QUANTITATIVE CHEMICAL ANALYSIS
BY
ELECTROLYSIS

BY

PROF. ALEXANDER CLASSEN, PH.D.
PRIVY COUNCILLOR
Director of the Laboratory of Electrochemistry and Inorganic Chemistry in the Royal Institute of Technology at Aachen

AUTHORIZED TRANSLATION

FOURTH ENGLISH FROM THE FOURTH GERMAN EDITION

REVISED AND ENLARGED

BY

BERTRAM B. BOLTWOOD, PH.D.
Formerly Instructor in Physical and Analytical Chemistry in the Sheffield Scientific School of Yale University

FIRST THOUSAND

NEW YORK
JOHN WILEY & SONS
LONDON: CHAPMAN & HALL, LIMITED
1906

ROBERT DRUMMOND, PRINTER, NEW YORK.

TRANSLATOR'S PREFACE.

THE chief object in preparing the present English edition of this book has been to include a considerable number of new electroanalytical methods which have been published since the appearance of the fourth German edition in 1897.

This task has been greatly simplified by the very kind assistance of Professor Classen, who has generously placed his new and valuable work on "Ausgewählte Methoden der Analytischen Chemie," published in Braunschweig in 1901, at the disposal of the translator. This book covers a wide field in analytical chemistry and embraces a variety of special subjects. It has been freely used in preparing the present English edition.

Part First of the German original has been divided into two sections, and the arrangement of the text has been altered to permit of a more systematic treatment of the subject. Much new material has been introduced into this part, and acknowledgment is especially due to Professors Hastings and Beach, from whose Text-Book of General Physics many of the descriptions of electrical apparatus have been taken.

To Part Second many new methods of analysis have been added, the source of these being Professor Classen's book mentioned above and the original papers in the chemical journals.

The translator has attempted to retain all of the valuable material contained in the fourth German edition and is solely responsible for any errors or mistakes in the new material which has been inserted. He desires to express here his thanks to Professor H. A. Bumstead of the Sheffield Scientific School for his valuable advice and criticism.

B. B. BOLTWOOD.

NEW HAVEN, Conn., April, 1903.

CONTENTS.

PART FIRST.

SECTION I.—INTRODUCTORY.

SECTION II.—DESCRIPTIVE.

PART SECOND.

SPECIAL.

PART THIRD.

QUANTITATIVE ANALYSIS BY ELECTROLYSIS.

PART FIRST.

SECTION I.—INTRODUCTORY.

CHAPTER I.

HISTORICAL.

THE development of electrochemical analysis has been almost wholly empirical. The most suitable conditions for the quantitative separation of metals by electricity have been determined from a great number of experiments, conducted with diligence and perseverance, while the nature of the reactions involved has not always at the time been 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 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, not as metals at the negative pole, but in the form of oxides on the positive pole, a property which permitted these metals to be readily separated from others. Investigations on the qualitative decomposition of inorganic salts of the metals were also carried out by Despretz (1857), Nickles (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 was comparatively rapid.

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 then directed principally to the chemical reactions which took place when different sources of current were used and when the other physical conditions were varied. The salts of the metals and the solvents suitable for use and the proper substances to be added to the solutions were investigated and determined. 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.

Simultaneous 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 tartaric acid solution containing an alkali acetate.

We are indebted to Richert (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 of 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.

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 electrolysed the uranium was completely precipitated as a hydrated protosesquioxide; 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 oxidised to sulphates. He summed up the results of his observations in a law, that in general the electric current exerts a reducing action on acid, and an oxidising 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 as and quite independently of Classen, 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) for the determination of zinc.

Since the year 1886 a great number of publications on electrochemical analysis have appeared, and the most important of these will be mentioned later.

Especially worthy of mention at this point, however, are the experiments conducted by Vortmann (1894) on the electrolytic determination of the halogens.

The investigations of Kiliani (1883), on the significance of the potential-difference in electrolytic determinations, served to draw attention to this important factor, and the later work of Le Blanc (1889) on the potential-differences 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 by carefully regulating the potential-difference of the current which he employed.

CHAPTER II.

THEORY OF SOLUTION.

THE modern theory of solution is the foundation of the science of electrochemistry. It is therefore most essential that this theory should be clearly understood by all workers in this branch of chemical science.

Until recent years solutions were considered to be mere mechanical mixtures of solvent and solute and no general laws governing such mixtures had been discovered. A theory assuming chemical interaction between solvent and solute, the so-called hydrate theory, involving the chemical combination of the molecules of the solute with the molecules of water, was proposed, but since this theory did not prove to be a satisfactory working hypothesis it was gradually abandoned.

The phenomenon of diffusion was well known. This is exhibited when solutions of dissolved substances are placed in contact with the pure solvent. In such cases the dissolved substance gradually works its way from the stronger solution through the entire solvent until finally after sufficient time has elapsed the mixture of solvent and solute is found to be absolutely uniform and all portions of the solution are of uniform concentration. This behavior of dissolved substances suggests the existence of a force tending to drive the particles out into the adjoining solvent, and in 1877 Pfeffer *

---

* Osmotische Untersuchungen. Leipzig 1877.

showed by a series of experiments that when the dissolved substance was prevented from diffusing into the solvent a pressure of considerable magnitude was exerted upon the retarding membranes which he employed. One of the membranes which he used was copper ferrocyanide precipitated in the walls of a porous earthenware cylindrical jar. This membrane allows the water used as a solvent, but not the substance contained in the solution, to pass through it (semi-permeable membrane), and by placing a solution in the jar which was surrounded by pure water, he was able to measure approximately the pressure which was exerted.

This pressure is known as the *osmotic pressure* of the substance in solution, and as a result of his experiments Pfeffer reached the following conclusions:

1. That the pressure is dependent on the nature of the dissolved substance.

2. That for any given substance the pressure depends on the concentration of the solution and is in direct proportion to this.

3. That the pressure at a given concentration is dependent on the temperature, and shows a regular increase with rising temperature.

Pfeffer also concluded that the magnitude of the pressure was influenced by the nature of the membrane, but this assumption was later shown to be erroneous.

Pfeffer's investigations attracted but little attention at the time they were published. It was not until the year 1885 that their important bearing on the theory of solution was appreciated.

In 1885 Van't Hoff called attention * to the fact that there

---

* Lois de l'Équilibre Chimique. Mémoire présenté a l'Académie Roy. des Sciences de Suède le 14 Octobre 1885.

seemed to be a very close and striking relation between the laws of gas pressure and the laws of osmotic pressure, and showed that the osmotic pressures of the dilute solutions measured by Pfeffer could be calculated from the gas laws alone, the values thus obtained corresponding within the limits of experimental error with the values measured by Pfeffer. He thus demonstrated that substances in dilute solutions have an osmotic pressure which is equal to the pressure which they would exert if they were in a gaseous form at the same temperature and occupied under these conditions a volume equal to the volume of the solution. Not only does the osmotic pressure vary inversely as the volume (Boyle's law), but the osmotic pressure is also directly proportional to the absolute temperature (Gay-Lussac's law).

If it be assumed, therefore, that the laws of gases apply generally to substances in solution, Avogadro's hypothesis may be applied in the following form:

Equal volumes of solutions of different substances at the same temperature and having the same osmotic pressure contain an equal number of molecules. This is known as Van't Hoff's law for solutions.

This law furnishes a valuable means for determining the molecular weight of chemical compounds. It is only necessary to determine the osmotic pressure and temperature of a solution containing a known weight of the compound in a given volume of solution. From the data thus obtained the molecular weight of the substance in solution can be readily calculated.

Since the direct measurement of the osmotic pressure is, for various reasons, a very difficult operation it is seldom resorted to in practice. Indirect methods which are more convenient are employed instead. These methods are based on the determination of other properties of solutions which show a direct variation with changes in the osmotic pressure. Chief among these indirect methods are those which depend on the measurement of the depression of the freezing point, the elevation of the boiling point, and the lowering of the vapor pressure of any pure solvent caused by the introduction of a known weight of any soluble substance. These are all directly proportional to the osmotic pressure of the substance in solution.

CHAPTER III.

ELECTROLYTES.

THE development of the theory of osmotic pressure brought to light the fact that a great number of chemical compounds when dissolved in water exerted osmotic pressures which did not agree with those which would be expected from Van't Hoff's law alone. These compounds, among which were included most of the substances used as reagents in analytical chemistry, could be divided into three general classes, *i.e.*, acids, bases, and salts.

These apparent exceptions to the law were raised as objections to its adoption, just as the abnormal gas density of ammonium chloride, before this was fully understood, was considered a proof of the fallacy of Avogadro's hypothesis.

Arrhenius * was the first to offer a satisfactory explanation of the cause of these abnormal osmotic pressures.

The theory proposed by him in 1887 may be stated as follows:

When a solid compound soluble in water is introduced into this liquid it passes into solution in the form of molecules. If the behavior of the compound is perfectly normal, *e.g.* if it gives an osmotic pressure which agrees with Van't Hoff's law, the molecules undergo no further alteration, but exist as such in the solution. If, however, the substance

---

* Zeit. f. phys. Chem., 1, 631 (1887).

belongs to that class of bodies which give abnormal osmotic pressures, then, *immediately* on passing into solution, some of the molecules dissociate into other particles which are called *ions*. These ions, which may be either single atoms or groups of atoms, have the same effect on the osmotic pressure as undissociated molecules. As a result of this increase in the number of particles in the solution the osmotic pressure is greater than if no dissociation had taken place.

The ratio of the number of dissociated molecules to the total number of molecules introduced into the solution is called the *degree of dissociation.*

If one gram molecule of a substance the composition of which is represented by AB is dissolved in a definite volume of solvent, and if this substance dissociates into two ions, A and B, the degree of dissociation being equal to x, the state of the substance in solution will be represented by the following expression:

$$xA + xB + (1-x)AB;$$

where 1 represents the gram molecule taken.

For a given solution having a known osmotic pressure the degree of dissociation can be calculated from the equation

$$x = \frac{P-p}{p(k-1)},$$

in which P stands for the osmotic pressure measured, p the theoretical osmotic pressure calculated from the gas laws, and k the number of ions into which each molecule dissociates.

The maximum value which x can attain is unity. This is its value when all of the substance contained in the solution is in the form of ions.

Several very important points with respect to the values of x have been brought out by experiment.

1. The degree of dissociation for a given substance dissolved in water is the same for all solutions of the same substance at the same concentration and temperature, *i.e.*, the degree of dissociation for a given solution at constant temperature is a constant.

2. On diluting a solution the degree of dissociation increases until the maximum value is attained. Beyond this point further dilution produces no change in the state of the dissolved substance.

3. Strong acids, strong bases and their salts even in fairly concentrated solutions are almost completely dissociated into their ions.

4. The degree of dissociation determined by measurements of the osmotic pressure or by any of the indirect methods already mentioned is found to agree exactly with the degree of dissociation as determined by an entirely separate and independent method depending upon the electrical conductivity of the solution (see p. 32).

A chemical compound which in a dissolved or melted condition conducts the electric current is called an *electrolyte*. If an electric current is passed through the aqueous solution of an electrolyte, certain chemical changes are produced. The process is called *electrolysis*. The points at which the current enters and leaves the solution are called the *electrodes*.

Arrhenius called attention to the fact that all solutions which contain dissociated substances have the property of conducting the electric current, indeed the greater the degree of dissociation the better the conductivity of the solution, while this property is not possessed to an appreciable extent by solutions of substances which correspond to Van't Hoff's law.

He therefore assumed that the undissociated molecules in a solution take no part in conducting the current and that the conductivity of the solution is due to the ions alone.

This view is borne out particularly by the fact that the conductivity of a solution per molecule of dissolved electrolyte increases with the dilution; namely, with increased dissociation.

In order to explain the property of conductivity, as well as other properties, the following conditions have been assumed:

1. That the separate ions are charged with electricity.
2. That a molecule is dissociated into two different kinds of ions, one kind being charged positively, the other negatively.
3. That the sum of the negative charges borne by the negative ions is exactly equal to the sum of the positive charges borne by the positive ions formed from the same molecule.
4. That the charges are inseparable from the ions as such and appear at the very instant of dissociation.
5. That the composition of the ions is similar to that of the substances which *primarily* appear at the electrodes when the solution is submitted to electrolysis.

Since bodies charged with electricity of unliko sign are known to attract each other, while the opposite is true for those which bear similar charges, the ions which appear at the negative electrode (*cathode*) are assumed to be charged positively (*cathions*) and those which appear at the positive electrode (*anode*) are assumed to be negatively charged (*anions*).

In the table given on p. 14 it is shown into what ions some of the more common acids, bases, and salts dissociate. The nature of the charge of each ion is denoted by a sign (+ or −) placed above it.

TABLE.

Acids.	Ions.	Bases.	Ions.
HCl	$\overset{+}{H}, \overset{-}{Cl}$	$NaOH$	$\overset{+}{Na}, \overset{-}{OH}$
HNO_3	$\overset{+}{H}, \overset{-}{NO_3}$	KOH	$\overset{+}{K}, \overset{-}{OH}$
HBr	$\overset{+}{H}, \overset{-}{Br}$	$Ca(OH)_2$	$\overset{+}{Ca}, \overset{-}{OH}, \overset{-}{OH}$
CH_3COOH	$\overset{+}{H}, \overset{-}{CH_3COO}$	$Ba(OH)_2$	$\overset{+}{Ba}, \overset{-}{OH}, \overset{-}{OH}$
H_2SO_4	$\overset{+}{H}, \overset{+}{H}, \overset{-}{SO_4}$ *		
H_2SO_3	$\overset{+}{H}, \overset{+}{H}, \overset{-}{SO_3}$		
$(COOH)_2$	$\overset{+}{H}, \overset{+}{H}, \overset{-}{C_2O_4}$		
H_3AsO_4	$\overset{+}{H}, \overset{+}{H}, \overset{+}{H}, \overset{-}{AsO_4}$		

Salts.	Ions.
$NaCl$	$\overset{+}{Na}, \overset{-}{Cl}$
$NaNO_3$	$\overset{+}{Na}, \overset{-}{NO_3}$
KBr	$\overset{+}{K}, \overset{-}{Br}$
$CaCl_2$	$\overset{+}{Ca}, \overset{-}{Cl}, \overset{-}{Cl}$
Na_2SO_4	$\overset{+}{Na}, \overset{+}{Na}, \overset{-}{SO_4}$
$(COONa)_2$	$\overset{+}{Na}, \overset{+}{Na}, \overset{-}{C_2O_4}$
$ZnSO_4$	$\overset{+}{Zn}, \overset{-}{SO_4}$
K_3AsO_4	$\overset{+}{K}, \overset{+}{K}, \overset{+}{K}, \overset{-}{AsO_4}$
$K_4Fe(CN)_6$	$\overset{+}{K}, \overset{+}{K}, \overset{+}{K}, \overset{+}{K}, \overset{-}{Fe(CN)_6}$
$HNaSO_4$	$\overset{+}{H}, \overset{+}{Na}, \overset{-}{SO_4}$

All acids dissociate into hydrogen cathions and acid radical anions, all bases into metal cathions and hydroxyl anions, and all neutral salts into metal cathions and acid

---

* In concentrated solutions: $\overset{+}{H}, \overset{-}{HSO_4}$.

radical anions. Acid salts furnish both metal and hydrogen cathions.

