under these conditions (2.3 to 2.4 volts and 0.01 ampere) the formation of the cobaltic oxide takes place so slowly that 0.08 gm. of cobalt is not precipitated in the course of 20 hours. A further difficulty lies in the fact that the electrolysis requires attention: only a small deposit of oxide should be allowed to form and for this reason the anode must be frequently changed during the process.

In the electrolysis of a lead solution it was possible to increase the concentration of hydrogen ions by the addition of a strong acid and thereby facilitate the discharge of such ions. This method is of no avail in the case of the cobalt determination, because no cobaltic oxide is precipitated from a strongly acid solution.

It will be remembered that in the case of the lead determination some authors recommended adding copper ions to the solution, as such ions are discharged more readily than hydrogen ions. In this case, however, nickel is to be determined in the solution after the cobalt has been deposited and thus the addition of copper is not permissible.

A third expedient is to remove the hydrogen ions as fast as possible by adding a depolarizer to the electrolyte; *i.e.*, a substance upon which the neutral hydrogen will react as fast as its ions are discharged, and if this reaction velocity is so great that no hydrogen gas is evolved, even when high current densities are used, the desired end is attained.

Coehn and Gläser have found potassium dichromate to be a satisfactory depolarizer. Their method is as follows:

The solution, containing about 0.08 gm. of cobalt and 0.02 to 0.08 gm. of nickel is treated with 0.1 to 0.2 gm. of potassium dichromate and with 3 to 4 gms. of potassium sulphate to improve the conductivity of the solution. After diluting to about 500 cc., the solution is heated and electrolyzed at a constant potential of 2.3 to 2.4 volts (see p. 212) and a current strength of 0.10 to 0.15 ampere for 10 hours. As cathode a platinized foil electrode may be used (p. 78), 5 × 9.5 cm. and as anode an equally large platinum gauze electrodes. Two such anodes are necessary but they are not weighed. As soon as the gauze has become covered with a dark coating it is taken out of the solution, washed and replaced by the other electrode. During the electrolysis it is necessary to change the anode about five times; at first, when the solution is more concentrated, the exchange is made at more frequent intervals than toward the last. When no further deposit of oxide is noticed, the electrolysis is finished.

Each time the anode is removed from the solution the deposited oxide is dissolved by dilute sulphuric acid to which a little sulphurous acid has been added. The excess of the latter is removed by heating and the cobalt determined as on page 191.

For the nickel determination the chromate remaining in the solution is reduced by heating with sulphurous acid, the excess of the latter is removed, and the analysis is continued as described on page 185.

Enough has been said to show the complexity of this method of analysis. The cobalt is all precipitated from the solution but the oxide usually contains a little nickel. To make sure that no nickel is present, the solution in sulphuric acid, after the removal of the sulphurous acid, should be neutralized with ammonia, the excess of ammonia removed by evaporation and the electrolysis carried out anew with the addition of dichromate, etc.

As compared with the simultaneous determination of nickel and cobalt from ammoniacal solution and the determination of the nickel with dimethyl glyoxime, this method is of little value although it does furnish a good means of testing a nickel solution to see if any cobalt is present. The dilute solution of the neutral salts is treated with potassium dichromate and potassium sulphate, heated to boiling and electrolyzed between two platinum wires for a few minutes with a current at 2.3 to 2.4 volts. If the anode becomes darkened, cobalt is probably present and can be confirmed by the borax-bead test.

LEAD.

Separation of Lead from Other Metals.

In the electrolytic determination of lead, the metal is usually deposited as peroxide upon the anode (*cf.* p. 194). The large quantity of nitric acid, which it is advisable that the electrolyte should contain, makes it possible to effect a separation from nearly all other metals although another metal cannot always be deposited simultaneously upon the cathode. The method that serves for the separation of small quantities of lead from larger quantities of copper was described on page 230, and the procedure to be followed when a large quantity of lead is present was also described.

According to the researches of G. Vortmann,* an accurate separation of lead from other metals is possible only in the case of copper. He found that small quantities of other metals invariably contaminated the lead-peroxide deposit. These results have not been confirmed by other investigators and further work is needed to settle the matter. It would seem advisable, however, for the most accurate results, to dissolve the peroxide deposit in nitric acid to which a little oxalic acid is added, and to repeat the electrolytic deposition. In the presence of arsenic, tellurium, silver, bismuth and chlorides, the results are too high, as Vortmann and other experimenters have found.

In a solution containing 15 to 20 per cent by volume of free nitric acid (sp. gr. 1.35 to 1.38)† the lead can be separated from the following metals under the experimental conditions given on page 194: alkalies, aluminium, barium, beryllium, chromium, cadmium, calcium, cobalt, iron, magnesium, mercury, nickel, strontium, uranium, zinc and zirconium.

Separation of Lead from Antimony.

There is no known method of separating these two metals electrolytically. According to H. Nissenson and B. Neumann,‡ however, it is easy to separate the two elements chemically and then determine each separately. For example, in the analysis

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* Ann. Chem., **351**, 283 (1907).

† In the presence of phosphoric acid, this quantity of nitric acid does not prevent the deposition of metallic lead upon the cathode (*cf.* p. 197).

‡ Chem.-Ztg., **19**, 1142 (1895).

of hard lead, type metal, etc., about 2.5 gms. of the borings are placed in a 250-cc. graduated flask, 10 gms. of tartaric acid, 15 cc. of water and 4 cc. of nitric acid (sp. gr. 1.4) are added and the alloy is dissolved by heating the acid. The resulting clear solution is treated with 4 cc. of concentrated sulphuric acid, diluted with water, cooled and brought to the graduation mark. The precipitate of lead sulphate, owing to the presence of the tartaric acid, is perfectly free from antimony, as the authors have proved by experiment. The solution is mixed thoroughly by pouring it back and forth several times into a dry beaker and, after allowing the precipitate to settle, it is filtered through a dry filter. An aliquot part of the filtrate (50 cc. = one fifth) is made strongly alkaline with caustic-soda solution, boiled with 50 cc. of a saturated sodium-sulphide solution, filtered immediately and the precipitate washed with water containing a little sodium sulphide. The precipitate usually consists of a little copper sulphide. The electrolytic deposition of the antimony is carried out in a hot solution after the addition of potassium cyanide (*cf.* p. 290).

If it is desired to determine the lead as well, the entire precipitate from 2.5 gms. of the alloy is too large for the electrolytic method described on page 231. The precipitate is washed with water, containing about 10 gms. of tartaric acid and 4 cc. of concentrated sulphuric acid in 250 cc., until free from antimony. The tartaric and sulphuric acids are removed by washing with alcohol and the precipitate weighed in the usual manner.

MOLYBDENUM.

Separation of Molybdenum from Vanadium.

R. E. Myers,* using the mercury cathode described by E. F. Smith (p. 205), obtained satisfactory deposits of molybdenum in the presence of vanadium under the following conditions. In one case the solution contained 0.095 gm. of molybdenum and 0.1 gm. of vanadium present as sodium molybdate and vanadate. The solution was acidified with 20 drops of concentrated sulphuric acid and electrolyzed with a current of 1.6 to 2 amperes at 6.5 volts potential. After 15 or 17 hours the free sulphuric acid was exactly neutralized with caustic potash solution, 15 drops of sulphuric acid added, and in this way the acidity kept the same at the end of the electrolysis as at the start. This regulation of the acidity has proved advantageous for the deposition of the last traces of molybdenum. The electrolysis was continued 3 hours at 1 to 1.5 amperes at 5.5 volts.

In another case, 0.19 gm. molybdenum and 0.01 gm. vanadium were present in the original solution. Then, the first addition of sulphuric acid amounted to 30 drops and the current was 1.5 amperes at 4.5 volts. After the neutralization with alkali, 20 drops of acid were added and the electrolysis finished with 1.2 to 1.5 amperes at 5.5 to 6 volts.

If the acidity of the solution is cut down too much, some oxide of vanadium will deposit on the anode. The end of the electrolysis is recognized by the green color of the solution.

The molybdenum deposits in the form of a lustrous, white amalgam which is washed with water, alcohol and ether, dried and weighed together with the electrolyzing vessel (*cf.* p. 205).

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* J. Am. Chem. Soc., **26**, 1130 (1904).

PART IV.

SPECIAL ANALYSES.

The methods of electro-analysis, up to the present time, have not been adapted to the determination of the composition of substances of a complicated nature; they are used more like volumetric methods as aids to ordinary gravimetric analysis. The following examples of practical analyses should be judged from this viewpoint.

Analysis of Commercial Copper.

Method of A. Hollard and L. Bertiaux. The following scheme of analysis includes the determination of these impurities: lead, bismuth, nickel, cobalt, iron, zinc, manganese, tin, antimony, arsenic, silver and sulphur. Manganese is not a common constituent of the metal, but is found sometimes as slag or matte inclusions.

In the case of an ordinary analysis, the nature and quantity of the impurities present are usually determined and the percentage of copper is determined by difference; if the copper is determined electrolytically, it is only as a check upon the process. Thus, an error of, say, 0.1 per cent in the determination of the copper would not be regarded as a serious analytical mistake in the electrolysis, but the presence of this amount of impurity is, in some cases, a very serious matter. The electrolytic deposition of copper is usually carried out chiefly for the purpose of obtaining a solution in which the impurities can be determined.

A brief summary of the principal operations will be given.

1. *Determination of the Copper.* A solution of the metal in nitric and sulphuric acid is electrolyzed, with the addition of ferric sulphate and lead sulphate if the original metal is very impure. These substances are added to prevent the electrolytic deposition of arsenic, antimony and bismuth (p. 290). The deposited copper contains all the silver which is determined as

described below (8) and the corresponding weight deducted from the weight of silver and copper.

The addition of lead sulphate only prevents the injurious effect of small quantities of bismuth. If considerable bismuth is present, the lead and bismuth must be removed before determining the copper, by the precipitation method outlined under 2.

2. *Determination of Lead and Bismuth.* The nitric-acid solution of another portion of the metal is evaporated with sulphuric acid till it fumes strongly; after diluting, the residue will contain the lead as sulphate and a part of the bismuth as arsenate and antimonate. The remainder of the bismuth is precipitated as phosphate by the addition of phosphoric acid.

From the nitric-acid solution of the residue, the lead is again precipitated by sulphuric acid. The lead is determined by electrolysis and likewise the bismuth in the solution free from lead.