To one who meets the suggestion for the first time it may appear surprising that separate particles of sodium and chlorine can exist free in an aqueous solution of sodium chloride, since metallic sodium reacts so violently with water and with gaseous chlorine. But these reactions are between *molecular* sodium and water on the one hand, and between *molecular* sodium and *molecular* chlorine on the other.

When molecular quantities of metallic sodium and gaseous chlorine combine to form sodium chloride a considerable quantity of energy, which usually appears in the form of heat, is set free. The reaction is

$$Na_2 + Cl_2 = 2NaCl \text{ (solid)} + \cdot \cdot \cdot \cdot 97.6 \text{ Cal.}$$

The solid sodium chloride possesses none of the properties of either metallic sodium or gaseous chlorine, but nevertheless it is considered to contain the quantities of these *elements* originally taken. When dissolved in water the sodium chloride splits up into sodium *ions* and chlorine *ions*, these *ions* resembling sodium *atoms* and chlorine *atoms* in *no particular except that of composition.*

A satisfactory explanation of the cause for the difference in the properties of *atomic* sodium and chlorine and the same elements in the form of *ions* lies in the fact that the *quantity of energy which is associated with the former is* greater than that associated with equivalent quantities of the latter. It is reasonable to assume that the energy which is set free when molecular sodium and chlorine enter into chemical combination results from the loss of energy by both of these elements.

CHAPTER IV.

CURRENT-STRENGTH, POTENTIAL.

SUPPOSE that two electrodes composed of a metal which undergoes no alteration during the subsequent action are immersed in the solution of an electrolyte, and that the electrodes are connected with the positive and negative poles of a suitable source of current. Under these conditions the electrodes will be charged positively and negatively respectively. The negatively charged ions in the solution will be attracted to the anode and the positively charged ions to the cathode, and on coming into contact with the electrodes the ions will receive from them equivalent quantities of electricity of a sign opposite to that which they bear, that is, the positive ions will receive negative charges equal to the positive charges which they possess, and correspondingly the negative ions will receive positive charges from the anode equivalent to the negative charges of which they are the carriers. This neutralisation of the charges of the ions having taken place these particles instantly acquire the properties of atoms or atomic radicals.

As a result of the process described, electricity will disappear from both of the electrodes and the effect on these will be comparable to that which would take place if they were connected with each other by means of a metallic conductor.

If the wire connecting one of the electrodes to the source of current be considered, then as electricity disappears from the electrode, as a result of the neutralisation of the charges of the ions, more electricity will flow along the wire to take its place, and this movement of electricity will continue so long as there are ions in the solution.

Such a movement of electricity through a conductor is called a *current*, and since it is evident that certain quantities of electricity must pass along the wire in a given time, it is possible to speak of the *strength* of the current.

The *current-strength* in any conductor is the quantity of electricity passing any cross-section in the unit time (per second).

A peculiar significance is attached to the term "strength of current" if the flow of both positive and negative electricity along the conductor be considered. Thus, for example, at the *surface* of the positive electrode, where the contact of the negative ions takes place, two conceptions of the passage of electricity are permissible. It may be considered that, on the one hand, in one second a certain quantity of positive electricity n, exactly equivalent to the quantity of negative electricity n' borne by the discharging ions, passes from the electrode to the ions, and produces their electrical neutrality; or, on the other hand, the view may be taken that in the same time a quantity of positive electricity equal to $\frac{n}{2}$ passes from the electrode to the ions while simultaneously a quantity of negative electricity equal to $\frac{n'}{2}$ passes from the ions to the electrode. In the latter case the effect is the same as in the former, since a quantity of positive electricity equal to n disappears from the electrode, and the current-strength, *i.e.*, the total quantity of electricity passing this cross-section, is equal to n in both cases.

For the purpose of generality, therefore, the current-strength through any cross-section of a conductor will be considered as equal to N as defined by the following equation:

$$N = n + n',$$

n being the quantity of positive electricity passing in the unit time, and n' the quantity of negative electricity passing in the same period but in an opposite direction.

In order that electricity can flow from one point to another a difference of electrical pressure between the two points is necessary. This electrical pressure is called *potential* and the movement of electricity along the conductor is said to be due to a *difference of potential.* Potential bears a striking resemblance to pressure in fluids and to temperature in heat, but the analogy is not rigid and care must be taken that they are not confounded. Since two kinds of electricity are recognised it is important to remember that while positive electricity moves from a point of higher to a point of lower potential, negative electricity always moves in the opposite direction, *i.e.* from a point of lower to a point of higher potential.

CHAPTER V.

FARADAY'S LAW.

THIS law, which applies to the passage of electricity through the solution of an electrolyte, includes two propositions:

1. The weights of the ions which separate at an electrode during equal intervals of time are directly proportional to the current-strength.

2. The current-strength remaining constant, the weights of different ions which separate at the electrodes in equal intervals of time are in direct proportion to the chemical equivalent weights of the ions.

The truth of the first proposition can be readily demonstrated by electrolysing a copper sulphate solution for a certain length of time with a current of given strength and determining the weight of the separated copper. If the experiment is repeated, but with a current of twice the former strength, the weight of the copper will be twice that precipitated in the first experiment.

The truth of the second proposition can be similarly shown by passing currents of equal strength through solutions of different electrolytes for equal periods of time. If a series of solutions containing the ions $\overset{+}{\mathrm{H}}$, $\overset{+}{\mathrm{Ag}}$, $\overset{+}{\mathrm{Cu}}$ (cuprous), $\overset{+}{\mathrm{Cu}}$ (cupric), $\overset{+}{\mathrm{Fe}}$ (ferric), $\overset{-}{\mathrm{Cl}}$, and $\overset{-}{\mathrm{Br}}$ are electrolysed with the same current for the same length of time, it will be found that the weights of the elements set free at the electrodes are in the ratio

$$1:107.9:63.6:\frac{63.6}{2}:\frac{56}{3}:35.5:80,$$

respectively.

These two propositions lead to the following assumptions:

1. That the quantities of electricity borne by equal weights of similar ions are equal.

2. That the quantity of electricity borne by any ion is exactly equal to the charge borne by every other similar ion.

3. That the magnitude of the charge borne by any univalent ion is the same as that borne by every other univalent ion.

4. That the quantity of electricity associated with every ion is directly proportional to the valence of the ion, the quantity associated with a bivalent ion being twice as great as that of a univalent ion, etc.

The *unit quantity of electricity* has been chosen as that quantity of electricity *equivalent* to the charge borne by 1.118 milligrams* of silver ions. This quantity of electricity is called a *coulomb*.

A *current* is of *unit strength* when the quantity of electricity (p. 18) which passes a cross-section of the conductor in one second is equal to one coulomb. The name for the unit of current-strength is the *ampere*.

The magnitude of the charge borne by a gram-equivalent of ions can be readily calculated from the definition of the coulomb. It is only necessary to divide the chemical equiv-

---

* After a careful study of the results obtained by different investigators, Richards and Heimrod (Zeit. phys. Chem., **41**, **302** (**1902**)) have decided that the most probable value is 1.1175 mg.

alent weight of silver, 107.9, by 0.001118. The result obtained is approximately 96,540.* This quantity of electricity is denoted by the symbol *F* and may also be defined as that quantity of electricity required for the discharge, or, better, for the electrical neutralisation, of one gram-equivalent of ions at the electrodes.

The weight (in milligrams) of the different ions set free per second at the electrodes by the passage of a current of one ampere is known as the electrochemical equivalent of the ions. A table of the electrochemical equivalents of a number of ions is given below.

Element.	Atomic Weight.	Ion.	Valence.	Weight of Ions Discharged by Current of One Ampere		
				in one second, milligrams.	in one minute, milligrams.	in one hour, grams.
Antimony	120.2	Sb'''	3	0.414	24.86	1.492
		Sb''''	5	0.249	14.92	0.895
Cadmium	112.4	Cd''	2	0.582	34.93	2.096
Chlorine	35.45	Cl'	1	0.367	22.03	1.322
Copper	63.6	Cu'	1	0.659	39.53	2.372
		Cu''	2	0.329	19.76	1.186
Iron	55.9	Fe''	2	0.289	17.37	1.042
		Fe'''	3	0.193	11.58	0.695
Lead	206.9	Pb''	2	1.072	64.30	3.858
Mercury	200.0	Hg'	1	2.072	124.32	7.459
		Hg''	2	1.036	62.16	3.730
Nickel	58.7	Ni''	2	0.304	18.24	1.094
Silver	107.93	Ag'	1	1.118	67.08	4.025
Tin	119.0	Sn''	2	0.616	36.98	2.219
		Sn''''	4	0.308	18.49	1.109
Zinc	65.4	Zn''	2	0.339	20.32	1.219

---

* 96,580 according to Richards and Heimrod, *loc. cit*

CHAPTER VI.

OHM'S LAW.

THE basis of this law as first discovered by Ohm may be stated as follows:

In any metallic conductor through which a current of electricity is flowing, the current-strength is directly proportional to the difference of potential existing between the ends of the conductor.

If the difference of potential between the ends of the conductor be represented by $(V_1 - V_2)$ and the current-strength by C, the law can be expressed as follows:

$$\frac{V_1 - V_2}{C} = K \text{ (at constant temperature),}$$

where K is a constant depending only on the conductor.

For conductors of similar shape but of different materials the values of K are different. For wires composed of the same metal the following laws have been determined:

1. The cross-section of the wires being uniform throughout, the value of K is in direct proportion to the length of the wires.

2. The length of the wires being the same, the values of K are inversely proportional to the cross-section of the wires.

These two propositions apply only when the temperature is the same in all cases. The value of K for a given metal is found to increase with increasing temperature.

It is evident from the above that if, with a given difference of electrical potential, the length of the wire is increased, the current-strength will be diminished. It is therefore customary to speak of the constant K, which has been defined above, as the resistance of the wire or body in question, since by increasing the length, or diminishing the cross-section, of the wire a certain opposition appears to be offered to the passage of electricity.

On the basis of this conception it is allowable to express the law in the following manner:

$$\frac{\text{Difference of potential}}{\text{Current-strength}} = \text{Resistance},$$

and representing the resistance by R,

$$\frac{V_1 - V_2}{C} = R.$$

The unit employed in practice for measuring differences of potential is called the *volt*. If the difference of potential between the ends of a conductor is equal to one volt and the current-strength through the conductor is equal to one ampere, the value of K in the above equation would be unity. Under these conditions the conductor is said to have *unit* resistance, and this unit has been named the *ohm*. The ohm may be defined as the resistance of a conductor, which with a difference of potential between its ends of one volt, permits of the passage of a current having a strength of one ampere.

A resistance equal to the unit just mentioned is possessed by a column of mercury, at 0° Centigrade, 106.3 centimeters in length and with a uniform cross-section of one square millimeter.

The mathematical expression

$$\text{Resistance in ohms} = \frac{\text{Difference of potential in volts}}{\text{Current-strength in amperes}}$$

is of great practical value, since it makes it possible to determine any one of the three factors when the other two are given.

The *specific resistance* of any substance is the number expressing the ratio between the resistance of a cylinder of the substance in question and the resistance of a similar cylinder of some standard substance taken as unity. The standard substance chosen is mercury at 0° Centigrade.

The form of the equation given above can be changed to

$$\frac{C}{V_1 - V_2} = \frac{1}{R},$$

and since R is a constant, the value of $\frac{1}{R}$ must be a constant also. This factor, $\frac{1}{R}$, can be represented by L and is called the *conductivity* or *conductance*.

The equation may then be written

$$\frac{C}{V_1 - V_2} = L.$$

If the current-strength is measured in amperes and the difference of potential in volts, the value of the conductivity will be obtained in *reciprocal ohms*. To this unit the name *mho* has been given.

TABLE OF THE SPECIFIC RESISTANCE AND CONDUCTIVITY OF SOME SUBSTANCES AT 18°.

	Resistance in Ohms of a Column 1 Meter Long and 1 sq. mm. in Cross-section.	Conductivity Referred to Mercury at 0°.
Silver	0.016	59
Copper	0.0172	55
Gold	0.023	41
Zinc	0.063	15
Iron	0.09 to 0.15	6 to 10
Platinum	0.14	6.5
Lead	0.21	4.6
Mercury	1.016	0.984
Gas carbon (about)	50	0.02
Brass	0.07 to 0.09	10 to 14
German silver	0.16 to 0.4	2.4 to 6

(Wiedemann and Ebert, Physikalisches Praktikum, Braunschweig, 1893.)

CHAPTER VII.

MIGRATION OF THE IONS.

If the solution of an electrolyte be submitted to electrolysis, a movement of the ions towards the electrodes and a discharge of the ions at the electrodes will take place. Equivalent quantities of positive and negative electricity must disappear simultaneously from the anode and cathode respectively,* and chemically equivalent quantities of anions and cathions must be discharged. This must be the case, since if it were not, the electrostatic equilibrium of the system would be disturbed, and under the conditions this is not possible. Thus, for example, if an excess of anions separated at the anode the solution would become as a whole charged negatively, and this condition would retard the separation of more anions and promote the discharge of more cathions until equilibrium was again established.

If the movement of electricity through the wires connecting the electrodes with the source of current be considered it will be obvious that the simplest conception of this is that equal quantities of positive and negative electricity flow in opposite directions through the metallic circuit. For this and for other reasons this is the general conception of the character of current through metallic conductors.

The movement of the ions toward the electrodes during electrolysis is called the *migration of the ions*. The effect

---

* **Faraday's law.**

of this migration on the concentration of the solution can be best understood by the use of the following diagram.

Let *A* and *B* be the positive and negative electrodes between which is a solution of a binary electrolyte (an electrolyte the molecules of which dissociate into two univalent ions), and let *C* be a cross-section of the solution equidistant from *A* and *B*. Let the form of the vessel be such that the volume of the solutions in *AC* and *BC* are equal, and for convenience let it be assumed that the quantity of the electrolyte contained in each compartment is equal to six molecules. If the velocities of migration of the cathion and anion are the same, then in a given interval of time if two anions pass through *C* from left to right, two cathions will pass through *C* in the opposite direction. The state of the solution after this has taken place is shown at *b*. In this figure the ions to the left of the anode and to the right of the cathode have been neutralised at the electrodes and have passed out from the solution.

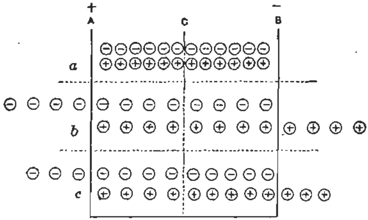


FIG. 1.

It is evident that under these conditions the following changes have taken place:

Two positive ions have passed into *CB* from *AC* and four positive ions have been neutralised at the cathode. Two negative ions have passed from *CB* into *AC* and four negative ions have been neutralised at the anode. Four equivalents of electricity have passed each of the electrodes, and four equivalents (two positive and two negative) have also passed the cross-section *C*. The current-strength through all cross-sections of the solution has been the same. Equal quantities of the electrolyte remain on both sides of the section *C*.

If the velocities of migration of the anion and cathion are not the same, a different condition of affairs will be recognised. Let it be assumed that the velocity of migration of the cathion is twice that of the anion (Fig. 1, *c*). Then in a given interval of time if two cathions pass through *C* from left to right, only one anion will have passed in the opposite direction. Three cathions and three anions have been neutralised at the electrodes and three equivalents of electricity have disappeared from each of the latter. Three equivalents of electricity have passed the cross-section *C*, two positive and one negative. The current-strength through all cross-sections has been the same.

The most important result which has been produced is the change in the relative concentration of the solution. In *AC* there are now *four* molecules of the electrolyte, while in *CB* there are *five* molecules.

In general when the velocities of migration of the ions are different one of the results of electrolysis is a change in the relative concentration of the solutions about the cathode and the anode.

The effect on the solution in *AC* has been to decrease the amount of material contained in it by two molecules, while from *CB* a quantity equal to one molecule has been removed. The following equation can be shown to express the conditions, both for the case mentioned as well as for all others:

$$\frac{\text{Velocity of migration of cathion}}{\text{Velocity of migration of anion}} = \frac{\text{Loss at anode}}{\text{Loss at cathode}}.$$

The terms "loss at anode" and "loss at cathode" must be understood to mean the decrease in concentration of the solutions in the neighborhood of the respective electrodes.

If the quantity of electricity supplied to the electrodes has been 96,540 coulombs, and further, if that portion of a gram-equivalent of the cathion which has migrated through any cross-section of the solution from the region of the anode toward the cathode be represented by n, then $1-n$ will represent that portion of a gram-equivalent of the anion which has moved from the region of the cathode toward the anode. Representing the velocities of migration of the cathion and anion by u and v respectively, we obtain the following equation:

$$\frac{u}{v} = \frac{n}{1-n} = \frac{\text{Loss at anode}}{\text{Loss at cathode}}.$$

The quantities n and $1-n$ are called the *shares of transport* or transport numbers of the cathion and anion.

In the following table * the relative velocities of migration of a number of cathions and anions are given:

(0.1 Normal solutions.)

$\overset{+}{K}$	= 55.8	$\overset{-}{Cl}$	= 56.5
Na	= 35.0	I	= 57.3
Li	= 26.1	NO_3	= 51.4
NH_4	= 54.8	$\frac{1}{2}SO_4$	= 41.9
Ag	= 43.3	$\frac{1}{2}CO_2$	= 38
H	= 296	OH	= 157

---

* Kohlrausch and Holborn, Leitvermögen der Elektrolyte.

CHAPTER VIII.

THE CONDUCTIVITY OF SOLUTIONS.

The unit taken for the conductivity of solutions is the conductivity of a body, a column of which one centimeter long and one square-centimeter in cross-section has the resistance of one ohm. The best conducting aqueous solutions of acids, at about 40°, have such a conductivity.

Formerly the electric conductivity was almost without exception referred to mercury at 0°. Since a centimeter-cube of mercury at 0° has a resistance of $\frac{1}{10630}$ ohm, the present unit is 10,630 times greater than the former one.*

Since the passage of electricity through the solution of an electrolyte is primarily dependent on the ions which are between the electrodes, and since the greater the number of the ions the greater the conductivity, this factor in the case of solutions is of more immediate significance than the resistance.

The simplest method of expressing the conductivities of solutions is in terms of the unit already defined, but since it is for many reasons desirable to compare solutions containing equal numbers of molecules, the conductivities are often expressed in terms of the ratio of the conductivity to the equivalent or molecular concentration.

Let a gram-molecule of some salt, say sodium chloride, be dissolved in sufficient water to make the total volume of the final solution equal to 1000 cc. and let this solution be

---

* Kohlrausch and Holborn, Leitvermögen der Elektrolyte, Leipzig, 1898.

introduced into a rectangular vessel having two parallel conducting walls, *A* and *B* (Fig. 2), which are separated by a distance of one centimeter, and let the two other sides and bottom be of non-conducting material. If the conductivity of the solution between the two electrodes be now measured it will be exactly 1000 times that of a cube with an edge of one centimeter, *i.e.*, 1000 times as great as the conductivity of the given normal solution expressed in the adopted units.

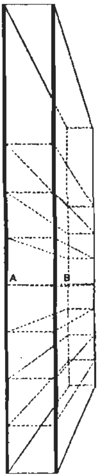


FIG. 2.

The *equivalent conductivity* of the solution may be defined as the conductivity divided by the equivalent concentration (the concentration measured according to the gram-equivalents of the dissolved substance in 1 cc. of the solution).

If the solution in the vessel be now diluted to 2000 cc. and the conductivity of the solution between the electrodes again measured, the value obtained will be 2000 times that of a cube of the solution with an edge of one centimeter.

Since the *quantity* of sodium chloride between the two electrodes is exactly the same as that in the first measurement (one gram-molecule) and the distance between the electrodes is unaltered, any change in the observed conductivities would be due entirely to a change in the *state* of the dissolved electrolyte. Since the degree of dissociation increases with increased dilution the more dilute solution would contain the greater number of ions, and the conductivity would be, and in practice is found to be, greater in the second case than in the first.

If the vessel were of sufficient capacity so that the solution could be diluted until all of the dissolved electrolyte was in the form of ions, then the maximum value for the conductivity would be obtained. There would then be one gram-equivalent (23 grams) of sodium ions and one gram-equivalent (35.5 grams) of chlorine ions between the two electrodes.

A description of the apparatus and method used in actual practice for measuring the conductivity of solutions is beyond the scope of the present work. It may be stated that the general principle depends upon the measurement of the resistance of the solution which is contained in a suitable vessel provided with platinum electrodes. In calculating the conductivity of the solutions from the values thus obtained use is made of the so-called "resistance capacity" of the vessel, a factor which depends upon the shape and size of, and the distance between, the electrodes. Since direct currents would produce a decomposition of the solution only alternating currents of high frequency and low current-strength are employed in measuring the conductivity.

Since strong acids, strong bases and salts are completely dissociated in solutions which are not so dilute as to make accurate measurements of their conductivities impossible, the equivalent conductivities of a large number of these compounds have been determined under all conditions of dilution. If the equivalent conductivity of an electrolyte at any given concentration be divided by the equivalent conductivity of a solution in which the dissociation is complete the quotient will be the degree of dissociation of the dissolved substance at the given concentration (see p. 12).

As a general summary of the theory of electrolytic conductivity it may be said that since the passage of electricity through an electrolyte is always accompanied by the transfer of matter, the power which a solution has for conducting the electric current must depend directly on the nature of the substances which are in the solution. The ions alone are the bearers of electric charges, the undissociated molecules taking no part in the transportation of electricity. The conductivity of a solution depends, therefore, upon the number of ions which it contains and the nature of the ions themselves. The speed at which the electricity is transported depends upon the velocity of migration of the ions. The general relations are expressed in the law known as Kohlrausch's law, which states that:

The equivalent conductivity of an electrolyte is equal to the sum of two values, one of which depends solely upon the cathion, the other upon the anion.

The effect of a rise in temperature is, in general, to increase the conductivity of solutions.

The conductivity of solutions is governed by Ohm's law.

CONDUCTIVITY * OF AQUEOUS SOLUTIONS (18° C.).

Concentration expressed in per cent. of dissolved substance.	Substance.	Conductivity in terms of unit defined p. .
10	HCl	0.63
10	HBr	0.35
12.4	HNO_3	0.54
10	H_2SO_4	0.39
9.8	Acetic acid	0.0015
10	Tartaric acid	0.0081
7	Oxalic acid	0.078
10	H_3PO_4	0.056
8.4	KOH	0.27
10	NaOH	0.31
8	NH_3	0.001
6.5	KCN	0.10
10	$AgNO_3$	0.047
10	$Cu(NO_3)_2$	0.063
10	K_2SO_4	0.086
10	Na_2SO_4	0.068
10	$(NH_4)_2SO_4$	0.101
10	$ZnSO_4$	0.032
10	$CuSO_4$	0.032
13	$NiSO_4$	0.045
10	$K_2C_2O_4$	0.091
10	KH_2PO_4	0.040

* Kohlrausch and Holborn, Leitvermögen der Elektrolyte.

CHAPTER IX.

ELECTROLYSIS.

SINCE an electrolyte is already dissociated into its ions in a solution, the action of the current during electrolysis is not the *decomposition* of the dissolved substance but is confined to the *transportation and discharge of the ions* at the electrodes. When the electrical charges of the ions are neutralised at the electrodes these particles instantly acquire the properties of atoms or atomic radicals.

When a solution of potassium sulphate is electrolysed between platinum electrodes, hydrogen is liberated at the cathode and oxygen at the anode. Chemically equivalent quantities of the two gases appear, *i.e.* two volumes of hydrogen to every one volume of oxygen. It might be assumed from this that the ions in the solution are hydrogen and oxygen; but if after the electrolysis has proceeded some time the solutions about the electrodes are examined it is found that the solution about the cathode contains potassium hydroxide, while that about the anode contains sulphuric acid, and further, the quantities (measured in gram-equivalents) of hydrogen and oxygen set free are exactly equivalent to the quantities of the acid and base in the solution, measured in the same units.

It was formerly customary to speak of the base and acid as resulting from the *secondary* action of the atomic potassium and SO_4 on the water of the solution, and to express the complete reaction by the following equations:

$$K_2SO_4 \text{ (solid)} = \overset{+}{K} + \overset{+}{K} + \overset{-}{SO_4} \text{ (solution)}.$$

On electrolysis—

$$\begin{aligned} &\overset{+}{K} + \overset{+}{K} + \overset{-}{SO_4} \text{ (ions)} = K_2 + SO_4 \text{ (atomic)}, \\ &2K_2 + 2H_2O = 2KOH + 2H_2 \text{ (gaseous)}, \\ &2SO_4 + 2H_2O = 2H_2SO_4 + O_2 \text{ (gaseous)}. \end{aligned}$$

This view of the behavior of the ions at the electrodes, while it has certain advantages as a method of expressing the reactions, has the disadvantage that it does not presumably give an accurate idea of the theoretical course of the electrolysis. It is therefore preferable to assume that the hydrogen and oxygen which appear in the above electrolysis are due to the *primary* dissociation of the water, and the course of the electrolysis can then be assumed to be the following:

Under the influence of the charged electrodes the $\overset{+}{K}$ and $\overset{-}{SO_4}$ ions in the solution migrate to the cathode and anode, and when they arrive there, those ions whose separation is attended with the least expenditure of energy will separate on the electrodes. Thus, for example, in the region of the cathode there will be potassium ions and hydrogen ions (the latter from the primary dissociation of the water). When an excess of positive electricity is present in this portion of the solution, and a discharge of cathions takes place, the hydrogen ions will be the first to discharge, since the separation of these is attended with a smaller expenditure of energy than would be required for the separation of the potassium ions. The OH residue of the water and the potassium ions constitute the potassium hydroxide found in this portion of the solution. The action at the anode is explained in an analogous manner. It must be remembered, however, that the degree of dissociation of the solvent water is extremely small, so small in fact as to contribute to the conductivity of the solution to a scarcely appreciable extent. But this does not limit the actual quantity of hydrogen and oxygen ions which in a given time can be supplied from this source to the electrodes since no sooner are the ions present removed than a new supply is instantly furnished by the dissociation of a fresh quantity of water.

If the electrolysis of a potassium sulphate solution be conducted with a mercury cathode and the current be suitably regulated, hydrogen will not appear. Instead of this an amalgam of potassium with the mercury of the cathode will be obtained. This is explained by the fact that the potassium ions, since they can immediately enter into combination with the mercury, separate more readily than the hydrogen ions under these conditions.

If a solution of chromic acid, H_2CrO_4, containing sulphuric acid is electrolysed, chromic sulphate, Cr_2SO_4, is formed at the cathode and no hydrogen appears. In this case the reaction can be explained by assuming that hydrogen is first set free, and then as a secondary reaction reduces the chromic acid to the divalent chromium compound; but it is more logical to assume that under the electrical conditions existing at the cathode the $\overset{-}{Cr}O_4$ ion changes to three $\overset{+}{Cr}$ ions, since the electrical equivalence of the change is the same and there is no actual evidence that the hydrogen is even temporarily deposited on the electrode. As a method of expression, however, the former assumption is the more convenient and for this reason will be followed. The reaction at the cathode can therefore be expressed by the following equations:

$$H_2CrO_4 = H_2 + CrO_4,$$
$$2CrO_4 + 5H_2 + 3H_2SO_4 = Cr_2(SO_4)_3 + 8H_2O.$$

The most important factor in electrolytic experiments, next to the actual composition of the solution, is the ratio of the current-strength to the surface-area of the electrodes. It is obvious that the reactions which take place at an electrode must be greatly influenced by the relative number of ions which are neutralised per unit area of electrode surface. The ratio mentioned above is known as the *current-density*, and as unit a current-strength of one ampere for 100 square centimeters of electrode surface has been chosen. This unit is known as the *normal density*, and current-densities expressed in terms of this unit are denoted by the symbol ND_{100}. The expression $ND_{100} = 1.2$ amperes, denotes that for every 100 square centimeters of the given electrode a current of 1.2 amperes is passing through the circuit.

Although the current-strength is the same through every cross-section of the circuit, the current-densities at the cathode and anode have the same value only when the surfaces of these in contact with the solution are exactly equal.

When a solution of copper sulphate is electrolysed and the current-density at the cathode is properly regulated, only metallic copper is deposited; but when the current-density is too high the metallic copper is mixed with copper oxide, and hydrogen is also set free. Similarly, in the case of cupric chloride solutions, copper or cuprous chloride appears at the cathode; while variations in the current-density at the anode in the electrolysis of sulphuric acid solutions result in the appearance of oxygen, ozone, hydrogen peroxide, or persulphuric acid. A classical illustration of the effect of the current-density, described by Bunsen, is furnished by the electrolysis of a solution of chromium chloride where either hydrogen, chromic oxide, chromous oxide, or metallic chromium can be obtained. The concentration and temperature of the solution is also an important factor in these reactions.

In the electrolysis of hydrochloric acid the chlorine set free at the anode reacts with water, forming hypochlorous acid, chloric acid, perchloric acid, etc. Similar secondary reactions are observed in the electrolysis of chlorides. If a solution of ammonium chloride, for example, is submitted to electrolysis the nascent chlorine acts on the undecomposed salt, with the production, among other substances, of nitrogen or nitrogen chloride. Halogen salts of the alkaline earths show similar phenomena.

Nitric acid, on electrolysis, gives in the first place

$$8HNO_3 = 4H_2 \text{ (cathion)} + 8NO_3 \text{ (anion)}.$$

The latter then splits up further:

$$4N_2O_6 = 4N_2O_5 + 2O_2 \text{ (anion)}.$$

The oxygen is given off, while the anhydride forms nitric acid again with water:

$$4N_2O_5 + 4H_2O = 8HNO_3.$$

The hydrogen, on the contrary, which appears as cathion, is not set free but acts reducingly on the nitric acid present:

$$4H_2 + HNO_3 = NH_3 + 3H_2O.$$

In the presence of sulphuric acid, or a sulphate, this decomposition is complete, the final product being ammonium sulphate.

In the electrolysis of organic compounds the ions as they are released from the solution at the electrodes may enter into secondary reactions in a manner analogous to that described in the case of inorganic compounds.