If the quantity of bismuth present is large, the copper is determined in the solution from which the bismuth was precipitated as phosphate, arsenate and antimonate.

3. *Determination of Nickel, Cobalt, Iron and Zinc.* In a new sample, the copper is deposited as under 1, but without the addition of any substances to the acid bath, because in this case it makes no difference whether or not a pure deposit of copper is obtained. The four metals in question are sure to remain in solution after the electrolysis, and the remaining metals of the copper group are precipitated by the introduction of hydrogen sulphide into the slightly acid solution. The filtered sulphide precipitate, which also contains the tin, is saved for the determination of the metals in it, and the filtrate is used for the separation of nickel, cobalt, iron and zinc.

Nickel and cobalt are determined together by the electrolysis of an ammoniacal solution in the presence of precipitated ferric hydroxide.

The ferric hydroxide is dissolved in oxalic acid and the iron determined electrolytically.

The solution, in which only the zinc remains, is transformed into a citrate solution and the zinc deposited by the current.

4. *Determination of the Tin.* The sulphide precipitate obtained under 3 may contain some lead and antimony as well as tin. The sulphides are changed to oxalates, as described on page 302, and, after precipitating the antimony with hydrogen sulphide,

the tin can be determined electrolytically in the oxalic-acid solution.

5. *Determination of Manganese.* The electrolytic determination of the manganese can be effected in the solution freed from zinc as described under 3.

6. *Determination of Arsenic.* A sample of the original metal is dissolved in hydrochloric acid and ferric sulphate, and the arsenious chloride distilled in a current of hydrogen chloride (see below).

7. *Determination of Antimony.* The solution freed from copper, as described under 1, may be used for this determination. After the removal of the nitric acid, antimony sulphide is precipitated by introducing hydrogen-sulphide gas and the antimony sulphide is extracted from the precipitate by treating it with sodium-sulphide solution. This solution is used for the electrolysis.

8. *Determination of Silver.* The nitric-acid solution of a portion of the original metal is treated with a little hydrochloric acid. The silver chloride is filtered off, dissolved in potassium cyanide, and the resulting solution electrolyzed.

9. *Determination of Sulphur.* According to G. L. Heath * the sulphur is best determined gravimetrically as barium sulphate in the solution freed from copper electrolytically. Naturally no ferric sulphate should be added to the bath in this case.

Details of the Method for the Analysis of Commercial Copper.

1. *Copper.* The metal borings are freed from grease by treatment with ether and from particles of iron (from the drill) by means of a magnet. 10 gms. of the metal are then dissolved in a beaker about 6.5 cm. in diameter and 18 cm. tall; this small diameter of the beaker is desirable because the glass is to be used as electrolyzing vessel and considerable electrode surface can be used without unnecessarily diluting, and because the tall sides of the beaker tend to prevent loss by spattering during the solution of the metal. A funnel is placed in the beaker and the contact between the sides of the beaker and the funnel is made air-tight with a little water.

After covering the borings with water, about 0.4 gm. of finely powdered lead sulphate (see below), 12 cc. of concentrated sul-

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* Chem.-Ztg., 20, rep. 113 (1896).

phuric acid, and 25 cc. of nitric acid (sp. gr. 1.33) are added and the reaction is hastened by warming slightly. Refined copper usually dissolves completely but unrefined metal usually leaves behind a slight residue which can be freed from copper by warming for some time.

The solution is diluted to about 300 cc. and pure ferric sulphate, corresponding to about 0.1 gm. of iron, is added. The ferric salt helps to keep the arsenic in the quinquevalent condition and thus prevents its deposition upon the cathode with the copper. The addition of lead sulphate has been found by Hollard and Bertiaux to prevent the deposition of antimony and bismuth on the cathode while the copper is being deposited; the deposition of the lead peroxide upon the anode favors the deposition of bismuth upon the anode as peroxide. If considerable bismuth is present, the expedient of adding lead sulphate is of little avail and it is necessary to remove the bismuth as described under 2 before attempting to determine the copper.

After the solution has become clear, the gauze electrodes are introduced and the electrolysis is conducted with a current of 1 ampere; at the end of 7 or 8 hours most of the copper will have been deposited. When the blue color of the solution has disappeared, a little water is added to the bath and it is noticed whether there is any further deposit of copper formed on the freshly exposed electrode surface (*cf.* p. 125). The complete removal of the copper requires not more than 12 hours. Then, without turning off the current, the beaker is quickly removed from beneath the electrodes and replaced by another beaker containing distilled water. This wash water is added to the main solution which is used for the further analysis (see 7). The further treatment of the copper is as described on page 99, but it must be borne in mind that all the silver is present and its weight must be deducted.

2. *Lead and Bismuth.* The solution of 10 gms. of copper in 50 cc. nitric acid is evaporated to dryness with the addition of 10 cc. of sulphuric acid. The residue is treated with 5 cc. of sulphuric acid and 200 cc. of water; the undissolved part contains lead sulphate, bismuth arsenate and bismuth antimonate. If much bismuth is present, some of it remains in solution, so that 10 cc. of phosphoric acid (60° Bé. = sp. gr. 1.90) are added to precipitate the remaining bismuth as phosphate. The precipitate, containing all

the lead and bismuth, is allowed to settle, is filtered after standing 12 hours, and washed with dilute sulphuric acid. (The filtrate may be used for the determination of copper as in 1.)

The precipitate containing the lead and bismuth is dissolved by heating with nitric acid and a little hydrochloric acid, 7 cc. of concentrated sulphuric acid are added, and the solution is evaporated until fumes are evolved. The residue, after cooling, is treated with 100 cc. of water, a little alcohol is added, and the precipitate, which now consists wholly of lead sulphate, is filtered off. After washing with water containing sulphuric acid and alcohol, the lead sulphate is dissolved and electrolyzed according to page 197.

The solution, from which the lead sulphate was precipitated last, is diluted to 300 cc. and the bismuth deposited upon the cathode by electrolyzing with a current of 0.1 ampere; the alcohol present does no harm. This method is suitable only for the determination of small quantities of bismuth and requires considerable time (about 24 hours). If the necessary apparatus is available, the method described on page 147 *et seq.* is to be preferred.

3. *Nickel, Cobalt, Iron, Zinc.* Without the addition of any lead sulphate or ferric sulphate, 5 gms. of the copper are dissolved as under 1, and the greater part of the copper is deposited electrolytically while the four metals in question remain in solution. If a deposit of lead peroxide forms upon the anode, it may contain some iron. It is dissolved, therefore, in the solution from which the copper has been removed, adding, if necessary, a little hydrogen peroxide. The solution is evaporated to remove the nitric acid and finally diluted with water. By introducing hydrogen sulphide into the hot, slightly acid solution, all the members of the copper and arsenic groups are precipitated as sulphides. The precipitate is filtered, washed and set aside for the determination of tin as in 4.

The filtrate is boiled to remove hydrogen sulphide and the last traces of this gas are oxidized by adding hydrogen peroxide, and at the same time the ferrous ions are converted into ferric ions. The separation of the nickel and cobalt from the zinc is accomplished in an ammoniacal solution in which ferric hydroxide is suspended (p. 284). In preparing the electrolyte, the excess of hydrogen peroxide must be removed by boiling before the sulphite is added.

The nickel may be determined, if necessary, by the dimethylglyoxime method and the cobalt determined by difference. Formerly it was customary to determine the cobalt by the potassium-cobaltic nitrite method and to get the nickel by difference.

The ferric hydroxide is filtered off, freed from any zinc by repeatedly dissolving in hydrochloric acid and precipitating by ammonia, and the iron is determined by titration or by the electrolytic method described on page 183.

The ammoniacal liquid is used for the determination of the zinc as described below.

If, as is the case with certain very impure grades of copper, more than 2 per cent of iron is present, some ferric hydroxide may contaminate the deposit of nickel and cobalt. In such a case the deposit is dissolved in nitric acid, the solution evaporated with sulphuric acid, and in this way a solution is obtained containing so little iron that there is no danger of contamination when the nickel and cobalt are deposited again from an ammoniacal solution.

All the solutions from which the nickel and cobalt have been precipitated are combined, freed from ferric hydroxide (purifying the precipitate as mentioned above) and concentrated by evaporation. According to Hollard and Bertiaux the solution is prepared for the zinc determination as follows: After neutralizing the sulphuric acid, 5 gms. of sodium hydroxide in excess are added, followed by 2 gms. of citric acid, and the excess of the alkali is neutralized with sulphuric acid. Then the solution is made slightly alkaline with a few drops of sodium hydroxide and finally 2 gms. more of citric acid are added. The solution is diluted to 400 cc. and the zinc deposited upon a coppered platinum cathode with a current of 1 ampere.

4. *Tin.* The sulphide precipitate obtained under 2 is heated with sodium sulphide to dissolve the tin and free it from sulphides of copper, etc. The filtered solution is decomposed by introducing hydrogen-sulphide gas and the tin sulphide is dissolved in oxalic acid; since antimony is also present in this solution it must be precipitated by the introduction of more hydrogen sulphide into the hot solution. The presence of oxalic acid prevents the precipitation of the tin (see p. 302).

5. *Manganese.* The determination of manganese can be combined with that of zinc, if Scholl's method, described on pages 201 and 289 is used.

6. *Arsenic.* 1 to 5 gms. of copper are dissolved in the presence of about 8 times as much pure ferric sulphate and heated with 150 cc. of concentrated hydrochloric acid in a distilling flask. The escaping vapors are led into water and the distillation is continued, until the contents of the flask have become nearly dry. In this way all the arsenic trichloride is distilled over into the water. The arsenic trichloride solution thus obtained is neutralized with ammonia, made slightly acid with hydrochloric acid and titrated with iodine in the presence of sodium bicarbonate; or, the arsenic may be precipitated as sulphide and determined gravimetrically. Care must be taken to run a blank on the acid used, as most commercial hydrochloric acid contains arsenic.

7. *Antimony.* The solution freed from copper under 1 is used for the antimony determination after any deposited lead peroxide has been dissolved off the anode. The nitric acid is removed by evaporation, the solution is diluted and hydrogen sulphide is introduced in the cold; under these conditions the arsenic will remain in solution. The sulphide precipitate on being treated with sodium sulphide yields a solution from which the antimony may be deposited electrolytically by the method given on page 158.