Thus potassium acetate might be expected to yield potassium (potassium hydroxide) and acetic acid as final products, but instead of the latter the acetic ion splits up into carbon dioxide and ethane, according to the equation:

$$\left.\begin{matrix}CH_3COO\\CH_3COO\end{matrix}\right> = C_2H_6 + 2CO_2,$$

and ethylene may also be formed from the oxidation of ethane at the anode.

Potassium valerate yields, in addition to valeric acid, carbon dioxide and octane; and by continued electrolysis the latter is oxidised into isobutylene and water. In the electrolysis of sodium succinate among the products formed are ethylene and carbon dioxide; potassium lactate breaks up into carbon dioxide and acetaldehyde; potassium tartrate gives carbon dioxide, carbon monoxide, oxygen, formic aldehyde, and formic acid; and potassium cyanide is converted into potassium cyanate.

The electrolysis of warm solutions of oxalic acid lead to the complete decomposition of the acid according to the equation

$$C_2H_2O_4 = 2CO_2(\text{anode}) + H_2(\text{cathode}).$$

In cold solutions carbon monoxide, as well as carbon dioxide, appears at the positive electrode.

When potassium oxalate is subjected to electrolysis the principal reactions are:

$$K_2C_2O_4 = 2CO_2(\text{anode}) + K_2(\text{cathode}),$$
$$K_2 + 2H_2O = 2KOH + H_2,$$
$$2KOH + 2CO_2 = 2KHCO_3.$$

When ammonium oxalate is used the decomposed solution contains hydrogen ammonium carbonate; a part of the latter splits up into ammonia and carbon dioxide.

In the electrolysis of double oxalates, *e.g.* zinc ammonium oxalate, decomposition takes place as follows: Zinc oxalate breaks up into zinc and carbon dioxide, and ammonium oxalate into ammonia and carbon dioxide. The carbon dioxide which separates at the anode combines with the ammonia in the solution to form hydrogen ammonium carbonate as explained above.

The simplest conditions are met in electrolysis in those cases where the ions in the solution on reaching the electrodes are immediately deposited and thus removed from the solution. Such is the case for example in the electrolysis of a solution of stannous chloride between a platinum cathode and a silver anode: the stannous ions are deposited on the cathode as metallic tin, and the chlorine ions at the moment of electrical neutralisation combine with the silver of the anode to form an insoluble coating of chloride of silver.

So also in the case of the electrolysis of a copper sulphate solution between copper electrodes, metallic copper is deposited at the cathode, while an exactly equal quantity of copper passes into solution at the anode.

For the continuous electrolysis of any solution between electrodes which are not attacked, a certain minimum potential difference is essential. This factor, which is of great importance in electrochemical analysis, is called the *decomposition potential*, and by it is denoted that difference of potential at which the electric current is just able to transform ions into atoms at the electrodes.* Le Blanc, who measured the de-

---

* The significance of this factor will be discussed later in the chapter on Polarisation

composition potential of a large number of solutions, determined the following values:

SALTS.

Normal (Molecular) Solutions.

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

ACIDS.

Sulphuric acid	1.67 volts.	Pyroracemic acid	1.57 volts.
Nitric acid	1.69 "	Trichloracetic acid	1.51 "
Phosphoric acid	1.70 "	Hydrochloric acid	1.31 "
Monochloracetic acid	1.72 "	Hydrazoic acid	1.29 "
Dichloracetic acid	1.66 "	Oxalic acid	0.95 "
Malonic acid	1.69 "	Hydrobromic acid	0.94 "
Perchloric acid	1.65 "	Hydriodic acid	0.52 "
Dextrotartaric acid	1.62 "		

BASES.

Sodium hydroxide	1.69 volts.	0.4N. Methylamine	1.75 volts.
Potassium hydroxide	1.67 "	0.2N. Diethylamine	1.68 "
Ammonium hydroxide	1.74 "	0.8N. Tetramethyl ammonium hydroxide	1.74 "

The sulphates and nitrates of the alkalies and alkaline earths have all nearly the same decomposition potential, namely, about 2.20 volts.

CHAPTER X.

ELECTROMOTIVE FORCE.

If a strip of metal, zinc for example, be dipped into a solution of a zinc salt, the zinc ions present in the solution will have a tendency to discharge their electricity upon the zinc and to pass over into the atomic condition. This tendency may be considered as a pressure striving to force the ions from the solution toward the metal, and is known as the *osmotic pressure of the ions.** The metallic zinc, however, may be considered to exert a pressure in the opposite direction, which is due to the tendency of the zinc atoms to pass into the solution and assume the condition of ions. This pressure is known as the *electrolytic solution pressure* of the zinc. Since the ions are bearers of electric charges it is evident that the simultaneous action of these two pressure-forces is intimately connected with the production of an electric current, and that as one or the other of these predominates, positive electricity will pass from the region of higher pressure to the region of lower, and a difference of potential between the solution and the metal will result. The osmotic pressure of the ions and the electrolytic solution pressure of the metal tend to cause currents in opposite directions. The positively charged ions of the solution strive to give up their charges to the exposed metal and to charge this positive; while, on the other hand, the electrolytic solution pressure

---

* Nernst, Zeit. f. physik. Chem., 4, 129 (1889).

strives to force positive ions out from the metal and into the solution, leaving an equivalent negative charge on the metal itself.

Since the operation of all galvanic elements depends upon the difference of potential between conductors of the first order * and solutions of electrolytes, the hypothesis just enunciated is of great value in offering an explanation of the working of these cells.

A very simple cell is furnished by the combination, metallic silver, silver nitrate solution (concentrated), silver nitrate solution (dilute), metallic silver. In this combination the metallic silver in contact with the concentrated silver nitrate solution is found to be positively charged with respect to the silver electrode dipping into the dilute solution. When the solutions are 0.1 normal and 0.01 normal respectively, the difference of potential is 0.055 volt (at 18°). The theory offers the following explanation of this cell: The electrolytic solution pressure of the metallic silver is the same at both poles, but in the concentrated solution the osmotic pressure of the silver ions is greater than in the dilute solution. There will therefore be a tendency for silver ions to pass out of the concentrated solution and to deposit as metallic silver on the electrode in this solution, and, simultaneously, for silver atoms to pass out as ions from the silver electrode into the dilute solution. The silver electrode in the concentrated solution will thus become positively charged with respect to that in the dilute solution. As this process continues the electrostatic condition will become such that the difference of potential between the solution and the electrodes will oppose the precipitation and formation of any further ions, and a state of

---

* Substances which conduct the electric current without undergoing chemical decomposition, *i.e.* metals, carbon, etc.

equilibrium will be reached which will depend upon the relative concentrations of the two solutions, and will be measured by the difference of potential between the two poles, as stated above. If, however, the two poles of the cell are connected with one another by a metallic conductor, so that this electrostatic difference of potential is prevented, the process of precipitation and solution will continue until both solutions are of equal concentration.

The electrolytic solution pressures of a number of metals have been calculated by Neumann* and their values are given in the following list:

Zinc	$=9.9\times10^{18}$	atmospheres.
Cadmium	$=2.7\times10^{6}$	"
Iron	$=1.2\times10^{4}$	"
Nickel	$=1.3\times10^{0}$	"
Lead	$=1.1\times10^{-3}$	"
Hydrogen	$=9.9\times10^{-4}$	"
Copper	$=4.8\times10^{-20}$	"
Mercury	$=1.1\times10^{-16}$	"
Silver	$=2.3\times10^{-17}$	"

Assuming the osmotic pressure of the ions in a totally dissociated normal solution to be 22 atmospheres, it is evident from the above list that electrodes of zinc, cadmium, and iron will always be charged negatively with respect to normal solutions of their ions with which they are in contact, while solutions of nickel, lead, hydrogen, copper, mercury and silver, under similar conditions, will always be charged positively.

A familiar galvanic cell is the so-called Daniell's element. This consists of a zinc electrode surrounded by a solution of zinc sulphate, and a copper sulphate solution

---

* Zeit. f. phys. Chem., 14, 229 (1894).

containing an electrode of metallic copper. If the solutions are both normal, then the electrolytic solution pressure of the zinc will greatly exceed the osmotic pressure of the zinc ions in the solution, and positive zinc ions will pass from the metal to the solution, leaving a negative charge on the former. The osmotic pressure of the copper ions in the copper sulphate solution will exceed the electrolytic solution pressure of the copper, and accordingly copper ions will pass from the solution to this electrode and charge it positive. The difference of potential thus produced will consist primarily of the sum of two differences, namely, that between the zinc and the zinc sulphate solution, and that between the copper sulphate solution and the copper. This total difference of potential is equal to 1.1 volts.

TABLE.

SINGLE POTENTIAL DIFFERENCES OF METALS IN NORMAL SOLUTIONS OF THEIR SALTS.*

Zinc	+0.51 volt.
Cadmium	+0.16 "
Iron	+0.09 "
Nickel	−0.02 "
Lead	−0.10 "
Hydrogen	−0.25 "
Copper	−0.59 "
Mercury	−1.03 "
Silver	−1.06 "

The signs denote the charge of the solution when the potential of the metal is placed at zero.

It is evident that if the two electrodes (or poles) of the cell are connected by a metallic conductor their charges will be removed and the difference of potential between them will

---

* Ostwald, Grundriss der Allgemeinen Chemie, 3 Auf., 1899, p. 468.

be diminished. This fall in potential between them will be proportional to the resistance of the connecting conductor. It is evident also that this difference of potential between them will have a maximum value when they are not externally connected. Since this maximum value is the true measure of the electrical factors in the cell, it will be given a special name and will be called the *electromotive force of the cell*.

The *internal resistance* of a cell is the resistance of the solution, or solutions, which it contains and the porous separating wall, if one is used to separate the solutions.

CHAPTER XI.

POLARISATION.

IF a solution of zinc sulphate is electrolysed between platinum electrodes, metallic zinc will be deposited on the cathode and oxygen on the anode. As soon, however, as the metal and the oxygen have passed over into the atomic condition, the electrolytic solution pressure of each comes into action and operates to drive them back into the form of ions. The electrodes can no longer be regarded as consisting of platinum, but behave exactly as if composed of zinc and oxygen. Under these conditions the electrodes are said to have become *polarised* and the phenomenon is known as *polarisation*. The combination may then be considered as a galvanic cell consisting of zinc, sulphuric acid, and oxygen, with an electromotive force opposed to that of the first or primary current.

If the primary current be now interrupted, and the two electrodes are connected by a metallic conductor, a current will flow between them through the conductor in a direction opposite to that of the original current. The current thus obtained is called the *polarisation current*. Polarisation will always take place when the electrodes are composed of a metal like platinum, which is not attacked during the electrolysis.

For the continuous electrolytic decomposition of any solution a difference of potential must therefore be maintained between the electrodes greater than the back electromotive force due to polarisation. Unless this is the case no current will pass through the cell.*

It is evident that a very close relation must exist between the electromotive force due to polarisation and the decomposition potential of solutions measured by Le Blanc (page 41), since these latter values represent the difference of potential between the electrodes necessary in order to overcome the back electromotive force due to polarisation.

The current-strength through any circuit containing an electrolytic cell may be calculated from the equation:

$$C=\frac{P-p}{R},$$

where P is the primary difference of potential, p is the electromotive force due to polarisation, and R is the total resistance of the circuit.

---

* It has been observed that very small currents will flow through a cell even when the difference of potential between the electrodes is considerably lower than the values obtained for the decomposition potential by Le Blanc (p. 41). A satisfactory explanation of this phenomenon is yet to be discovered.

SECTION II.—DESCRIPTIVE.

CHAPTER XII.

ELECTROCHEMICAL ANALYSIS.

THE object of electrochemical analysis is the quantitative determination of certain elements, chiefly metals, by the use of the electric current. For this purpose the elements, or their compounds, are precipitated in an adherent form on weighed electrodes and their quantity is determined from the increase in weight of the electrode. Electrolytic reactions are also employed for separating an element from one or several others, since the conditions favorable for the precipitation of one element are often such as entirely prevent the precipitation of another. One of the chief advantages of the electrochemical method is that when the electrolytic process is once started it requires little or no attention until completed. Another advantage lies in the fact that many separations of different elements can be effected without difficulty by this means which are extremely troublesome when conducted by the ordinary gravimetric methods. The extreme accuracy of many of the electrolytic determinations is also a strong point in their favor.

Quantitative electrochemical determinations may be divided into two general classes according to whether the determination of a cathion (metal) or an anion (halogen or metal peroxide) is involved. The metals are precipitated as metallic coatings on the cathode, and the halogens are determined by the employment of a silver anode with which they combine to form silver halogen compounds. The process in the separation of the metal peroxides is somewhat more complicated. Formerly the formation of lead and manganese peroxides was attributed to an oxidation brought about by the electrolytically generated oxygen. The investigations of Liebenow * and Löb † have made it appear that lead peroxide and manganese peroxide ions are already present in the solutions. Since the peroxides are deposited from strong nitric acid solutions, it is necessary to assume that, through the oxidising power of this acid, oxygen ions are formed in the solutions, and that these oxygen ions combine with the lead and manganese ions to form peroxide ions. Since in the peroxides of the bivalent metals the two positive charges of the metal are combined with the four negative charges of the two oxygen ions, the resulting peroxide ion possesses two negative charges and consequently behaves like a bivalent anion. It is precipitated on the positive electrode in a smooth, adherent coating.

In electrochemical analysis the composition of the solution from which a metal is separated is of the very greatest importance, since, in general, the metals do not separate from solutions of their pure salts in a form which is suitable for quantitative determination. For this reason solutions of mixed electrolytes are employed almost without exception for this purpose, since the addition of other substances to the solution of the metal salt has a very important influence on the physical character of the precipitated metal. By

---

* Zeit. für Elektrochemie, 3, 653 (1896–97).

† *Ibid.*, 3, 100 (1896–97).

the addition of suitable substances to the solution the precipitated metal can be obtained as a smooth, compact and firmly adherent coating on the electrode in cases where if a solution of the pure salt were used the metal would be deposited as a crystalline or amorphous crust totally unsuited to accurate determination. Substances are also added to the solutions to permit the *complete* precipitation of certain metals. Their action is then to neutralise or counteract the effect of deleterious substances formed during the process of electrolysis. Thus by the addition of ammonium oxalate to a solution of zinc sulphate, the zinc can be completely precipitated, which would not be the case if the action of the sulphuric acid formed at the anode were not neutralised by the ammonium oxalate in the solution. Chemical substances other than the salts of the metals to be determined are also added to solutions in order to permit the separation of one metal from one or several others. Thus the addition of nitric acid to a solution containing the sulphates of copper, iron, and zinc, makes it possible to completely separate the copper by electrolysis without, at the same time, bringing down even traces of the other two metals.

If the position of hydrogen is represented by a dash, and those elements which separate more readily than hydrogen are placed below this line, while those which separate less readily are placed above it, the conditions existing in various different solutions may be represented as given below:*

in potassium cyanide solution $\frac{\text{Cu, Pt, As, Ni, Co, Fe, Zn}}{\text{Au, Ag, Hg, Cd}}$;

in sodium sulphide (conc.) solution $\frac{\text{As, Sn}}{\text{Sb}}$;

---

* Haber, Grundriss der Technischen Elektrochemie, Leipzig, 1898.

in ammonium sulphide (dil.) solution $\frac{-}{\mathrm{Sb, As, Sn}}$;

in strong inorganic acids $\frac{\mathrm{Zn, Cd, Fe, CO, Ni, Pb}}{\mathrm{Bi, As, Sb, Sn, Cu, Hg, Ag, Pd, Pt, Au}}$.

Substances are also added to the electrolytic solutions to increase their conductivity.

The nature of the added substance is, in general, dependent on the chemical properties of the metals in the solutions. A fundamental requirement, however, may be stated. The substance must be a good conductor of the current and must form no decomposition products which are insoluble or which are detrimental to the analysis. Alkalies, and acids which after their decomposition are again generated at the electrodes, are therefore frequently suitable, as are also organic acids, the decomposition products of which are given off in a gaseous form. This last condition is fulfilled by oxalic acid especially, which also on account of its ready solubility is of special importance in the electrolysis of metals, particularly in the form of the double oxalates.

Since solutions of mixed salts are used in electrochemical analysis, Faraday's law does not apply to the electrolytic separation of metals under these conditions; *i.e.* the quantity of metal separated is not proportional to the quantity of electricity passed through the solution. Especially the last traces of a metal in a solution require a large excess of current to effect their complete precipitation. For this reason in many determinations the time required is largely independent of the quantity of metal to be separated.

The values of the decomposition potential of solutions of metallic salts have an important bearing* on electrochemical

---

* Kiliani, Berg- und Hüttenm. Ztg., 1883. Freudenberg, Zeit. f. phys. Chem., 1893.

analysis, since they give the minimum potential-difference required for the precipitation of the metals from such solutions. They also afford a means of quantitatively separating several metals successively from the same solution through a variation of the potential-difference of the primary current. For example, zinc is not precipitated from a normal zinc sulphate solution when the difference of potential between the electrodes is less than 2.35 volts. From a normal silver nitrate solution, however, the silver is deposited when the potential-difference is equal to 0.70 volt. Therefore, from a mixture of these two solutions, the silver can be separated by keeping the potential-difference below 2.35 volts, the zinc remaining meanwhile in solution. After the silver has been separated, the zinc can be deposited by increasing the potential-difference to over 2.35 volts.

Kiliani was the first to point out the importance of the difference of potential in electrolytic separations. Somewhat later, Freudenberg, basing his work on Le Blanc's studies, carried out a careful investigation of the exact relations.

The physical state of the precipitated metal (or peroxide) is largely dependent on the current-density at the cathode (anode), since this determines the number of the ions which in the unit time separate as molecules on a unit surface of the electrode, *i.e.* the rate of deposit of the metal (peroxide). If the current-density is high the individual atoms are deposited upon one another in such rapid succession that the precipitated metal does not adhere firmly to the electrode, but scales off. When the current-density is too low a compact layer does not form and the metal is deposited on the electrode in isolated patches, a condition which is undesirable in quantitative determinations. The current-density is therefore an important factor in quantitative electrolysis.

The necessity of accurate data in the performance of electrochemical analysis is obvious, for unless all the important factors are determined and recorded the experiment cannot be accurately repeated.

Since the determination of the resistance of the liquid in the cell is beyond the scope of analytical work, therefore, instead of this, the exact volume and composition of the solution, as well as the size and shape of the electrodes, must be stated. In addition to this, the difference of potential between the electrodes, the current-strength as read directly on the amperemeter, and the calculation of the current-density from the current-strength, for the electrode on .which the quantitative precipitation has taken place, must be given. All electrical relations are influenced by the temperature, so that an exact knowledge of this is most essential. The length of time required for the electrolysis, and the nature of the source of current having been specified, all adequate and necessary data are at hand to enable every one to repeat the analysis under exactly similar conditions.

CHAPTER XIII.

DETERMINATION OF THE ELECTRICAL MAGNITUDES.

MEASUREMENT OF THE CURRENT-STRENGTH.

THE current-strength can be measured either by means of the chemical or the electromagnetic action of the current.

The chemical instruments are the gas voltameter and the weight voltameter.

The electromagnetic instruments are the galvanometer and the amperemeter.

Gas Voltameter (Coulombmeter).—The principle upon which this instrument depends is the measurement of the volume of the combined oxygen and hydrogen gas liberated in a given period of time by passing the current to be measured through a solution of sulphuric acid or sodium hydroxide.

A common form of the gas voltameter is shown in Fig. 3. The inner vessel *A* contains the dilute sulphuric acid (33%) solution and is surrounded by an outer vessel *cc* containing water for cooling purposes. The apparatus is connected with the circuit in which the current is to be measured by the binding-screws *bb* attached to the platinum electrodes *aa*. The hydrogen and oxygen which are liberated at the electrodes are conducted through the tube *ef* to a gas-burette, where the combined volume is measured. When the volume of the gas obtained is reduced to standard conditions, *i.e.* 760 mm pressure and 0° C., the strength of the current can be calculated, since a current of 1 ampere liberates 10.44 cc of oxyhydrogen gas per minute.

The use of sulphuric acid as the electrolyte is objectionable, however, since owing to the formation of ozone and per-

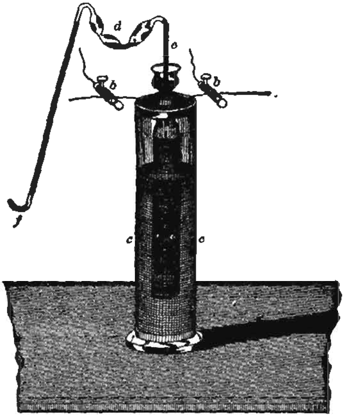


Fig. 3.

sulphuric acid at the anode, and to other secondary reactions, the results obtained with it are often far from accurate. A much more satisfactory electrolyte is a two-per-cent. solution of sodium hydroxide. With this nickel electrodes are employed.

The *amperemanometer* described by Bredig (Zeit. f. Elektrochemie, **7**, 259) is an extremely simple modification of the gas voltameter. It consists of a glass vessel *a* (Fig. 4) partially filled with a sodium hydroxide (2%) solution. It is closed with a tight-fitting rubber stopper through which pass nickel wires connecting the cylindrical nickel electrodes, *c* and *b*, to binding-screws on the outside, and also the tube *de*. This tube is curved as shown and is closed at *e* by a small rubber stopper through which passes a capillary tube *f*. A small manometer *g* containing colored water is connected with the tube *de*. The operation of this apparatus is very simple; the escape of the gas generated by the electrolysis is retarded by the capillary opening through which it must pass and a pressure is created in the interior which is shown by the manometer. A plug of loose cotton wool is inserted at *c* to filter the escaping gases and prevent the capillary from clogging. The instrument must be empirically calibrated by comparison with a standard amperemeter. Its range of measurement can be greatly increased by providing a series of capillaries of different sizes. Each capillary must of course be standardised separately. The obvious advantage of this form of apparatus is that when once calibrated its readings are obtained directly in amperes without calculation.

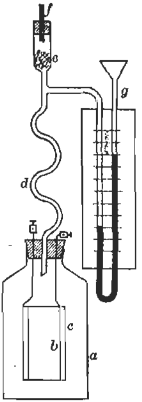


FIG. 4.

The chief objection to the use of gas voltameters is that their back-electromotive force due to polarisation is considerable (1.7–2.5 volts) and it is therefore nearly always necessary to keep them permanently in the circuit, which is often very inconvenient.

Weight Voltameter (Coulombmeter).—In this instrument the current-strength is determined from the weight of metal *(silver or copper) deposited in a given time.*

The silver voltameter is employed chiefly for determining the electrochemical equivalent of silver, which has been adopted as the standard for the electrochemical equivalents of the elements. In practice it usually consists of a platinum dish cathode and an anode of pure silver. A silver nitrate solution is used as electrolyte.* A description of its details will be omitted.

The copper voltameter, however, furnishes a very convenient and inexpensive apparatus for measuring the strength of currents. In its simplest form it consists of a thin sheet of copper, which serves as cathode, suspended between two somewhat thicker sheets of copper, which are the anodes. As electrolyte a solution containing the following constituents has proved very satisfactory: †

15 g	Copper sulphate (cryst.),
5 g	Conc. sulphuric acid,
5 cc	Alcohol,
100 cc	Water.

With this solution the current-density may vary from 0.06 to 1.5 ampere per square decimeter cathode surface.‡ The

---

* A silver voltameter in which a solution of silver cyanide and potassium cyanide is used as electrolyte is described by Farup, Zeit. f. Elektrochem., **8**, 569.

† Oettel, Chem. Ztg., **17**, 543 (1893).

‡ Shepard (Am. Journ. Science, **12**, 49 (1901) recommends the following solution: a conceptrated solution of copper sulphate (sp. gr. 1.2) which has been digested with metallic copper for one hour at 100° C., and to which a trace of ammonium chloride has been added. This is recommended especially when high current-densities are employed.

difference of potential between the cathode and anode when a current is passing from is 0.1 to 0.5 volt.

The current-strength is determined by connecting the voltameter in the circuit and allowing the current to pass for a given length of time. Since a current of one ampere will deposit

0.0197 gram of copper per minute
and 1.181 grams of copper per hour,

the current-strength can be calculated by determining the increase in weight of the cathode.

The copper voltameter is used chiefly for calibrating amperemeters and for measuring the quantity of electricity passing through circuits when the current-strength is subject to considerable and frequent variations. Since, like the other voltameters, it actually measures coulombs and not amperes, the name *coulombmeter* has been very appropriately suggested * for this type of instruments, to distinguish them from *voltmeters*, which they in no way resemble and with which they are continually confounded.

GALVANOMETERS.

The term *galvanometer* is commonly applied to any instrument used to detect the existence of, or to measure, a current by the deflection produced in a magnetic needle or its equivalent.

Tangent Galvanometer.—The name of this instrument is derived from the fact that the current-strength is calculated from the tangent of the angle of deflection of the needle. It consists (Fig. 5) of a short magnetic needle suspended at the center, or on the axis, of one or more circular coils of wire,

---

* **Richards and Heimrod, Zeit. f. physik. Chem., 41, 302 (1902).**

through which the current passes. The plane of the coil is set in the magnetic meridian.

The current-strength is calculated from the equation

$$C = \frac{rH}{2\pi n} \tan \theta,$$

where r is the radius of the coil, H is the horizontal component of the earth's magnetic field, n is the number of turns of wire in the coil, and θ is the angle of deflection of the needle from the magnetic meridian.

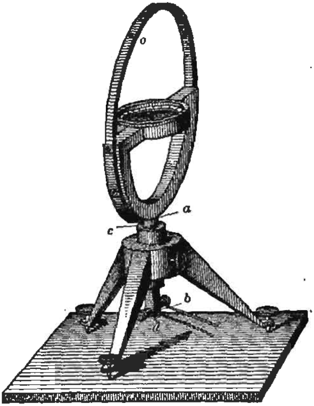


FIG. 5.

Sine Galvanometer. — The essential difference between the sine galvanometer (Fig. 6) and the tangent galvanometer is that the plane of the coil is not fixed in the meridian but can be revolved about a vertical axis. When a current is passing through the instrument the coil is turned until its plane corresponds exactly with that of the needle. The current-strength is then obtained from the equation

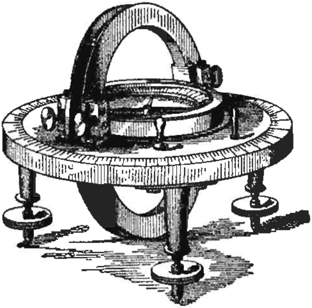


FIG. 6.

$$C=\frac{rH}{2\pi n}\sin\theta,$$

θ being the angle between the needle and the magnetic meridian.

Other Galvanometers.—Where great sensitiveness is required in a galvanometer it may be obtained by combining two or more needles in an *astatic* system, *i.e.* by suspending them in the same plane but with their poles reversed and rigidly connected with one another, so that the effect of the earth's magnetic field on the system is almost entirely eliminated. This increases the sensitiveness of the needles, and the effect of the current on them is greatly increased by surrounding them with different coils containing a large number of turns of the same wire. The compound needle, to which a small mirror is attached, is suspended by a silk fiber, and its deflection is measured with a telescope and scale. A galvanometer of this type is shown in Fig. 7.

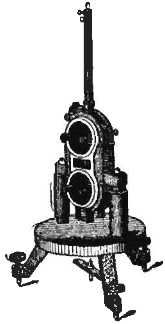


FIG. 7.

Another method of constructing a sensitive galvanometer is by suspending the coil through which the current passes in an intense magnetic field.

In the Rowland d'Arsonval galvanometer (Figs. 8 and 9) the coil C is suspended between the poles, NS, of a strong permanent magnet, by a thin strip of phosphor-bronze. The deflection

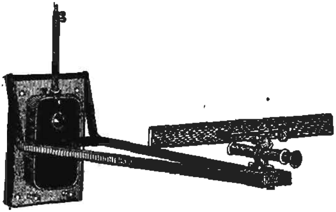


FIG. 8.

of the coil is measured by observing the reflection of the scale in the mirror M through the telescope attached to the *instrument*.

Amperemeters.—The name *amperemeter* is applied to those galvanometers in which the current-strength is indicated directly in amperes, usually by a pointer which moves over a graduated scale. Owing to their simplicity of operation they are by all means the most convenient and satisfactory instruments for measuring the current-strength in analytical electrochemical experiments.

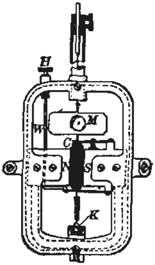


Fig. 9.

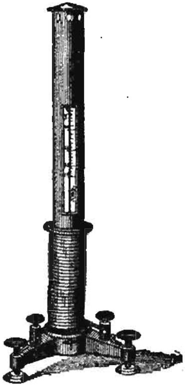


Fig. 10.

In the *spring amperemeter* devised by Kohlrausch (Fig. 10) a hollow cylinder of sheet iron is suspended by a spiral spring just above a coil of wire having the form of a vertical helix. When a current passes through the coil the iron cylinder is drawn into it until the force of attraction is balanced by the tension of the spring. A small pointer attached to the cylinder moves over a vertical scale attached to the front of the instrument.

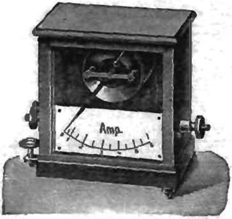


FIG. 11.

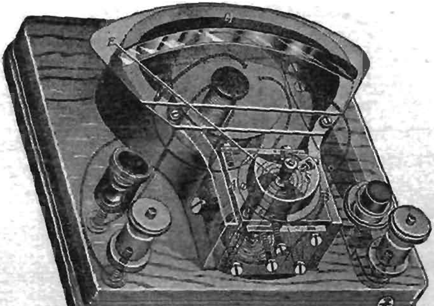


FIG. 12.

In the amperemeter shown in Fig. 11 the coil is horizontal and a curved piece of thin sheet-iron to which a pointer is attached is pivoted eccentrically within it. The pointer moves over a scale on the front of the instrument.