8. *Silver* and 9. *Sulphur,* see page 289.

Determination of Copper in Materials Rich in Iron.

The difficulties involved in the determination of copper in a solution containing considerable iron (*cf.* pp. 127, 237) were found particularly annoying by Fairlie and Bone (*cf.* p. 72) in the rapid electrodeposition of copper. Thus, if a solution obtained from 3 gms. of copper slag, containing 40 to 50 per cent ferrous oxide, is electrolyzed at a volume of about 150 cc. in the presence of 2 cc. or more of nitric acid with a current of 3 amperes and rotating anode, the copper at once begins to deposit upon the cathode. At the same time the solution begins to assume a brown color and the color deepens until nearly all the copper is deposited. Then the solution suddenly becomes colorless and the copper begins to dissolve in the electrolyte which now contains only a very little ferrous iron.

The cause of the brown color lies in the fact that some of the ferric iron is reduced to ferrous iron and unites with nitric oxide which is present to some extent as a reduction product of the nitric acid. This compound, of variable composition, between ferrous salt and nitric oxide, is formed in the well-known qualitative test for nitric acid. As long as the ferrous salt is forming, the deposition of the copper continues, because ferrous ions exert no solvent effect upon the copper deposit. As soon, however, as the unstable compound of ferrous salt with nitric oxide decomposes, which change is recognized by the solution suddenly becoming colorless, all the iron is oxidized back into ferric salt and this exerts a solvent action upon the deposit. This solvent action is considerably increased, as a number of investigators have found, if considerable nitric acid is present at the same time. If little nitric acid is present, the solvent effect of the ferric salt is scarcely noticeable. Thus, if only 1 cc. of nitric acid is present in the electrolyte an accurate determination of the copper can be accomplished.

To determine the copper in a copper slag rich in iron, 3 gms. of the finely powdered substance are mixed with 15 cc. of hydrochloric acid (sp. gr. 1.2) in a porcelain dish, and 5 cc. of nitric acid (sp. gr. 1.42) are added. After heating for about 5 minutes, the solution is allowed to cool somewhat, 4 cc. of concentrated sulphuric acid are added, and the solution is evaporated until white fumes of sulphuric acid are evolved. After cooling, 30 cc. of water and exactly 1 cc. of concentrated nitric acid are added, and the solution is boiled and filtered. The filtrate is diluted to 150 cc., heated to 50° or 55° and electrolyzed with a current of ND_{100} = 3 amperes with the anode making 400 to 500 revolutions per minute (see p. 128). The deposition of the copper requires about 35 or 40 minutes.

The method to be followed when other disturbing elements, such as arsenic and antimony, are present, is described on page 287.

If the solution contains only a little iron, the presence of more nitric acid does no harm, as in the analysis of the following materials (*cf.* p. 237).

Crude Converter Copper. 5 gms. of copper are dissolved in 21 cc. of nitric acid (sp. gr. 1.42), 5 cc. of concentrated sulphuric acid are added, and the solution is evaporated to dryness. After the addition of 2.5 cc. of nitric acid, the residue is dissolved in water, diluted to 150 cc., and electrolyzed at 50° to 55° with a current of ND_{100} = 5 amperes. The anode makes 500 revolutions per minute and the electrolysis requires about 2 hours.

Copper Matte. One gram of the powdered material is dissolved in 15 cc. of strong nitric acid containing bromine and allowed to stand without heating until all the sulphur is oxidized. Then 4 cc. of concentrated hydrochloric acid are added, the decomposition is completed by gently boiling, and, after the addition of 2 cc. of concentrated sulphuric acid, the solution is evaporated to dryness. The dry residue is moistened with 2 cc. of sulphuric acid and 2 cc. of nitric acid, diluted with water to 150 cc., and electrolyzed at 50° to 55° with a current of ND_{100} = 3 amperes in 45 to 55 minutes. The anode revolves as in the preceding case (*cf.* p. 128).

Ores. 1 gm. of the powder is heated with 10 cc. of nitric acid and the solution is evaporated to dryness with 1 cc. of sulphuric acid. To the residue, 3 cc. of sulphuric acid and 2 cc. of nitric acid in water are added, and the filtered solution is diluted to 150 cc. The electrolysis is carried out at 50° to 55° with a current of ND_{100} = 2 amperes; the anode makes 400 to 500 revolutions per minute; time required, 40 to 50 minutes.

The filtration of the solution can be omitted in most cases of technical analysis. The presence of suspensions does no harm when the electrolysis is carried out with a rotating electrode (*cf.* p. 238).

If it is desired to obtain a copper solution free from iron in the analysis of ores low in copper, instead of hydrogen sulphide or sodium thiosulphate to precipitate the copper, the use of metallic aluminium, as recommended by Heidenreich,* gives satisfaction.

From 2 to 5 gms. of ore are dissolved in a deep porcelain dish with 40 to 100 cc. of a mixture of 3 volumes of concentrated nitric acid and 1 volume of concentrated hydrochloric acid; the action is assisted by gentle heating until all the sulphide present is oxidized. The nitric acid is all removed by twice evaporating to dryness with hydrochloric acid. The residue is moistened with 5 cc. of dilute hydrochloric acid and dissolved in 10 cc. of water. The solution is filtered into a flask and diluted to about 100 cc. A strip of metallic aluminium is added and the solution heated for a few minutes. The deposited copper is filtered off, washed with hot water till free from chloride, and the filter together with the deposited copper is ignited in a porcelain crucible. The residue is dissolved in dilute nitric acid and the filtered solution electrolyzed according to page 123.

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* Z. anal. Chem., **40,** 15 (1901).

H. Danneel determines the copper in ores very quickly by first depositing this metal in a nitric-acid solution without paying any attention to the other metals present or to the spongy nature of the deposit. In this way all the copper together with some impurity is obtained. The deposit is washed without interrupting the current, taking care not to lose any copper. It is not necessary to wash very carefully, and one washing will answer all purposes. The spongy copper in the platinum dish is covered with dilute nitric acid and the dish is now made the anode in another electrolysis, using a gauze or sieve cathode. In the second deposition, the copper is obtained sufficiently pure for most analytical purposes. If the ore contains arsenic, it is well to dissolve the first deposit in nitric acid and deposit the copper the second time from an ammoniacal solution.

Brass.

Weigh 1 gm. of the alloy into a slender beaker of about 125-cc. capacity. Add 8 cc. of 6-normal nitric acid, cover the beaker and heat gently till all the brass is dissolved.

If, owing to the presence of a little tin, a white precipitate of metastannic acid forms, evaporate to dryness but do not bake the residue. Add 2 cc. of nitric acid, 25 cc. of water and boil gently to dissolve the nitrates of copper and zinc. Filter off the metastannic acid, wash it with hot water and weigh as SnO_2 after ignition in a porcelain crucible.

Dilute the clear solution of the nitrates to about 75 cc. and boil gently for one minute to remove any nitrous oxides. Then wash down the sides of the beaker and the cover glass and electrolyze, using preferably a platinum gauze cathode and a rotating platinum gauze anode. Use a current of about $ND_{100} = 3$ amperes. More current can be used, but there is then danger of slight mechanical loss and more likelihood of obtaining a spongy, non-adherent deposit. It is advisable to keep the beaker covered with a split watch glass.

Usually a slight deposit of lead peroxide will form upon the anode. If the alloy contains more lead than is commonly met with in brass, it is better to deposit the lead peroxide upon a stationary gauze cathode and in that case a rotating crucible cathode gives satisfactory results.

After the solution has become colorless continue the electrolysis a few minutes longer, add 0.1 gm. of urea and wash down the sides of the beaker. This serves to expose fresh electrode surface to the bath, as well as to wash down any copper solution that may have spattered up from the solution. With a little practice one can usually estimate closely the time when all the copper is deposited. It is not desirable to continue the electrolysis any longer than necessary. The bath gradually becomes neutral, owing to the reduction of nitric acid, and then zinc will deposit. Moreover, enough nitrous acid may be formed to dissolve some of the deposited copper. To counteract this last influence the urea is added: if nitrous acid is present the solution effervesces and nitrogen gas is evolved.

When all the copper is deposited, it is important to wash both electrodes while breaking the circuit. The best way to accomplish this is to siphon off the solution while pouring fresh water into the beaker, continuing until the resistance of the bath becomes so great that an incandescent light in the circuit glows very faintly. This treatment, however, greatly dilutes the zinc solution and retards any further work with it. It is sufficient to wash the electrodes in this manner: Slowly lower the beaker with the left hand while washing both electrodes with a stream of water from the wash bottle held in the right hand. Then quickly replace the original beaker with one containing pure water. Turn off the current, remove the electrodes and treat them in the usual manner.

To make sure that all the copper has been deposited, add a slight excess of ammonia to the entire solution. There should be no evidence of blue color. If one is obtained, discharge the color by the careful addition of sulphuric acid and electrolyze again with clean electrodes.

In the commercial analysis of brass, the zinc is usually determined by difference. It may be determined electrolytically by the method of L. H. Ingham or, more suitably, gravimetrically by precipitation as zinc ammonium phosphate in neutral solution (*cf.* Treadwell-Hall, Analytical Chemistry, Vol. II.).

Copper Matte (Lead Matte).

These metallurgical products contain silicic acid, sulphur, arsenic, antimony, iron (nickel, cobalt, zinc), as well as copper and lead which are often the only metals to be determined. 1 gm. of the substance is dissolved in about 30 cc. of nitric acid (sp. gr. 1.4). If it is desired to determine the lead, the nitric-acid solution is diluted with hot water, filtered and electrolyzed with the platinum dish as anode (*cf.* p. 194).

If only the copper is to be determined, the solution should contain but little nitric acid on account of the disturbing effect of the large quantity of iron present (*cf.* p. 293). The solution, irrespective of whether the metal was dissolved in nitric acid containing bromine (*cf.* p. 295) or in aqua regia, is evaporated with sulphuric acid and the sulphate residue is dissolved in the small volume of nitric acid recommended on page 295. In this solution the copper is determined slowly (p. 123) or rapidly (p. 128).

If both lead and copper are to be determined, the former metal is deposited as peroxide as described above. Meanwhile a part of the copper deposits upon the cathode. This copper deposit is redissolved in the solution which has been freed of lead, the large excess of nitric acid is neutralized with ammonia, and the copper is deposited according to page 123. The large quantity of ferric salt present prevents any interference of the arsenic (*cf.* p. 290). If the matte contained antimony, some lead sulphate must be added, for the reason given on page 290. Any silver present is determined by dissolving the copper deposit in nitric acid, precipitating with hydrochloric acid, and weighing the silver chloride.

Bronzes.

A pure bronze contains only copper and tin but the qualitative examination of commercial bronzes shows such differences in purity that it is impossible to give suitable procedures to cover all cases. There are bronzes which are very pure (telephone and telegraph wire), being prepared from electrolytic copper and Banca tin and containing a little phosphorus, silicon, or similar constituent, to increase the tenacity. The ordinary alloys, on the other hand, may contain all the impurities present in the copper, tin or old metal which may have been used in their manufacture. Then there are special bronzes, such as manganese bronze, phosphor bronze, etc., to which one or more foreign elements have been added designedly. Since such alloys are, as a rule, decomposed by the action of nitric acid, the important point that first arises is the purity of the metastannic acid that is left behind as insoluble residue. Metastannic acid has the property of carrying down with it such elements as copper, lead, iron, arsenic, antimony and phosphorus, and when the highest accuracy is demanded this is a matter that causes considerable complication in the analysis. The first thing to be decided, therefore, is whether it is desired to determine the tin content with the greatest possible accuracy or whether it will suffice to regard the washed metastannic acid as pure. The contamination of the metastannic acid by other oxides can, in the analysis of bronzes, easily amount to one per cent or more; but in many cases, when phosphorus and antimony are absent, it is satisfactory in technical analysis to leave the impurities out of consideration. When antimony, arsenic or phosphorus is present it is quite another matter. All but a trace of the former will be precipitated with the tin and all the phosphorus and arsenic will be precipitated, provided six or eight times as much tin is present in the alloy as the weight of the phosphorus pentoxide or arsenic pentoxide formed by the action of the nitric acid on the alloy. Since one part by weight of phosphorus gives more than two parts by weight of phosphorus pentoxide, and as much as one per cent of phosphorus is often present, it is obvious that considerable error may be introduced if the phosphorus in the insoluble residue is not determined.

Leaving, for the present, the phosphorus bronzes out of consideration and remembering that it is not common to find much arsenic or antimony in a bronze, it may be said that in most cases of commercial analysis it is satisfactory to wash the metastannic acid with water containing nitric acid, ignite it and weigh it as stannic oxide, SnO_2. In this way results are obtained more quickly than by determining the tin electrolytically.

A number of methods have been proposed for obtaining a pure residue of metastannic acid, or for purifying it. To free it from iron, Künzel boils the metastannic acid with dilute sulphuric acid. It must be borne in mind, here, that if large quantities of iron are present some tin may dissolve in the nitric acid (Rose). Busse's method,* which was devised for the analysis of tin alloys containing about 4 per cent of tin, consists in treating the alloy with very concentrated nitric acid (sp. gr. 1.5), and the reaction is started by gradually adding a little water; the method does not give good results if much tin or impurity is present. The direct

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* Z. anal. Chem., **17,** 63 (1878).

purification of the metastannic acid by means of the electric current is discussed on page 244.

To determine the tin content of an impure metastannic acid, the filter together with the washed metastannic acid is placed in a flask, a small piece of pure sodium hydroxide is added, this is covered with a little water, and then, on gently heating, the stannic oxide will dissolve to form sodium stannate, provided too large an excess of sodium hydroxide is not used. By saturating this solution with hydrogen sulphide, sodium thiostannate is formed and sulphides of copper, lead, and iron are left behind. The black sulphide residue is filtered, washed, and the filtrate is acidified with acetic acid whereby stannic sulphide is precipitated together with arsenic and antimony sulphides, when these elements are present in the original alloy. If to this mixture of suspended sulphides there is added, without filtering, a hot solution of equal parts oxalic acid and ammonium oxalate (3.5 gms. oxalic acid and 3.5 gms. oxalate for each 0.1 gm. of tin present) then the tin sulphide will dissolve, forming a brown solution from which, after filtering, the tin can be determined electrolytically (*cf.* p. 160); a slight turbidity of sulphur does no harm (F. Henz).*

The precipitated copper, lead, and iron sulphides obtained in purifying the metastannic acid are ignited together with the filter in a porcelain crucible; the residue is dissolved in dilute nitric acid and added to the solution obtained by treating the original alloy with nitric acid. The copper is then determined according to page 123. The other metals present are determined by methods already given, and the phosphorus by precipitation (*cf.* Treadwell-Hall, Quantitative Analysis).

Alloys of Lead, Tin, Antimony and Copper.

According to the methods to be described, the following alloys may be analyzed.

1. Alloys containing less than 20 per cent tin, such as impure tin foil.
2. Solder composed of lead and tin, containing more than 20 per cent tin, with possibly some antimony.
3. Britannia metal and similar alloys of tin, antimony and copper.
4. Bronzes of copper and tin; phosphor bronzes.

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* Z. anorg. Chem., **37,** 40 (1903).

5. Bearing metal (Babbitt metal) of tin, lead, antimony and copper.

6. Type metal of lead, tin and antimony.

7. Antimonial lead (hard lead) of lead and antimony with traces of copper, arsenic, nickel, cobalt and iron.*

A solution is prepared of 500 cc. water, 25 gms. potassium chloride, 400 cc. concentrated hydrochloric acid, and 100 cc. nitric acid (sp. gr. 1.4). This solution decomposes only slightly in the cold.

1 gm. of alloy is heated with 70 to 100 gms. of the acid solution. When the action of the acid upon the metal is over, the solution is concentrated to about 50 cc. and cooled. After the greater part of the lead has deposited as chloride, gradually, under constant stirring, 100 cc. of 95 per cent alcohol are added and the solution is allowed to stand for 20 minutes, to allow all the lead chloride to crystallize. The solution is decanted through a weighed Gooch crucible, the crystals washed three times by decantation with a mixture of 4 volumes of alcohol and 1 volume of concentrated hydrochloric acid, after which the crystals are all transferred to the crucible and freed from hydrochloric acid by washing with absolute alcohol. The crucible is dried at 120° to 130°, cooled in a desiccator and weighed.

If it is desired to determine the lead electrolytically, which is advisable if the percentage is low, the chloride is transformed to nitrate by treatment with nitric acid and the electrolysis conducted as described on page **194**.

The separation of the tin from antimony is best accomplished by Clarke's method which was originally devised for the separation of these two elements only, but, as Thompson has shown, it may be also used for the separation of tin from copper. The method is based upon the different behavior of the metals toward hydrogen sulphide in a boiling solution of oxalic acid; antimony and copper are precipitated as sulphides while the tin remains in solution. This method is particularly suited here because the oxalic-acid solution can at once be electrolyzed for tin.

The solution freed from lead is evaporated to dryness on the water bath to remove the alcohol and hydrochloric acid; the

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* This classification of alloys was suggested by C. W. Thompson (J. Soc. Chem. Ind., **15**, 179 (1896)). Various details mentioned by Thompson are stated in the above text.

residual salts are dissolved in 10 gms. oxalic acid, 10 gms. ammonium oxalate and about 200 cc. of water. The solution is heated to boiling and, while it is kept at a temperature near the boiling point, a current of hydrogen sulphide is introduced for about 45 minutes. The sulphides of antimony and copper are promptly filtered off and washed with hot water containing hydrogen sulphide.

After the excess of hydrogen sulphide has been boiled off, the filtrate is concentrated as much as necessary and the electrolytic determination of tin carried out as described on page **160.**

The precipitate of copper and antimony sulphides is heated with a little sodium-sulphide solution and the treatment is repeated with successive portions of this reagent until all the antimony is extracted. The solution is filtered and the antimony determined, after destroying the polysulphide present, as described on page **158.**

The copper sulphide is dissolved in nitric acid, and, after filtering off any sulphur that is deposited, the copper is determined electrolytically as described on page **123.**

Inasmuch as a little lead invariably escapes precipitation as chloride, the anode is weighed in this last electrolysis and the last traces of lead will be deposited upon it as peroxide while the copper is being deposited on the anode.

White Metals.

These alloys, comprising Babbitt metal as well as other bearing and antifriction metals, contain tin as the principal ingredient in the presence of small quantities of antimony and copper; to some of the alloys lead is added and there are always impurities likely to be present as a result of impure metals being used in the manufacture of the alloys.

If the metal contains no lead, about 0.5 gm. is dissolved in 3 or 4 cc. of hot concentrated nitric acid; after cooling, the solution is diluted cautiously with water and a slight excess of sodium-hydroxide solution is added. This alkaline mixture is poured into 50 cc. of a sodium-sulphide solution which is saturated with the salt at the laboratory temperature; this precipitates the copper as sulphide together with some stannous sulphide. The latter is brought into solution by heating the solution and adding sodium polysulphide drop by drop, avoiding an excess. The stannous sulphide is thus converted into sodium thiostannate, soluble in water. The insoluble sulphide residue is filtered and washed with water containing sodium sulphide. The solution is saturated with sodium monosulphide, Na_2S, treated with the requisite amount of potassium cyanide and the antimony determined according to page 158.

The tin is determined in the oxalate solution, prepared as described on page 160.

For the determination of copper and any other metals present, the insoluble sulphides remaining after the above treatment with sodium sulphide are dissolved in nitric acid and the analysis continued by the separations that have already been given.

If the white metal contained lead, the alloy is dissolved in nitric acid to which tartaric acid is added, and the determination of lead and antimony accomplished according to page 284, and the tin according to page 255.

Analysis of Commercial Zinc.

As regards the determination of the impurities and the principal metal, the statements on page 287 apply here; the zinc is determined by difference.

A. Hollard and L. Bertiaux * have adopted the following procedure, which is a combination of methods already known.

The presence or absence of arsenic is determined by testing the metal with arsenic-free sulphuric acid in a Marsh apparatus. If no arsenic is found, or not enough to influence the determination of any other constituent, 10 gms. of zinc are dissolved with an equal quantity of pure copper in 87 cc. of nitric acid (sp. gr. 1.33) after covering the metal with water. The quantity of nitric acid is such that, after the solution of the metal is complete, about 12 cc. of free acid will remain. The solution is electrolyzed with a current strength of 0.3 ampere (*cf.* p. 195). In the presence of the copper a much denser deposit of lead peroxide is obtained and it adheres more firmly to the anode.