Another type of these instruments, known as the Weston amperemeters, are constructed on the principle of the d'Arsonval galvanometer. The essential parts of these instruments (Fig. 12) are a permanent magnet, *AGB*, of great constancy, a fixed soft-iron cylinder *C*, which concentrates the field, and a coil of wire *d*, wound about an aluminium frame which turns freely on pivots *V*, *V′*. *E* is a pointer fastened to the coil and moving over an empirically divided scale. On breaking the circuit, the coil is restored to the zero position by spiral springs *S*. Only a very small portion of the current passes through the pivoted coil, the greater part being deflected through a shunt of low resistance.

FIG. 18.

FIG. 14.

Fig. 13 shows a standard portable instrument, Fig. 14 a switchboard type; and a cheaper, but for electrochemical purposes equally satisfactory, instrument is shown in Fig. 15.

This make of instrument possesses many advantages; the

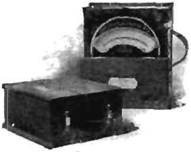


FIG. 15.

pointer comes to rest at once when the circuit is closed, owing to the damping effect of the aluminium frame on which the coil is mounted; the divisions of the scale from zero to the maximum *are practically uniform in size;* the construction permits of very accurate reading; and the resistance is so low that these instruments can be introduced into or removed from the circuit *without appreciably altering the strength of the current.*

For electrochemical analysis an instrument with a range of five amperes, with subdivisions corresponding to one-tenth ampere, will be found very satisfactory, although for some experiments an instrument of lower range capable of measuring 0.01 ampere may be required.

MEASUREMENT OF THE POTENTIAL.

For measuring the potential a large number of instruments are in use, their suitability depending upon the accuracy of measurement desired. Two instruments are employed in electrochemical analysis, the voltmeter and the torsion galvanometer; while for exact determinations of differences of potential and electromotive forces, especially small ones, the capillary electrometer and quadrant electrometer have been generally adopted.

Voltmeter.—In construction the voltmeter (Figs. 16 and 17) is essentially a high resistance galvanometer. This is accomplished in the Weston type of instruments by connecting a high resistance *in series* with the movable coil, through which the entire current furnished to the voltmeter passes. The scale of the instrument is empirically divided so that the position of the pointer indicates, in *volts*, the difference of potential between the binding posts.

In measuring the difference of potential between any two points the voltmeter is provided with a separate circuit of its own, the free terminals of which are attached to the points to be measured. Since the resistance of the instrument is very high (several thousand ohms in the low-range instruments), that portion of the current deflected through the voltmeter circuit may be neglected, and likewise the resistance of the connecting wires.

FIG. 16.

FIG. 17.

In the type of instruments in which an immovable coil acts on a movable magnet, the high resistance is obtained by constructing the coil of a large number of turns of exceedingly fine wire.

For the purposes of electrochemical analysis a voltmeter having a scale reading to 10 volts, in fractions of 0.1 volt, is satisfactory.

Torsion Galvanometer.—In this instrument a light bell-shaped magnet is suspended between two vertical coils by a spiral spring attached to a movable pointer. A second pointer is rigidly attached to the magnet, and the adjustment of the spring is such that, when no current is passing through the coils and the instrument is properly placed with respect to the magnetic meridian, both pointers indicate zero on a horizontal scale calibrated in volts and located just below the glass cover.

When a current passes through the coils the magnet is deflected, and in order to restore it to its original position the pointer from which it is suspended is turned in the opposite direction. The position of this pointer then indicates the potential difference in volts.

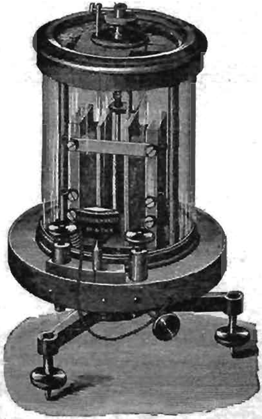


FIG. 18.

These instruments are made with high resistance and the vibrations of the magnet are damped by surrounding copper, but they are not as convenient as voltmeters, owing to the fact that it is necessary to adjust them for each separate reading. A torsion galvanometer is shown in Fig. 18.

Capillary Electrometer.—The principle upon which the action of this instrument depends is the following: If a small mercury electrode is in contact with dilute sulphuric acid, the change in the surface tension of the mercury is proportional to the change in the difference of potential between the solution and the electrode, provided that the difference of potential is small (not over 0.1 volt).

A very convenient form of this electrometer is shown in Fig. 19. The capillary *C* is partially filled by a short column of mercury which is a portion of a larger column of mercury contained in the vertical tube *M*, open at the top. The remainder of the capillary is filled with dilute sulphuric acid, as is also the short wide tube *S*. The bottom of *S* is covered with mercury, which is connected with a small mercury contact *P* by a platinum wire fused into the glass between them. The mercury in *M* is similarly connected with an external contact *N*. When *N* and *P* are connected with a small difference of potential the column of mercury in *C* rises or falls owing to a change in the surface tension at the meniscus. As already stated, the movements of the meniscus are proportional to the potential-difference when this does not exceed 0.1 volt. The movements of the mercury are usually observed through a low-power microscope containing a transparent glass scale.

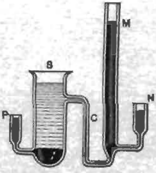


FIG. 19.

In practice the poles of a galvanic element are connected through a resistance of 1000 ohms. This resistance is provided with a series of contact plugs so distributed that the total resistance of 1000 ohms is divided into nine resistances of 100 ohms each and ten resistances of 10 ohms each. Since it follows from Ohm's law that the fall in potential through a conductor is proportional to the resistance, if the total difference of potential produced by the element at the ends of the resistance is equal to *one* volt, the difference of potential between any two contact plugs having a resistance of 100 ohms between them will be equal to 0.1 volt, and the difference of potential between two plugs having 10 ohms between them will be 0.01 volt.

The difference of potential to be measured is now connected by means of a movable contact with alternate plugs along the resistance, its polarity being opposed to that of the element furnishing the standard current. The movements of the mercury column of a capillary electrometer connected in the circuit of the unknown potential-difference, serve to indicate the point at which this difference of potential is balanced or compensated to within 0.01 volt by the known difference of potential along the resistance. The difference of potential is then read to within one one-thousandth volt by noting the diplacement of the meniscus from its normal position when the electrometer is short-circuited. This method is known as the Poggendorf compensation method. It is obvious that the known difference of potential between the ends of the resistance must always be greater than the difference to be determined.

Since no flow of current takes place through the electrometer under the conditions of final measurement, owing to the polarisation of the small mercury electrode, this method is particularly suited to the accurate determination of the true electromotive force of galvanic elements (see p. 46).

Quadrant Electrometer.—This important type of instrument (Fig. 20), devised by Lord Kelvin, is particularly suited for the measurement of small potential-differences and the electromotive forces of galvanic elements. Its construction is extremely simple. A flat, cylindrical metallic box is divided into four separate segments (Fig. 21), each of which is supported by an insulated standard. Each of these segments is called a *quadrant.** The opposite quadrants are connected by wires, and within them is suspended, by a quartz fiber, a light aluminium vane or needle (N, Fig. 21) bearing a mirror. When the instrument is in use the needle is charged to a relatively high potential by a water battery containing many elements or other suitable appliance, and contact with the needle is effected through a small wire attached to it and dipping into a vessel of concentrated sulphuric acid just beneath. One pair of quadrants is grounded, and the other pair is connected with one pole of the electromotive force to be determined. The second pole of the electromotive force is connected with the earth. This causes a deflection of the needle, which is measured with a telescope and scale.

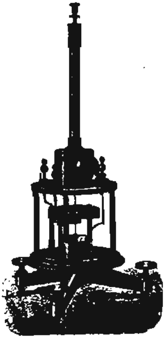


FIG. 20.

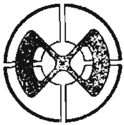


FIG. 21.

---

* In Fig. 20 one of the quadrants is removed.

The instrument may be used instead of a capillary electrometer in the compensation method, or may be used independently after having been calibrated by comparison with a standard electromotive force.

CHAPTER XIV.

SOURCE OF CURRENT.

THE source of current in electrochemical analysis may be either chemical or physical. The former includes the galvanic elements, which are divided into primary and secondary elements. The physical sources are the electromagnetic machines and the thermopiles.

PRIMARY ELEMENTS.

Leclanché Cell.—This cell consists of zinc, ammonium chloride solution, and carbon.* Electromotive force, 1.5 volt. When it is closed through a circuit, zinc goes into solution, and hydrogen ions, being more readily deposited than the NH_4 ions, separate as gaseous hydrogen at the carbon electrode. Owing to the absorbent action of carbon towards gases a small quantity of hydrogen can be deposited without producing marked polarisation, but when currents of any considerable strength are furnished by this element for even a short time polarisation takes place and the potential difference rapidly diminishes. In order to avoid this disadvantage these elements are usually modified by sur-

---

* In the descriptions of primary elements the external negative pole will be given first, the solution or solutions next, and last the external positive pole. It should be borne in mind, however, that the movement of the *positive* electricity *in the interior* of the cells is from the negative to the positive pole, and that of the negative electricity is in the opposite direction.

rounding the carbon rod with a porous earthenware jar containing a mixture of manganese dioxide and retort carbon, or the electrode itself is composed of a compressed mixture of these two substances (Fig. 22).

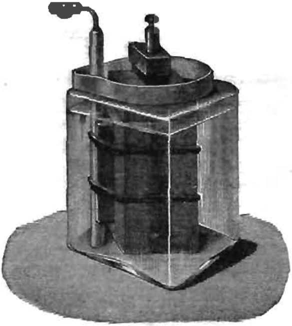


FIG. 22.

The manganese dioxide exerts an oxidising action on the hydrogen ions, and instead of hydrogen being set free on the electrode, water is formed in the solution about the positive pole. The depolarising action of the manganese dioxide is limited, however, and even those cells which contain it are not satisfactory as sources of current for electroanalysis. A large number of cells of this type are to be found on the market under special trade names. They differ from one another chiefly in the shapes of the containing jars, the electrodes, and similar minor details. They all possess the same disadvantages to a greater or less extent, and are suited only for ringing electric bells and similar open circuit work.

The so-called *dry cells* are mostly Leclanché elements in which the use of a fluid is avoided by moistening plaster of paris, sawdust, or absorbent paper with the electrolyte. The negative electrode of sheet-zinc usually forms the containing vessel.

The internal resistance of the Leclanché element varies with the construction, but is usually about 0.25 ohm. The internal resistance of the dry cells is considerably higher.

Daniell Cell.—This cell consists of zinc, zinc sulphate solution, copper sulphate solution, copper. Its electromotive force is approximately 1.1 volt.

The action of this cell when furnishing current has already been described on page 44. Its construction (Fig. 23) varies considerably, in the earlier form the zinc is placed in a porous earthenware cup containing the zinc sulphate solution, and

FIG. 23.

action. The electromotive force of this cell is about 1.8 volt and its internal resistance approximately 0.2 ohm.

In the Bunsen cell carbon is substituted for platinum. The reactions are the same, and the electromotive force and internal resistance are the same as for the Grove cell.

In another type (Fig. 26) of this same cell the depolarising action is produced by chromic acid. In this case both the zinc and the carbon electrode dip into the same solution, a mixture of potassium bichromate and dilute sulphuric acid.

Cupron Element.—This cell (Fig. 27) consists of zinc, dilute sodium hydroxide solution, cupric oxide. The zinc passing into solution in the sodium hydroxide solution tends to displace hydrogen ions at the other pole. The hydrogen ions react with the cupric oxide to form water and metallic copper.

The element has an electromotive force of 0.8 volt and an internal resistance of 0.05 ohm.

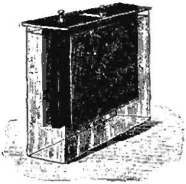


FIG. 27.

FIG. 28.

An element of this type, known as the Edison-Lelande cell (Fig. 28) has come largely into use in the United States. These cells are manufactured with capacities of from 50 to 600 ampere-hours and furnish a very convenient primary source of current for electrochemical experiments.

GALVANIC SECONDARY ELEMENTS.

Accumulators, or Storage Batteries.—Galvanic elements may be separated into two general groups, *i.e.* reversible cells and irreversible cells. Reversible cells are those which after having produced current and having undergone chemical change can be restored to their original condition by passing through them a current in the opposite direction to that which they have furnished. To this group belongs the Daniell cell. When this cell is furnishing current zinc passes into solution and copper is precipitated, the current within the cell flowing with respect to the positive electricity from the zinc to the copper. If this cell is so attached to a source of higher electromotive force that the current within the cell is forced to flow in the opposite direction, *i.e.* from the copper to the zinc; then copper will pass into solution and metallic zinc will be deposited on the zinc electrode. The original condition of the cell can thus be re-established.

Irreversible cells are those in which the original conditions are not re-established by the reversal of the direction of the current. Thus, for example, on passing a current through a partially exhausted Grove cell, in a direction opposite to that of the current which it has furnished, hydrogen will appear at the zinc pole and oxygen at the platinum. In the sense in which this expression is used, therefore, such a cell is not reversible.

When a reversible element is producing a current of electricity, a transformation of chemical energy into electrical energy is taking place. When the direction of the current is reversed, electrical energy is being transformed into chemical energy. Since the chemical energy which is thus stored up and accumulated within the cell may be again converted into electrical energy, this type of cell is known as a storage cell or accumulator.

The most satisfactory cell of this type is obtained by the combination spongy lead, dilute sulphuric acid, lead peroxide. Its electromotive force is approximately 2 volts. When this cell furnishes current the spongy lead passes into solution to form lead sulphate, which is deposited as an adherent coating on the surface of the lead electrode, and this tends to displace hydrogen at the other pole, as a result of which the lead peroxide (PbO_2) is reduced to lead oxide (PbO) which in turn is acted upon by the electrolyte to form lead sulphate.

In an external conductor connecting the two poles, the current, with respect to the positive electricity, will flow from the lead peroxide electrode to the lead electrode.

The simplest equation for representing the reaction * in this cell is the following:

$$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + H_2O.$$

If the current through the cell be now reversed, the lead sulphate at the negative (lead) electrode will be reduced to spongy lead, and the lead sulphate at the positive pole will be converted into lead peroxide, according to the equation

$$2PbSO_4 + H_2O = Pb + PbO_2 + H_2SO_4.$$

A large number of different types of this element have been, and still are, manufactured, and many of them have found very general practical application. In the construction of accumulators the chief objects aimed at are a long life, low internal resistance and a high "capacity" per

---

* The theory of the lead accumulator has been the cause of much scientific argument. Its discussion will be omitted.

pound of electrode material. By *capacity* is meant the current furnished by an accumulator expressed in ampere-hours (product of amperes and hours).

For the preparation of the electrodes two general methods are in use. One, originated by Planté, depends upon the behavior of lead plates in contact with sulphuric acid during electrolysis. If two such plates are immersed in dilute sulphuric acid and a current is passed between them, the surface of the plate connected with the positive pole of the source of current is converted into lead peroxide and hydrogen is evolved at the negative plate. If the direction of the current is now reversed, the lead peroxide is reduced to spongy lead and the other plate is superficially converted into lead peroxide. By occasionally reversing the direction of the current and continuing the operation for some time, the action finally penetrates to the interior of the plates, which are thus brought into a condition suitable for use in an accumulator. This process is called "forming," and is promoted by the addition to the electrolyte of certain chemical substances, particularly nitrates.