To determine the iron a sufficiently large quantity of the zinc is dissolved in dilute sulphuric acid, out of contact with the air, and the resulting ferrous salt titrated with potassium permanganate solution. This simple process is permissible, however,

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* Analyse des Métaux par Electrolyse.

only when the zinc contains no tin or other substance that will react with permanganate in dilute solution. If tin is present, after the solution has been accomplished a few grams of chemically pure zinc are added to precipitate the tin upon it.

If the metal contains arsenic, it must be removed, as it interferes with the determination of lead. About 5 gms. of zinc are dissolved by boiling dilute hydrochloric acid whereby the arsenic is volatilized as trichloride. If an insoluble residue remains behind, it is dissolved by adding a few potassium-chlorate crystals and the excess of chlorine is removed by boiling. Into this solution hydrogen-sulphide gas is conducted to precipitate the sulphides of lead, cadmium, copper and tin. The solution must not be too acid as otherwise the cadmium is not precipitated as sulphide; it is necessary, therefore, to neutralize a part of the acid with ammonia before introducing the hydrogen sulphide. It must be remembered that the solubility products of zinc sulphide and of cadmium sulphide are not far apart. It is better in this case to have the solution so slightly acid that some zinc sulphide precipitates, rather than so acid that some of the cadmium fails to come down. The filtered and washed sulphide precipitate is dissolved by heating with nitric acid and, to aid in the oxidation of the sulphur, some bromine water is added. The resulting solution is evaporated to dryness on the water bath, the residue moistened with nitric acid, diluted with water, and the deposited metastannic acid filtered off. After dissolving in oxalic acid and ammonium oxalate, the tin is determined electrolytically.

From the nitric-acid solution, which may contain lead, cadmium and copper, the lead is precipitated as sulphate after evaporating with sulphuric acid. After filtering and washing the precipitate in the usual manner, it is dissolved in a mixture of 40 cc. of ammonia (sp. gr. 0.925), 67 cc. of nitric acid (sp. gr. 1.33) and enough cupric nitrate to correspond to 10 gms. of copper. This mixture contains ammonium nitrate, in which lead sulphate dissolves, and it also contains enough free nitric acid to permit the electrolytic determination of lead as peroxide as well as sufficient copper to obtain a good deposit (*cf.* p. 195).

In the sulphuric-acid solution from which the lead was precipitated, the copper is determined by the method given on page 116.

Cadmium may be present in the solution from which the zinc was deposited. The solution is evaporated to expel the nitric acid and the cadmium determined in cyanide solution according to page 176.

The iron is found together with the zinc in the solution from which the sulphides of lead, cadmium, copper and tin have been removed. The hydrogen sulphide is expelled by boiling the solution and finally adding a little concentrated nitric acid whereby the iron is also oxidized to the ferric condition. An excess of ammonia is then added and the precipitated ferric hydroxide is dissolved in oxalic acid. After the addition of ammonium oxalate, the iron is determined according to page **183**.

Determination of Zinc in Zinc Dust, Blue Powder, Flue Dust and Zinc Ores.

K. Jene [*] determines the zinc in such products as the above by the sodium-zincate method as recommended by v. Foregger.[†]

The solution of about 0.5 gm. of the substance in aqua regia is evaporated to dryness with 1 or 2 cc. of sulphuric acid (1 : 1) and the residue heated. In this way the metals are converted to sulphates in which state it is necessary to have the zinc. The sulphates are dissolved by boiling water, the insoluble residue removed by filtration, and the solution treated with 4 to 7 gms. of sodium hydroxide. This solution is electrolyzed at 50° in a copper-coated platinum dish by means of a current of $ND_{100} =$ 1 ampere at 3.8 to 4.2 volts, no attention being paid to the precipitated hydroxides of iron, manganese, etc. (*cf.* p. 307). After $1\frac{1}{2}$ hours a bright piece of copper foil is suspended over the edge of the dish and it is noticed whether a deposit of zinc is formed upon it. If after 15 minutes this is not the case, the deposited zinc is washed without interrupting the current, rinsed, dried and weighed.

Owing to the evaporation of water during the electrolysis a black rim may form where the zinc comes in contact with the air. To prevent this, water is added to the dish from time to time. The zinc deposit dissolves readily in dilute nitric acid before the layer of copper is attacked so that it is possible to use the dish for another zinc determination without depositing more copper upon it.

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[*] Chem.-Ztg., **29**, 803 (1905).

[†] Inaug.-Dissert., Bern, 1896.

Sphalerite.

The method tested by Ingham (p. 168) for depositing zinc in an ammoniacal solution with the aid of a rotating anode was used by him for the determination of zinc in a sample of sphalerite. Of the powdered ore, 0.5 gm. is moistened with water in a porcelain dish and heated slightly on the sand bath with the addition of nitric acid (sp. gr. 1.42). When, at the end of about 20 minutes, the action of the acid has ceased, the watch glass covering the dish is rinsed with water and raised somewhat by placing a glass triangle under it. The contents of the dish are then evaporated to dryness, the residue moistened with hydrochloric acid (sp. gr. 1.21), again evaporated to dryness, and the operation repeated several times to remove all the nitric acid. Finally the residual salt is moistened with strong hydrochloric acid and dissolved in hot water. After the iron has been precipitated with ammonia, the precipitate containing ferric hydroxide and gangue is filtered, dissolved, without washing, in hydrochloric acid and the iron again precipitated with ammonia. For this entire operation about 10 cc. of hydrochloric acid should suffice; the quantity of ammonia added should be regulated so that at the last about 2 cc. remain in excess.

The combined filtrates are treated with 0.5 gm. of ammonium chloride and the solution electrolyzed at 125 cc., while still warm, with a current of 5 amperes at 6 volts (*cf.* p. 168). The zinc forms as a light gray deposit and adheres well enough to prevent loss on washing. The results are very satisfactory.

As has already been mentioned several times, it cannot be assumed as a general rule that the presence of suspensions in an electrolyte has no effect upon the purity of a metal deposit nor that any of the metal present as inclusion in the precipitate (*i.e.*, zinc in ferric hydroxide) will be dissolved out during the progress of the electrolysis. As regards the effect of the precipitate upon the purity of a deposit, it is not serious if the precipitate is not allowed to remain in permanent contact with the electrode; thus the electrolysis in a stirred electrolyte gives better results when suspensions are present than when a stationary electrolyte is used. As regards the second point, there are so many contradictions in the literature that it is advisable to exercise precaution in all cases.

According to Hollard and Bertiaux, the copper present in metastannic acid is removed during the progress of the electrolysis; these authors also found that nickel in an ammoniacal solution could be determined accurately in the presence of suspended ferric or aluminium hydroxide. Similarly K. Jene (p. 305) deposits zinc from an alkaline solution of sodium zincate containing hydroxides of iron and manganese in suspension and obtains accurate results. On the other hand, Ingham has found it impossible to obtain accurate results in the zinc determination when the electrolysis of the ammoniacal solution was carried out in the presence of suspended ferric hydroxide. He found that the precipitate invariably contained zinc which could not be obtained by the action of the electric current. It is worth noting, however, that Ingham only carried out the electrolysis for 20 minutes whereas Jene allowed the current to act about seven times as long (*cf.* p. 238).

Lead (Refined or Soft Lead).

The impurities likely to be present include antimony, tin, arsenic, silver, bismuth, copper, cadmium, zinc, iron, nickel and cobalt. Since the sum of all these impurities seldom amounts to more than a fraction of one per cent, it is necessary to take a large sample for analysis.

In a two-liter calibrated flask, 200 gms. of the finely cut metal are treated with 1275 cc. of water, and 325 cc. of nitric acid (sp. gr. 1.4); the dilute acid is heated until all the metal is dissolved. To the cooled solution, 62 cc. of concentrated sulphuric acid are added, the solution is cooled again, diluted up to the mark and the precipitated lead sulphate allowed to settle. The solution is filtered and 1750 cc. of the filtrate are evaporated to dryness in a porcelain dish. The dry residue is extracted with a little water and the insoluble residue transferred to a filter and washed with water; in this way a residue (*A*) and a filtrate (*B*) are obtained.

The residue (*A*) consists chiefly of lead sulphate. To extract small quantities of antimony from it, it is rinsed into a small flask, and treated with sodium hydroxide and 25 cc. of saturated sodium-sulphide solution. After heating a short time, the solution containing the antimony as sodium thioantimonate (*F*) is filtered and set aside for the time being.

The filtrate (*B*), which contains all the other impurities, is acidified with a little hydrochloric acid, and treated with hydrogen-sulphide gas until the liquid above the precipitated sulphides has become perfectly clear. Filtration now gives a precipitate (*C*) and a filtrate (*D*).

The precipitate (*C*) contains the metals antimony, tin, arsenic, silver, bismuth, copper and cadmium. It is heated with sodium-sulphide solution and filtered. This filtrate is combined with the above-mentioned filtrate (*F*) leaving behind a residue (*E*).

Antimony, tin, arsenic. If no arsenic is present the solution is ready for the electrolytic separation of tin and antimony after treatment with potassium cyanide and sodium hydroxide (see p. 252).

If, however, arsenic is present it is best to determine this element in a separate sample (see below) and to prepare a solution of antimony and tin, free from arsenic, in the following manner. The three sulphides are precipitated by adding dilute sulphuric acid to the solution of the soluble thio salts. After filtering, the precipitate is washed with water and the arsenic pentasulphide extracted by treatment with ammonium-carbonate solution at the ordinary temperature. The sulphides of antimony and tin are then redissolved in sodium-monosulphide solution and, after treatment with potassium cyanide and sodium hydroxide, the solution is electrolyzed as described on page 252.

The residue (*E*), obtained from the second treatment with sodium-sulphide solution, and which contains the sulphides of silver, bismuth, copper and cadmium, is boiled with aqua regia. After diluting, any residue of silver chloride is filtered off.

Inasmuch as a little lead is likely to be present in this solution, it is next evaporated to dryness with the addition of a few drops of sulphuric acid. The residue is extracted with water and the lead sulphate is removed by filtration.

Bismuth. In the filtrate, containing bismuth, copper and cadmium, the bismuth is obtained, after neutralization with ammonia, by adding ammonium carbonate. If it is desired to determine the bismuth electrolytically, the bismuth carbonate precipitate is dissolved in nitric or sulphuric acid and the electrolysis conducted according to page 145, or page 149. A satisfactory gravimetric method for determining the bismuth consists in dissolving the precipitate in nitric acid and evaporating to dryness in a weighed porcelain crucible. After ignition, bismuth oxide, Bi_2O_3, is obtained.

Cadmium, copper. The ammoniacal filtrate from the bismuth precipitate is heated to expel the ammonia, and then treated with potassium cyanide. The cadmium is deposited electrolytically as described on page 176, and, after transforming the solvent to nitric acid, the copper is determined according to page 123.

Zinc. The filtrate (*D*), obtained from the precipitation with hydrogen sulphide, may contain zinc, iron, nickel and cobalt. The excess of hydrogen sulphide is expelled by boiling, a little bromine water is added and then an excess of sodium hydroxide. The zinc stays in solution as sodium zincate and the iron, nickel and cobalt are precipitated as hydroxides. The zinc may be determined in the alkaline solution according to the method described on page 166.

Nickel, cobalt. The washed hydroxides of iron, nickel and cobalt are dissolved in sulphuric acid and the nickel and cobalt determined in ammoniacal solution according to page 187.

Iron. After the electrolysis of the nickel and cobalt, the precipitate of ferric hydroxide is filtered off, dissolved in sulphuric acid and the iron determined volumetrically with potassium permanganate after reduction with zinc.

Silver. The most accurate method for determining the silver is by cupellation, as small quantities of silver chloride are held in solution by lead nitrate. A method for the electrolytic determination of the silver in lead is given on page 246.

Arsenic. To determine the arsenic, 10 gms. of lead are heated with 30 cc. of concentrated sulphuric acid until all the lead is converted into sulphate. To the cold liquid, 30 gms. of ferrous sulphate are added together with 2 gms. of ferric sulphate which reacts with any sulphurous acid that may have been formed by the reduction of sulphuric acid. After the addition of 300 cc. of concentrated hydrochloric acid, the arsenic trichloride is distilled into a receiver containing cold water. The arsenic in the distillate is determined iodometrically or as sulphide (*cf.* p. 293).

In computing all the above results, except in the case of arsenic, it is to be remembered that the solution obtained from 200 gms. of metal was diluted to a volume of 2 liters. The precipitate of lead sulphate occupies a volume of 46 cc. so that the true volume of liquid was only 1954 cc. instead of 2000. For the analysis 1750 cc. were taken, corresponding to $\frac{1750}{1954} \cdot 200 = 179.1$ gms. of the original metal.

Hard Lead.

The determination of antimony in hard lead was outlined on page 218. If it is desired to determine the copper, lead, etc., present in the sulphides obtained on treatment with sodium-sulphide solution, the precipitate is dissolved in nitric acid and the various metals determined as in the analysis of soft lead.

Crude Lead.

The impurities are the same as those in refined lead but they are present in larger quantities (1 to 4 per cent). From 10 to 50 gms. of the metal are weighed into a graduated liter-flask, and for each 10 gms. of the metal 60 cc. of water and 16 cc. of nitric acid (sp. gr. 1.42) added; 10 gms. of tartaric acid suffice even for 50 gms. of the metal. After solution is effected, 3 cc. of concentrated sulphuric acid are added for each 10 gms. of lead, and the lead sulphate is removed as described on page 307. An aliquot part of the filtrate from the lead sulphate is concentrated by evaporation; then the determinations of antimony, tin and arsenic are carried out after separating from other metals by treatment with sodium-sulphide and sodium-hydroxide solutions, as in the analysis of hard lead.

The sulphides insoluble in sodium-sulphide solution are dissolved in aqua regia. After diluting and filtering off the silver chloride, the metals of the copper group are precipitated in dilute hydrochloric-acid solution by the introduction of hydrogen-sulphide gas, and thereby separated from the metals of the iron group. The analysis is continued as in the case of refined lead (p. 307).

In computing the percentage of impurities present, it may be assumed that the volume of lead sulphate from 10 gms. of the original metal is 2.15 cc. This value is lower than that given on page 309, but in this case the impurities are present to a greater extent.

Silver is determined by cupellation of the original metal.

Iron Ores, Iron and Steel.

In the analysis of these materials only copper and nickel have been determined electrolytically to any extent. The difficulties involved in the electrolysis of copper solutions containing considerable iron have been pointed out already (p. 293). For determining the very low copper content of an iron or steel, the difficulty can be overcome in the following manner.

100 gms. of the filings or borings are covered with 200 cc. of sulphuric acid (sp. gr. 1.26); when the action slows down, 200 cc. more of the same acid are added and solution promoted by heating. Finally, after diluting to about 500 cc., the black residue, which contains all the copper, is filtered off. The filter, with its contents, is incinerated in a 100-cc. porcelain crucible, the residue treated with a little strong hydrochloric acid, whereby all the copper goes into solution, and the contents of the crucible evaporated to dryness with the addition of a little concentrated sulphuric acid. The residue is treated with water, nitric acid is added, and the copper is deposited in the filtered solution according to page 123.

If the material analyzed contains much graphite (gray cast iron) the graphitic residue may include considerable iron. In that case the contents of the first filter are rinsed back into the original beaker and again treated with 200 cc. of the sulphuric acid for half an hour at the boiling temperature. After diluting, the liquid is filtered through the same filter and the process continued as described.* The nickel determination is outlined on page 313.

Nickel.

In the analysis of commercial nickel, the metals nickel, copper and iron may be determined electrolytically.

Five grams of the metal, or more if necessary, are dissolved in nitric acid and the excess of acid expelled by heating. The residue is diluted with water, and enough ammonia is added to dissolve the nickel. The precipitated hydroxides of iron and aluminium, which contain some silicic acid † as well as some manganese and nickel, are filtered after heating a short time. The precipitate is dissolved in sulphuric acid and the precipitation with an excess of ammonia is repeated; in this way all the nickel is obtained in the ammoniacal solution. The precipitate (A) is set aside.

The combined ammoniacal nickel filtrates ‡ are electrolyzed

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* H. Koch, Z. anal. Chem., **41,** 105 (1902).

† For an accurate determination of the silicic acid, the residue obtained by evaporating off the nitric acid must be heated till the nitrates are decomposed and again dissolved in nitric acid.

‡ Hollard and Bertiaux recommend the addition of a few cubic centimeters of hydrogen peroxide to the ammonia whereby the deposition of carbon (from carbide) with the nickel is said to be prevented.

under the conditions given on page 186. The deposit (*B*) contains all the nickel, cobalt and copper. It is dissolved in nitric acid and the copper determined according to page 123. In the solution freed from copper, the cobalt is determined as potassium cobaltinitrite.* By deducting the weight of copper and cobalt from the weight of copper, cobalt and nickel obtained in the first electrolysis, the percentage of nickel is obtained.

The precipitate (*A*) which contains all the iron together with arsenic and antimony (as ferric arsenate and antimonate) is dissolved in sulphuric acid and the solution united with the electrolyte from which the deposit (*B*) was obtained, the latter being first freed from the excess of ammonia by boiling and made acid with sulphuric acid. This combined solution is treated with hydrogen sulphide to precipitate arsenic and antimony, and in the filtrate from these sulphides the excess of hydrogen sulphide is expelled. The last traces of the gas are decomposed by means of bromine water, the excess of the latter is boiled off, and the solution is transformed into a proper electrolyte for iron by the addition of ammonium oxalate. The iron is then determined electrolytically under the conditions given on page 183.

Manganese, aluminium and the remaining impurities are determined in the usual analytical way from the solution after the removal of the iron.

Determination of Nickel in Nickel Steel.

Various methods have been proposed for determining the nickel electrolytically in the presence of precipitated ferric hydroxide.† When much iron is present, however, it is certain that some nickel will be retained by the ferric-hydroxide precipitate and the deposited nickel will be contaminated by contact with the precipitate. Although these two errors tend to compensate one another, still the only safe way is to remove at least the greater part of the iron. The best way of accomplishing this is by the method of Rothe which depends upon the fact that undissociated ferric chloride is very much more soluble in ether than it is in water, whereas nickel chloride is insoluble in ether. It is important in

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* *Cf.* Treadwell-Hall, Quantitative Analysis.

† Hollard and Bertiaux, Analyse des Métaux par Electrolyse; Ducru, Classen's Ausgewählte Methoden; Vortmann, *cf.* page 265.

carrying out the separation that the solution should be free from suspended matter and for this reason it is necessary to remove any silicic acid at the start. In many cases, therefore, the determination of silicon will be combined with this analysis. Otherwise, it is easier to volatilize the silicic acid in the form of silicon tetrafluoride, in which case a platinum dish is used in dissolving the sample. According to the nickel content of the steel, from 2.5 to 5 gms. of borings are dissolved by heating with 40 cc. of hydrochloric acid (sp. gr. 1.12) and the solution is evaporated to dryness in a platinum dish, adding a few drops of hydrofluoric acid toward the last.* The residue is dissolved in dilute hydrochloric acid, the solution transferred to a porcelain evaporating dish, heated to boiling and cautiously treated with 2 to 2.5 cc. of concentrated nitric acid, keeping the dish covered with a watch glass. The solution is evaporated to sirupy consistency, or until ferric chloride begins to separate, to remove free chlorine or nitric acid, both of which tend to decompose ether. The solution, concentrated to about 10 cc., is transferred to a separatory funnel and shaken with ether.†

The solution from the ether separation is nearly, if not quite, free from iron when the process is carried out properly; it contains all the nickel and nearly all of the other constituents of the steel.‡ The solution is heated on the water bath to expel the ether and any copper present is precipitated by treating the slightly acid solution with hydrogen sulphide, or by boiling with sodium thiosulphate. The copper sulphide is filtered off, the solution freed from hydrogen sulphide by heating, and then evaporated nearly to dryness with the addition of sulphuric acid. The residue is dissolved in water and a few drops of sulphuric acid, and the manganese is precipitated by a double precipitation with ammonia and hydrogen peroxide.

In the combined filtrates, the nickel is deposited slowly or quickly under the conditions given on page 186 *et seq.*

A slight coloration at the anode is due to traces of manganese

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* The greater part of the iron is in the ferrous condition but during the evaporation considerable ferric chloride is formed. This may have a harmful effect upon the platinum dish.