The other method is based upon the application to a hard lead frame or "grid," of a paste composed of lead oxide (litharge), sulphuric acid and sometimes other substances. The mixture on standing acquires a solid consistency and is afterwards formed into spongy lead and lead peroxide by electrolysis in a bath of dilute sulphuric acid.

In the "chloride process" the spongy lead plates are prepared by casting a hard lead frame around cubes composed of a mixture of zinc and lead chlorides. The plates are then connected as cathodes in an acid bath and the zinc chloride dissolves out, leaving a sponge-like frame of lead chloride which is converted into metallic lead by the electrolytic process.

As ordinarily constructed, an accumulator consists of a rectangular jar of glass or hard rubber, which contains the electrolyte, and a series of hard lead frames which carry the active materials. Two solid lead cross-bars or connectors are rigidly attached, one to all the positive plates, the other to all the negative plates, and the plates are so arranged that the positives and negatives alternate, one positive being placed between every two negatives, contact between them being prevented by suitable insulators. Electrical connection with the plates is effected through the medium of long lead lugs which are rigidly connected with the cross-bars.

The capacity of a given accumulator varies considerably with the strength of the current which it is required to furnish. This is shown in the following table, where the strength of the current, the number of hours which it is supplied, and the corresponding capacity, is given for a certain accumulator.

Current-strength in amperes.	Time in hours.	Capacity amperes × hours.
10	8	80
14	5	70
20	3	60

Fig. 29 shows a type of accumulator manufactured by the Electric Storage Battery Co. Portable cells (Fig. 30) are also made, in which the accumulators are contained in sealed rubber jars enclosed in hard-wood cases provided with handles and external binding-posts. Various capacities are furnished.

The internal resistance of accumulators varies with the size and construction between 0.001 and 0.02 ohm.

Accumulators furnish the most satisfactory source of current for electrochemical analysis. Their freedom from obnoxious fumes or vapors, the fact that their component parts require no renewal, and the great constancy of the potential difference which they furnish, are all important factors which make them particularly suited for work of this

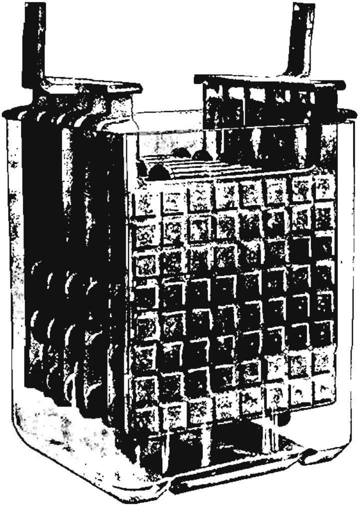


FIG. 29.

character. In the Aachen laboratory four pairs of accumulators have been constantly in use since 1888, without need of repair. Four accumulators are in use in the analytical laboratory, for which they have proved entirely sufficient, and four in the author's private laboratory.

REMARKS ON THE USE AND CARE OF ACCUMULATORS.

The type of accumulator which is ordinarily employed for the purpose of quantitative analysis is not shipped from the factory ready mounted for use, as are the smaller portable types of batteries, but the glass jars, cathode and anode plates,

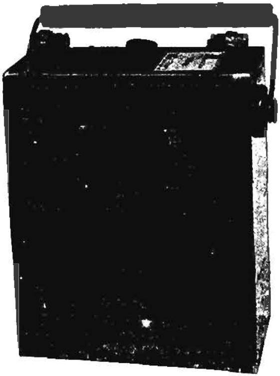


FIG. 30.

and the acid are packed separately. After the glass jars have been carefully cleaned, the plates are set in and the jars are filled with the acid electrolyte. Owing to the fact that they stand transportation much better under these conditions, the plates are not shipped in the primary state by the manufacturers, but are partially discharged and are then dried, the excess of sulphuric acid having first been removed from them. In order that they can be used as sources of current it is therefore first necessary to charge them. This operation should be begun *immediately* after the plates have been placed in the electrolyte, and consists in connecting the cells with some suitable source of current, the lead peroxide plates being connected with the positive pole, and the spongy lead plates with the negative pole, of the charging current. The most favorable conditions for charging are always specified by the manufacturers, and should always be closely complied with in order to obtain the most satisfactory results. The termination of the charging is denoted by the evolution of oxygen and hydrogen gases at the anode and cathode respectively.

The purity of the electrolyte is of the utmost importance. In preparing it only distilled water and strictly chemically pure sulphuric acid should be used. Among those substances which are particularly detrimental may be mentioned, chlorides, nitrates, iron salts, and arsenic. If only the commercial sulphuric acid is available it can be partially purified by passing hydrogen sulphide gas through it, which precipitates some of the metals as sulphides The precipitate is allowed to subside, the clear acid is decanted, and the dissolved hydrogen sulphide is expelled by blowing in air or by warming.

When an accumulator is fully charged it has an electromotive force of 2.2 volts, but when current is taken from it this falls rapidly to 2 volts and remains practically constant until the available supply of current is exhausted. The electromotive force then falls to 1.85 volt, and when this point is reached the use of the accumulator as a source of current should be discontinued and the process of recharging it should be begun immediately.

To insure the durability of accumulators, the following rules[*] must be observed:

1. They must be protected from short-circuit.

2. The maximum rate of discharge recommended by the manufacturers must not be exceeded.

3. An element must not be discharged until its electromotive force is below 1.85 volt.

4. An element must not be allowed to stand in an uncharged condition; and when not in use it must be charged at least once in every three or four months.

5. Violent shaking must be avoided, since this causes the active material to become loosened.

During the process of charging, and especially during supercharging, when gas is being generated at the cathode and anode, *an irritating vapor, which produces a choking sensation* in the throat and exerts a very corrosive action on exposed metal surfaces, is given off by the accumulators. This can be entirely prevented by pouring a thin layer of pure *mineral* oil on the surface of the electrolyte. An oil of the consistency of the so-called "cylinder oil" will be found most satisfactory. This treatment possesses other important advantages; *e.g.* the *creeping* of the electrolyte along the lugs to the connectors is entirely prevented; the electrolyte does not evaporate; single cells can be moved and carried about with much greater freedom, since the *viscosity of the oil greatly retards slopping. In batteries* containing a large number of single cells connected in series, leakage of current from one cell to another is reduced to a minimum not otherwise obtainable.

For charging accumulators the current may be furnished by a dynamo, a thermopile, or by primary elements.

---

[*] Anleitung zu elektrochemischen Versuchen von Dr. Felix Öttel, 1894.

If the charging current is taken from a dynamo, the number and arrangement of the separate accumulators should be such that the electromotive force of the dynamo current will exceed that of the accumulators by a small amount. A rheostat, for further regulating the current, should be included in the circuit, which should also contain an amperemeter for showing the strength of the current used in charging.

The maximum charging current recommended by the manufacturers for the particular model of accumulator in use should never be exceeded.

If the number of accumulators is not sufficient to nearly compensate the primary potential of the charging current, a rheostat with sufficient resistance to reduce the charging current to the desired strength may be used.

The *direct current* furnished in many places for electric lighting can be very conveniently used for charging accumulators. Where only three or four cells are to be charged, and this number is sufficient for all ordinary electroanalytical purposes, they may be connected together *in series* (p. 96) and charged from the lighting circuit by interposing a suitable incandescent lamp resistance. Thus, for example, if the normal charging rate of the accumulators is 5 amperes, and the difference of potential of the lighting circuit is 110 volts, the charging may be effected by inserting, in the circuit containing the accumulators, a resistance consisting of ten sixteen-candle-power lamps connected in *parallel*. Since each 16 CP. lamp requires a current of one-half ampere, the total current passing the accumulators will be equal to 5 amperes.

Since it is perfectly feasible to charge accumulators with a current *below* the normal, the simplest and most convenient method is often to connect the accumulators in parallel in a loop of the main conductor supplying a number of lights. When the lights are turned on the current will pass through the cells, and the effect of the back-electromotive force of the cells will not appreciably diminish the brilliancy of the lights in the circuit.

If a thermopile or primary galvanic elements are used for charging accumulators, it is usually necessary to connect the accumulators *in parallel* (p. 96). This method of charging is extremely tedious and inconvenient, and should be resorted to only under the force of necessity.

When no dynamo or circuit suitable for charging is to be had on the premises, it is best to use the portable type of accumulator shown in Fig. 30, which can be charged outside the building at some point where current is available.

It is very desirable to have a pair of lead safety-fuses inserted in the circuit with the accumulators to protect against excessively high currents. The capacity of these fuses should be such that they will "blow-out" when the current-strength exceeds the maximum recommended for the given accumulators.

PHYSICAL METHODS OF PRODUCING THE CURRENT.

Dynamos.—The production of current by dynamo machines depends upon the principle that when a conductor is moved through a magnetic field a current is set up in the conductor, the direction of the current being such as to oppose the change which produced it. The induced electromotive force is proportional to the number of lines of force which are cut per second by the conductor.

In dynamos, as they are commonly constructed, the magnetic field is produced between the poles of powerful electromagnets, and the conductors in which the current is generated consist of insulated copper wires wound about an iron core which serves to concentrate the magnetic field. The core is attached to a shaft or spindle supported by lubricated bearings, and through the application of power to the shaft the core and attached conductors are rapidly rotated in the magnetic field. In order to secure a direct current of practically uniform strength and potential, the moving conductor is divided into a number of sections which are separately connected to insulated bars of copper placed in the form of a ring about the spindle. Metallic brushes attached to the frame of the machine make electric contact with the copper bars on the spindle.

The electromagnets which produce the field are known as the *field-magnets;* the iron core with the attached conductors is called the *armature;* and the ring built up of copper bars is called the *commutator.*

Direct-current dynamos are classified, according to the manner in which the field magnets are excited, as:

1. *Series dynamos*, in which the whole current from the armature passes through the coils of the field-magnets, their resistance having been made as small as possible (Fig. 31).

2. *Shunt dynamos*, in which only a portion of the current is allowed to pass through the coils of the field-magnets by joining them in parallel with the main circuit (Fig. 32).

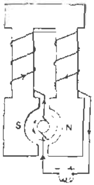


FIG. 31.

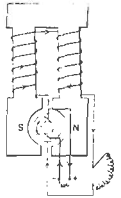


FIG. 32.

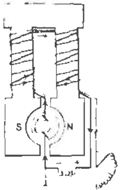


FIG. 33.

3. *Compound dynamos*, in which the field-magnets are

excited partly by a few turns of wire in series with the armature, and partly by a coil connected in parallel with the main circuit (Fig. 33).

Series dynamos are used where the conditions of the external circuit are unchanging. Shunt and compound dynamos are used where changes in the external circuit are desirable or unavoidable.

Shunt dynamos (Fig. 34) are the most satisfactory type for electrochemical purposes, since, by introducing a variable resistance in the circuit of the field coils (Fig. 32), the *strength of the field, and correspondingly the electromotive force of the external circuit*, can be changed and regulated.

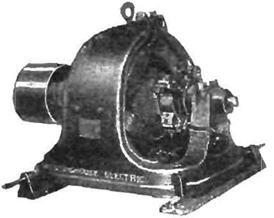


FIG. 34.

When, after having been at rest, the dynamos are started, the weak residual magnetism remaining in the field-magnets serves to build up the current in the armature.

The power for running a dynamo may be taken from an engine or may be furnished by an electric motor. If the former is used, the most efficient results are obtained by connecting the engine and dynamo directly together, and transmitting the power by a single shaft from one to the other. The small dynamos, such as are suitable for currents used in electroanalysis, may be driven by belts attached to pulleys on suitable counter-shafts. Where an electric motor is employed, the dynamo can be connected with it by a belt, but in such cases it is usually more satisfactory to use a motor-dynamo (rotary transformer) which may consist of a motor and dynamo mounted on the same frame and connected by a single shaft (Fig. 35), or of a single set of field-magnets and an armature containing two independent windings (Fig. 36).

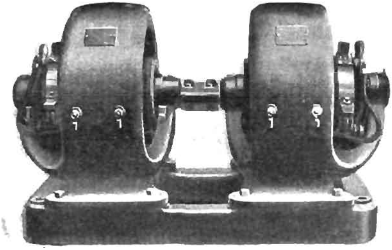


FIG. 35.

The most convenient plan in electrochemical analysis is to use the current from a dynamo only for charging storage batteries, but it is perfectly practical to use it directly as will be described later in Chapter XV. If it is to be used directly, an electromotive force of about 10 volts will meet every requirement. If it is to be used for charging accumulators, its capacity will depend upon the number and size of these.

The horse-power required for driving a given dynamo can be approximately determined by multiplying the current in amperes by the potential in volts, and dividing the product by 625.

Thermopiles.—If two strips of dissimilar metals are connected at their ends, and one of the junctions thus formed is

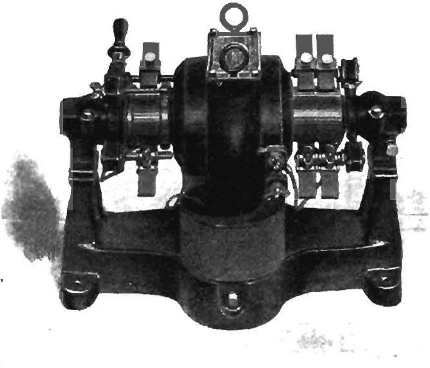


FIG. 36.

maintained at a different temperature from the other, an electric current will be produced in this circuit. If the strips consist of copper and bismuth, a continuous current will flow from the bismuth to the copper across the warmer junction, the work done by the current being mechanically equivalent to the heat which is absorbed at the warmer junction. The electromotive force of such a couple is small, but by combining a sufficient number of such pairs in series, it can be increased to a point where the combination is suitable as a source of primary current. An arrangement of this sort is called a *thermopile*, and the separate couples are called *thermo-elements*.

Practical thermopiles have been designed by Clamond, Noë, and Gülcher.

The general appearance of Gülcher's thermopile is shown in Fig. 37. The two metals forming the elements are a nickel alloy (known as *argentan*) and a special alloy the chief ingredient of which is antimony. The heating is done by gas, and the separate elements are so constructed that a mixture of gas and air is conducted through an argentan tube and burns with a non-luminous flame just at the point where the top of the tube is in intimate metallic contact with a flat bar of the antimony alloy. These points of contact between the tubes and the antimony bars constitute the hot junctions, and the cool junctions lie at those points where each bar of antimony is connected with the bottom of the argentan tube of the next adjoining element. Contact between the antimony bars and the bottoms of the burner-tubes is effected by means of thin plates of sheet copper which offer a large surface for the radiation of heat and thus tend to maintain the cooler junctions at a relatively low temperature. The separate

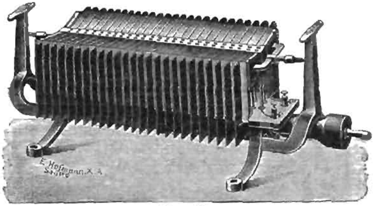


FIG. 37.

elements are assembled in series in two rows on an insulated iron frame, and the mixture of gas and air is supplied to them from a large pipe running directly beneath them.

The electromotive force of the thermopile varies with changes in the temperature and since this is to a considerable extent dependent on the gas pressure, the latter must be carefully regulated if a constant electromotive force is required. Of the various regulators constructed for this purpose, that designed by Danneel * is the simplest and most efficient.