† For fuller details of the ether separation, see Treadwell-Hall, Quantitative Analysis.

‡ Blair has found that molybdenum follows the iron in the analysis of alloy steels.

which were not precipitated by the ammoniacal solution of hydrogen peroxide.

Chrome-nickel Steel.

The removal of the iron is accomplished as described on page 313. Hydrogen sulphide is introduced into the filtrate and any precipitate of copper sulphide is filtered off, dissolved in nitric acid and the copper determined electrolytically (p. 123). The filtrate, which contains nickel, chromium and manganese, is evaporated to dryness with sulphuric acid and the residue prepared for the nickel electrolysis as described on page 190. If it is desired to determine the nickel quickly, the residue is treated with a solution of 10 gms. ammonium oxalate, heated to 80° and electrolyzed with a current of 6.5 to 7 amperes at 5.3 volts. Manganese is then precipitated as dioxide but does not adhere to the rotating anode.

To obtain pure nickel from this deposit which is usually contaminated with manganese, carbon and iron, the deposit is dissolved in nitric acid, the excess of acid removed by evaporation and the iron and manganese precipitated by treatment with ammonia and hydrogen peroxide. The precipitated ferric hydroxide and manganese dioxide are dissolved in sulphuric acid and a little hydrogen peroxide, and the precipitation is repeated in order to remove traces of nickel. In the combined ammoniacal filtrate the nickel is determined according to page 186.

For the chromium determination, the solution from the first nickel electrolysis, in which the chromium is present as chromic salt, is transferred to a platinum dish, to be used as anode, and the chromium is oxidized to chromate by electrolyzing at 60° with a current of 5 amperes at 6 to 9 volts potential. The oxidation requires nearly an hour.

The solution of chromate is acidified with acetic acid, treated with lead acetate, and the precipitated lead chromate determined in the usual analytical way.

Tin.

Of the impurities present in commercial tin, the antimony, lead, copper and bismuth may be determined electrolytically. The arsenic, iron and sulphur should be determined by the usual methods.

For the electro-analysis, 5 gms. or more of the sample are dissolved in hydrochloric acid with a little nitric acid. To separate the sulphides of tin, antimony and arsenic from the sulphides insoluble in alkaline sulphide, the solution is treated with an excess of ammonia, and hydrogen-sulphide gas is introduced until all the ammonia has been converted into monosulphide. The sulphides of lead, bismuth, copper and iron are filtered off, dissolved in acid, and the first three metals separated from iron by a second precipitation with hydrogen sulphide, this time having the solution slightly acid with hydrochloric acid.

To separate the lead from the bismuth and copper, the three sulphides are dissolved in aqua regia, the solution made ammoniacal and potassium cyanide added. If hydrogen sulphide is conducted into this ammoniacal-cyanide solution, the lead and bismuth are precipitated as sulphides while the copper remains in solution as ammonium cuprocyanide. The precipitated sulphides are dissolved in aqua regia and the resulting solution evaporated with sulphuric acid. To the residue, dilute alcohol is added, and the lead sulphate is filtered off. The precipitate is washed with water containing sulphuric acid and alcohol and the lead is determined as described on page 232.

In the alcoholic filtrate the bismuth is determined under the conditions given on page 291.

In the filtrate containing the iron, the hydrogen sulphide is expelled by boiling, the ferrous salt is oxidized to ferric salt by bromine water, and the iron precipitated by ammonia. The iron may be determined gravimetrically, volumetrically, or electrolytically.

The copper is determined best in a separate portion of metal. About 5 gms. are oxidized by treatment with nitric acid and the residue of metastannic acid is washed with water containing nitric acid; the solution will then contain the greater part of the copper. The metastannic acid is dissolved by adding solid potassium hydroxide and water (*cf.* p. 299), and hydrogen sulphide is introduced until all the potassium hydroxide has been converted into sulphide. The copper-sulphide precipitate is filtered off, dissolved in nitric acid, and this solution united with that obtained by the original treatment of the tin with nitric acid. The greater part of the nitric acid is neutralized with ammonia and the copper determined by electrolysis under the conditions given on page 123.

There is no danger of the deposited copper containing antimony or arsenic as these elements have followed the tin in the above treatment.

For the determination of antimony, another portion of the tin is taken and the solution of the thio salts is prepared as above by treatment with nitric acid, potassium hydroxide and hydrogen sulphide. The insoluble sulphides are filtered off, the polysulphides reduced by the addition of potassium cyanide (*cf.* p. 157) and the antimony deposited electrolytically. Since the antimony is likely to contain tin if the electrolysis is continued long, the deposit is dissolved in sodium-polysulphide solution (obtained by heating a little sodium-monosulphide solution with some free sulphur), the solution decolorized by the addition of potassium cyanide, and the electrolysis repeated.

The arsenic is volatilized as trichloride; 5 gms. of borings are dissolved in 150 cc. of hydrochloric acid in the presence of 50 gms. ferric sulphate (*cf.* p. 293), and the distillation carried out as usual.

Antimony.

From 5 to 10 gms. of the metal are dissolved in aqua regia, by first covering the borings with hydrochloric acid and adding nitric acid in small quantities until all the metal is dissolved. To get the antimony in the form of soluble thio salt, for the purpose of separating it from most of the impurities, the best way is to make the solution ammoniacal and then saturate it with hydrogen-sulphide gas; in this way the ammonium sulphide is formed in the presence of the substances upon which it is to act. The precipitated sulphides of copper, lead, bismuth, iron, etc., are filtered off.

It may be mentioned here that it is advisable to determine the copper in another sample of the metal. This is partly because copper sulphide is not absolutely insoluble in ammonium-sulphide solution and partly because the potassium-cyanide solution obtained in the further course of the analysis is not altogether suited for the copper determination.

After the washed sulphide precipitate has been dissolved in hydrochloric acid and bromine, the excess of the latter reagent is removed by boiling, and the metals of the copper group are separated from those of the iron group by the introduction of hydrogen sulphide into the slightly acid solution.

The precipitated sulphides of copper, lead and bismuth may contain traces of antimony which, however, are removed together with the copper by the following treatment. The sulphides are dissolved again in hydrochloric acid and bromine, the excess of the latter expelled by boiling, and, after making ammoniacal, an excess of potassium cyanide is added. If hydrogen sulphide is introduced into this solution, the sulphides of lead and bismuth will be precipitated. The filtrate containing the copper, and possibly some antimony, is rejected.

The sulphides of lead and bismuth are dissolved in aqua regia and the lead is precipitated as sulphate by evaporation with sulphuric acid; for the further treatment see page 232.

The filtrate containing the bismuth is electrolyzed as on page 291.

If the original metal contained cadmium, this element will be found in the bismuth solution. In this case the solution is neutralized with caustic soda and the separation of bismuth and cadmium accomplished as on page 260.

In the solution containing the iron, this metal is determined as described on page 183. If nickel is present, the process given on page 265 is followed.

Determination of the Copper. About 5 gms. of the antimony sample are dissolved as described on the preceding page and the excess of acid is expelled by heating, taking care to leave enough acid to prevent the precipitation of antimony oxychloride upon dilution with water. The solution is poured into one of sodium sulphide prepared with an excess of sodium hydroxide and in this way the copper is all precipitated as sulphide while all the antimony remains dissolved as sodium thioantimonate. The precipitated sulphide is filtered, washed with water and the copper determined according to page 123.

Copper-manganese.

The copper and manganese content of this alloy have been determined by A. Fischer and Reissmann in the Aachen laboratory. About 0.5 gm. of alloy is dissolved in nitric acid (sp. gr. 1.2), using an excess of 15 to 20 cc., and the solution is electrolyzed using a dish as cathode and a rotating disk, making 800 revolutions per minute, as anode. The current strength is adjusted to 1 ampere and the electrolysis is conducted at the laboratory temperature (see table on page 128).

The solution, free from copper, is neutralized with caustic soda and treated with hydrogen peroxide. The precipitate of hydrated manganese dioxide is filtered off, dissolved in acetic acid with the addition of hydrogen peroxide and the excess of the latter removed by the addition of a little chromic acid. In this solution containing acetate and chromic salt, the manganese is determined as described on page 191.

Ordinarily, only the manganese and copper are determined in this alloy and no attention is paid to a small iron content. If much iron is present, the acetic-acid solution obtained above is neutralized with ammonia, formic acid is added and the manganese and iron are determined as described on page 268.

Manganese Silicide.

From the experiments conducted by A. Fischer and Reissmann, it has been found that the manganese may be determined as follows: About 0.5 gm. of the substance is weighed into a platinum dish and moistened with hydrofluoric acid, sulphuric acid and a little nitric acid. After the first action is over the mixture is heated and the solution evaporated to dryness.

From the aqueous extract of the residue, the iron is precipitated as basic acetate, the precipitate dissolved in as little nitric acid as possible, and the basic acetate separation repeated. The combined filtrates are treated with acetic acid and chrome alum and the manganese is deposited electrolytically as described on page 191.

If it is desired to determine the iron, the basic ferric acetate may be dissolved in oxalic acid and, after neutralization with ammonia, the iron determined as on page 183.

Determination of Mercury in Cinnabar.

The transformation of mercuric sulphide into chloride, by heating with aqua regia, and the replacement of the nitric acid with hydrochloric acid is a tedious process and there is danger of volatilizing some mercury chloride. W. B. Rising and V. Lenher * have found that a more rapid method of effecting the solution of natural as well as artificial mercuric sulphide is by the use of hydrobromic acid; and that by adding potassium hydroxide and

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* J. Am. Chem. Soc., **18,** 96 (1896).

potassium cyanide to such a solution, an electrolytic determination of the mercury can be made at once.

The precipitated sulphide is dissolved in 12 per cent hydrobromic acid and the natural sulphide in 20 per cent hydrobromic acid, avoiding an excess. The precipitated sulphide dissolves in the cold but when the natural cinnabar is contaminated with silicate, a long digestion at the boiling temperature is required.

When all the mercury has dissolved, the solution is filtered, if necessary, and the free hydrobromic acid is neutralized with potassium-hydroxide solution. After adding an excess of potassium cyanide, the solution is electrolyzed with a platinum dish and disk anode and a current density of $ND_{100} = 0.025$ ampere (*cf.* p. 136).

* J. Am. Chem. Soc., **18,** 96 (1896).

INTERNATIONAL ATOMIC WEIGHTS, 1918.

	Symbol.	Atomic weight.		Symbol.	Atomic weight.
Aluminium	Al	27.1	Neodymium	Nd	144.3
Antimony	Sb	120.2	Neon	Ne	20.2
Argon	A	39.88	Nickel	Ni	58.68
Arsenic	As	74.96	Niton (radium emanation)	Nt	222.4
Barium	Ba	137.37	Nitrogen	N	14.01
Bismuth	Bi	208.0	Osmium	Os	190.9
Boron	B	11.0	Oxygen	O	16.00
Bromine	Br	79.92	Palladium	Pd	106.7
Cadmium	Cd	112.40	Phosphorus	P	31.04
Caesium	Cs	132.81	Platinum	Pt	195.2
Calcium	Ca	40.07	Potassium	K	39.10
Carbon	C	12.05	Praseodymium	Pr	140.9
Cerium	Ce	140.25	Radium	Ra	226.0
Chlorine	Cl	35.46	Rhodium	Rh	102.9
Chromium	Cr	52.0	Rubidium	Rb	85.45
Cobalt	Co	58.97	Ruthenium	Ru	101.7
Columbium	Cb	93.1	Samarium	Sa	150.4
Copper	Cu	63.57	Scandium	Sc	44.1
Dysprosium	Dy	162.5	Selenium	Se	79.2
Erbium	Er	167.7	Silicon	Si	28.3
Europium	Eu	152.0	Silver	Ag	107.88
Fluorine	F	19.0	Sodium	Na	23.00
Gadolinium	Gd	157.3	Strontium	Sr	87.63
Gallium	Ga	69.9	Sulfur	S	32.06
Germanium	Ge	72.5	Tantalum	Ta	181.5
Glucinum *	Gl	9.1	Tellurium	Te	127.5
Gold	Au	197.2	Terbium	Tb	159.2
Helium	He	4.0	Thallium	Tl	204.0
Holmium	Ho	163.5	Thorium	Th	232.4
Hydrogen	H	1.008	Thulium	Tm	168.5
Indium	In	114.8	Tin	Sn	118.7
Iodine	I	126.92	Titanium	Ti	48.1
Iridium	Ir	193.1	Tungsten	W	184.0
Iron	Fe	55.84	Uranium	U	238.2
Krypton	Kr	82.92	Vanadium	V	51.0
Lanthanum	La	139.0	Xenon	Xe	130.2
Lead	Pb	207.20	Ytterbium (Neoytterbium)	Yb	173.5
Lithium	Li	6.94	Yttrium	Yt	88.7
Lutecium	Lu	175.0	Zinc	Zn	65.37
Magnesium	Mg	24.32	Zirconium	Zr	90.6
Manganese	Mn	54.93			
Mercury	Hg	200.6			
Molybdenum	Mo	96.0			

* Also called *beryllium*, as in the text of this book.

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

0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS.								
										1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
8976	8982	8987	8993	8998	9004	9009	9015	9020	9026	1	1	2	2	3	3	4	4	5
9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
9777	9782	9787	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

Loga-rithms.	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS.								
											1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.43	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

ANTILOGARITHMS.

Logarithms.	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
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.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
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.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
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.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
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INDEX

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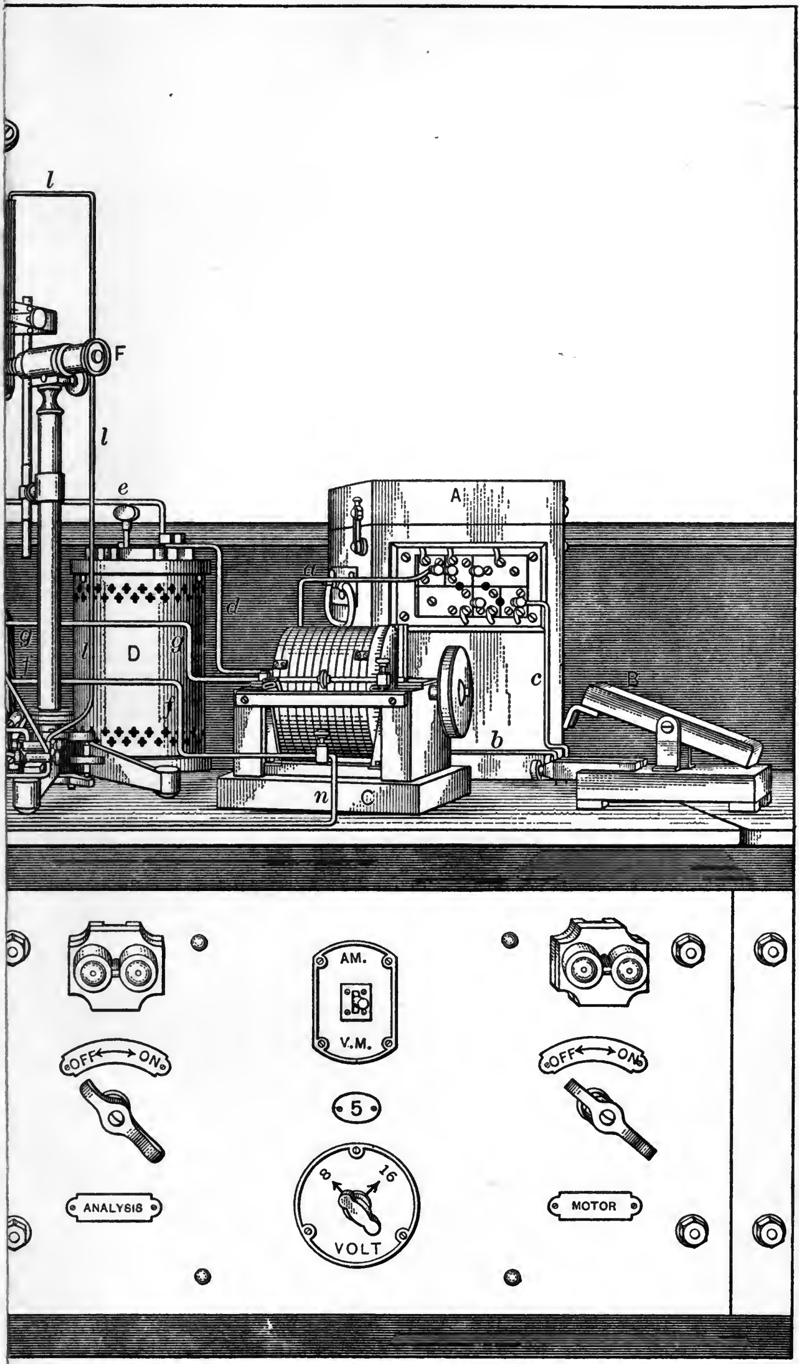
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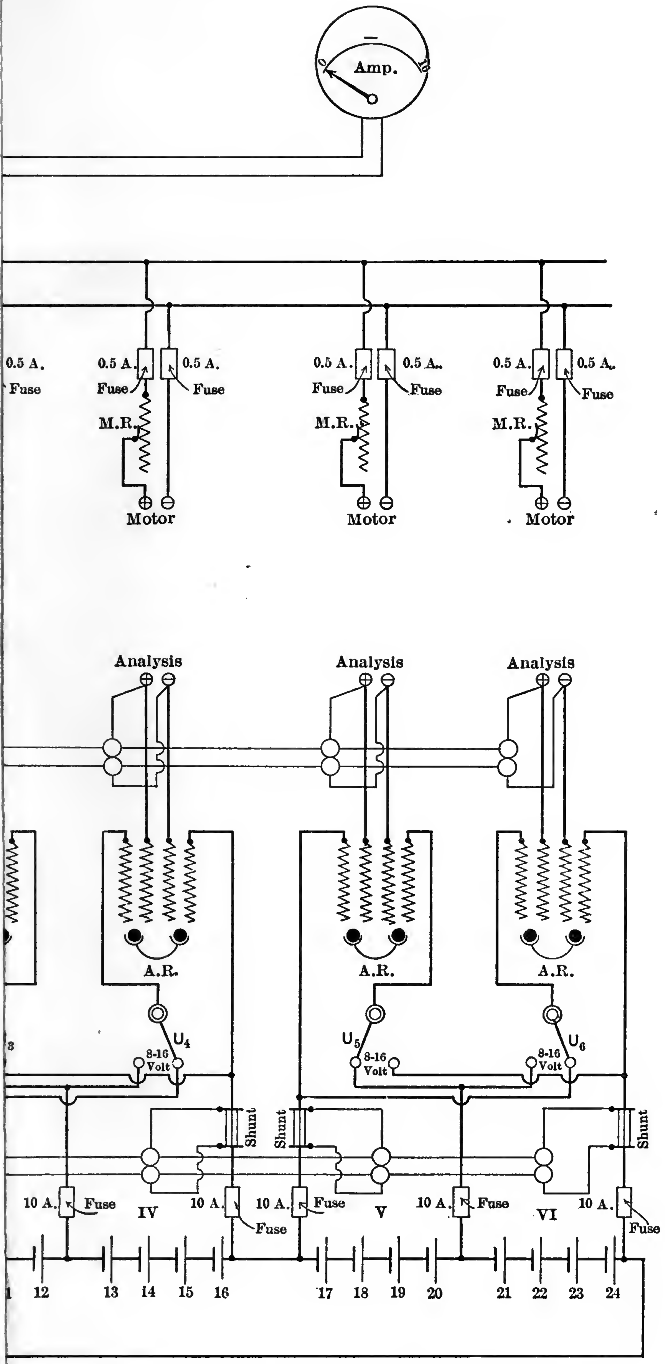
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CIVIL ENGINEERING—*Continued*

5e Highways; Municipal Engineering; Sanitary Engineering; Water Supply. **Forestry. Horticulture, Botany and Landscape Gardening.**

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10c Machine Design and Mechanism; Power Transmission; Steam Power and Power Plants; Thermodynamics and Heat Power.

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12—Medicine. Pharmacy. Medical and Pharmaceutical Chemistry. Sanitary Science and Engineering. Bacteriology and Biology.

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13—General; Assaying; Excavation, Earthwork, Tunneling, Etc.; Explosives; Geology; Metallurgy; Mineralogy; Prospecting; Ventilation.

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Quantitive analysis.

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To be reset.