The construction of this instrument is shown in the adjoining sketch (Fig. 38). The solenoid *S* is connected by wires to the binding-posts of the thermopile, and the gas supplied to the thermopile passes through the regulator, entering at *B* and leaving at *A*. The solenoid fits over a glass tube, within which is a permanent magnet *M* suspended by a spiral spring capable of adjustment. An increase in the electromotive force of the thermopile, due to a rise in temperature at the junctions, causes more current to flow through the coil, and the magnet is drawn further into it. The lowering of the magnet forces a disc down on the orifice of the gas supply pipe and reduces the supply of gas passing to the thermopile. *C* is a thumb-screw by which a second opening from *B* to *A* can be so regulated that just sufficient gas passes through it to keep the burners of the thermopile from being extinguished when the other valve is completely closed.

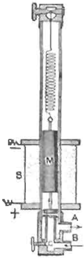


FIG. 38.

---

* Zeit. f. Elektrochemie, 3, 81 (1896–97).

CHAPTER XV.

METHODS OF REGULATING THE CURRENT-STRENGTH AND POTENTIAL.

THE relations between the current-strength, the difference of potential, and the resistance are expressed by the equation

$$\text{Current-strength} = \frac{\text{Difference of potential}}{\text{Resistance}}.$$

In any given system consisting of a source of current and an *external circuit, the above equation in order to express* the exact relations may be written

$$C = \frac{\epsilon}{R+r};$$

in which ϵ represents the electromotive force of the source of current, R the resistance of the external circuit, and r the internal resistance of the source of current. In the case of galvanic cells, the factor r represents the internal resistance of the cell, and where the source of current is a dynamo, r represents the resistance of the circuit through which the current passes *within* the dynamo.

In any given circuit having a definite external resistance, the *simplest method of altering the current-strength* is by a direct change in the difference of potential. Where the source of current is a galvanic element, the difference of potential can be increased by connecting two or more of these elements *in series*.

The process of connecting two galvanic elements in series consists in connecting the positive pole of the one to the negative pole of the other. The current is then taken from the two remaining poles. Any number of elements can be connected in this manner, as shown in Fig. 39, and the *electromotive force* of the combination, when the elements are all alike, is equal to the electromotive force of one element *multiplied by the total number of elements thus connected.*

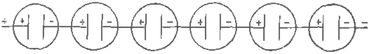


FIG. 39.

When two or more elements are connected in *series*, the current-strength in the circuit is represented by the equation

$$C = \frac{x\epsilon}{R + xr},$$

in which x is the number of elements and ϵ is the electromotive force of each element.

Another method of increasing the current-strength in a circuit is by connecting two or more elements *in parallel.*

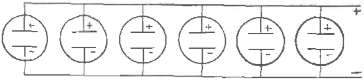


FIG. 40.

This consists in connecting all of the positive poles of the several elements to one conductor, and all of the negative poles to another, as shown in Fig. 40. The external circuit is then connected with the two conductors. The electromotive force of such an arrangement is the same as the electromotive force of a single cell, but the internal resistance is equal to the resistance of one element *divided* by the total number of elements. The current-strength under these conditions is determined by the equation

$$C = \frac{\epsilon}{R + \frac{r}{x}}.$$

The effect of this arrangement on the current-strength is largely dependent on the relative values of the internal and external resistances, since the smaller the value of R with respect to r, the greater will be the increase of the current produced by thus connecting the elements in parallel.

Another means for altering the current-strength in a circuit is afforded by the introduction or removal of resistance. This is usually effected through the use of rheostats or resistance-boxes.

The name *rheostat* is given to any appliance containing a liquid or metal conductor the electrical resistance of which can be altered at pleasure. Instruments of this sort, constructed on various patterns, can be purchased from dealers in electrical instruments. Only a few of these will be here mentioned.

Fig. 41 shows a general form of instrument known as a "resistance-box." The resistances, in the form of coils of fine wire, are contained in the interior, and the terminals of these coils are attached to metal blocks fastened to the top of the box. By inserting metal plugs between adjoining blocks the resistances can be short-circuited and removed from the path of the current. As ordinarily constructed these instruments are ill adapted to use in a chemical laboratory, because the exposed metal parts are quickly attacked by acid vapors. This difficulty has been met by the use of mercury contacts, instead of plugs, to connect the metal plates. An instrument of this sort, made at the author's suggestion by Fraas Brothers of Wunsiedel (Germany), is shown in Fig. 42. This is so constructed as to give resist-

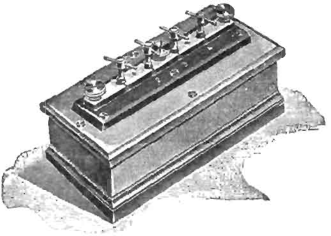


FIG. 41.

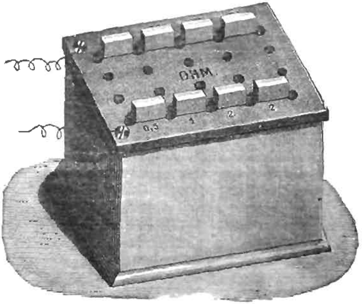


FIG. 42.

ances from 0.5 to 80 ohms, in multiples of 0.5 ohm. Continued use has established the fact that such a rheostat is extremely convenient and satisfactory.

Another commercial form of rheostat is shown in Fig. 43. The variable resistance is a circular coil of wire one end of which is attached to one of the binding posts shown at the corners of the base. The other post is connected with the pivot of a movable lever. To the end of the lever is fastened a *sliding contact* which *presses* on the coil of wire. In the rheostat shown in Fig. 44, the lever can be moved over a number of metal studs arranged in a semicircle on an insulated base. One terminal of the circuit is connected with the lever, the other with a coil of wire attached to the frame. By moving the lever over the studs the current is forced to pass through any number of the separate sections into which the resistance coil is divided.

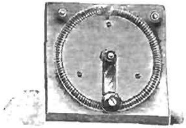


FIG. 43.

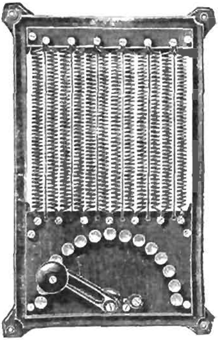


FIG. 44.

A commercial type of rheostat much used in the United States is known under the trade-name of "Iron-Clad." In these rheostats the wire resistance is fused into a protecting enamel, and the possibility of corrosion or mechanical injury is entirely excluded.

It is often possible to construct simple rheostats, which serve all the purposes required in the ordinary course of electrochemical analysis, rather than to purchase the more costly ones from dealers.

An arrangement * of this sort is shown in Fig. 45. It consists of a light wooden frame, in the form of a parallelogram, back and forth across which is strung a galvanised iron wire, supported on small porcelain or glass insulators. If currents of low potential only are to be used, the insulators can be entirely dispensed with, and the wire can be passed simply through iron screw-eyes inserted in the woodwork. One end of the wire is attached to a binding-post with which one terminal of the circuit can be connected, and the other terminal of the circuit is fastened to a brass clamp (*a*) which can be clamped on the iron wire at any point along it. The resistance which can thus be introduced is only limited by the total resistance of the iron wire, and any fraction of this total can be inserted by attaching the clamp at the proper position. The frame can be attached to the wall and the strands of wire can run up and down across it, in which case contact can be made with the bottoms of the separate strands. In many cases such an arrangement is extremely convenient.

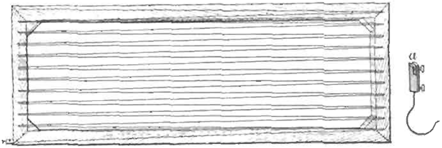


FIG. 45.

---

* Edgar F. Smith, Electro-Chemical Analysis, 1894.

Another simple and very convenient arrangement is shown in Fig. 46. Two separate resistances composed of narrow strips of sheet-zinc (or galvanised sheet-iron) are fastened to the opposite sides of a wooden frame, and one end of each of these strips is connected with a separate binding-post. To these binding-posts the terminals of the circuit are connected, and the resistance between them is varied by moving a sliding clamp (S) which is in contact with both strips, along the top of the frame. Fig. 46 (A) shows the end view of such a rheostat, and B in the same figure shows how the strips can be cut from a sheet of zinc. The thickness of the sheet-zinc used and the width of the strips determine the resistance for a given length of conductor. The frame is provided with feet so that it can stand upright, and it can be placed on the floor in the neighborhood of the work-bench.

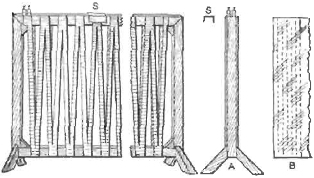


FIG. 46.

The plan of a simple rheostat described by Oettel * is given in Fig. 47. Spirals of wire forming the variable resistance are attached to a wooden frame at the top and to heavier copper wires at the bottom. The ends of the copper wires dip into cavities in the base-board containing mercury. The ends of the wire resistance are connected with binding-

---

* Anleitung zu Elektrochemischen Versuchen, 1894.

posts, by which the *rheostat* is inserted in the circuit. The most convenient arrangement is obtained by having the length of the wire in the different spirals in the ratios

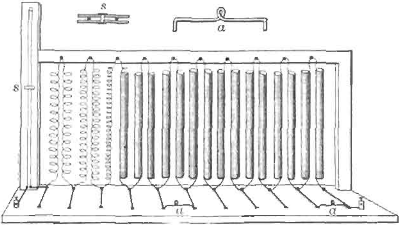


FIG. 47

1 : 2 : 4 : 8 : 16 : 32, etc., by which any number of units of resistance can be introduced. The resistance of the circuit passing through the rheostat is reduced at will by placing copper-wire bridges (*a*) between adjacent mercury cups. If a fine adjustment of the resistance is desired, this can be accomplished by stretching a wire, of a length slightly greater than that in the smallest spiral, in the form of a loop with parallel sides along an upright wooden strip attached to the end of the frame supporting the spirals. This loop carries a slider (*S*) in contact with both strands, and, by moving this slider up or down, a very delicate adjustment of the resistance can be effected.

The *methods for regulating the potential of the current,* which are more or less independent of the electromotive force of the source of supply, depend in general upon the fact that the fall in potential along any conductor through which a current is passing is proportional to the resistance.

Thus, for example, if A (Fig. 48) is the source of a current flowing through the circuit $ABCA$, and the conditions are such that *the difference of potential between B and C* is

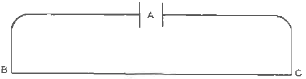


FIG. 48.

equal to x volts, the difference of potential between any two points on the conductor BC will be represented by the equation

$$V_1' - V_2' = \frac{xR'}{R};$$

where R' is the resistance between the two points in question and R is the total resistance of the conductor BC. If x is equal to 10 volts, and the conductor BC is 100 centimeters long and of uniform material and cross-section, the difference of potential between any two points 1 cm apart will be 0.1 volt.

By connecting one electrode of an electrolytic cell with the point B and the other electrode with some point along the conductor BC, any difference of potential less than 10 volts can be maintained between the two electrodes.

An arrangement of this sort, where a second circuit is connected in parallel with another circuit, is called a *shunt* connection, and the second circuit is known as the *shunt circuit.*

A shunt circuit attached to the conductor BC is shown in Fig. 49. If R represents the total resistance of the circuit, R_1 the resistance of the portion CAB (consisting of the resistance of the conductors BA and CA and the internal resistance of the source A), R_2 the resistance of BD, R_3 the resistance of DC, R_4 the resistance of the shunt circuit containing the electrolytic cell E, and if ϵ is the electromotive force of the source of current, then the current C flowing through the entire circuit will be represented by the equation

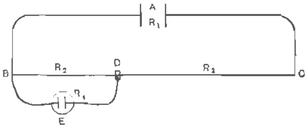


Fig. 49.

$$C=\frac{\epsilon}{R},$$

and the value of R is given by the equation

$$R=R_1+R_3+\frac{R_2R_4}{R_2+R_4}.$$

The values for the current-strengths through the parallel circuits BD (c_2) and BED (c_4) are determined by the equations

$$c_2=\frac{CR_4}{R_2+R_4}, \quad c_4=\frac{CR_2}{R_2+R_4}.$$

Finally, the difference of potential (x) between the points B and D can be calculated from the equation

$$R:\frac{R_2R_4}{R_2+R_4}=\epsilon:x.$$

From an examination of these equations it will be evident that when R_2+R_3 is large with respect to R_1, and R_4 is large with respect to R_2, the current-strength through the main circuit will be but little altered by connecting or disconnecting the shunt circuit *BED*.

The simplest practical arrangement for thus utilising the variable difference of potential which can be obtained in a shunt circuit is suggested by Fig. 49. The conductors *BA* and *AC* can consist of stout copper wires, and the points *B* and *C* can be connected by a wire of German-silver having a resistance of say 10 ohms. If the source of current is two accumulators connected in series, a difference of potential of approximately 4 volts will exist between *B* and *C*. By means of a sliding contact on *BC* any difference of potential less than 4 volts can be brought into action in the cell *E*.

A simple instrument has been designed by the author for this purpose (Fig. 50).

The current from the battery enters at *a*, passes through the German-silver resistance *NN*, and returns to the battery

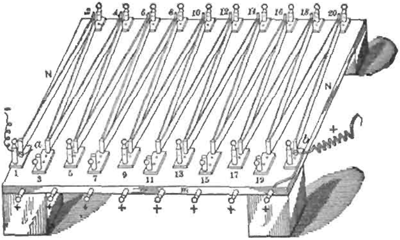


Fig. 50.

through *b*. In making electrolytic determinations the platinum dish serving as cathodes are connected with any one of the binding-posts numbered from 1 to 20, while the platinum anodes are connected with the binding-posts marked with the + sign. With this apparatus eight different operations can be conducted simultaneously.

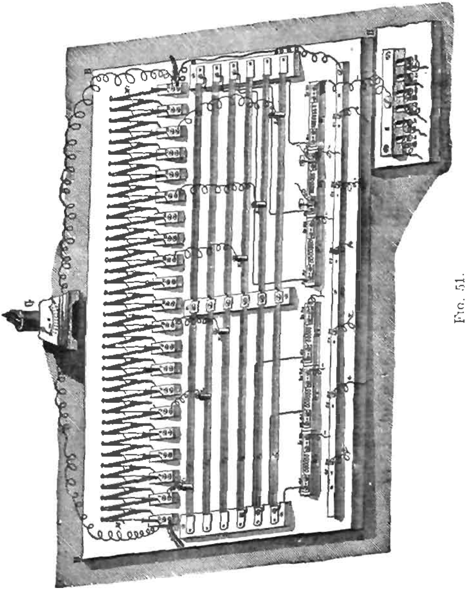


FIG. 51.

Another larger and more complicated instrument for the same purpose was constructed for the author's laboratory by the firm of Siemens & Halske (Fig. 51). With this instrument a large number of electrolytic determinations, requiring currents differing in strength and potential, *can be carried on independently of one another.* The current from a dynamo with a potential of 10 volts enters by the cables attached to the ends of the resistance MM_1. This resistance is composed of brass wire-gauze in strips arranged in a zigzag across the top of the base of the instrument and is divided into 20 divisions by the contact-bars 0, 1, 2, 3 · · · 20, to which it is fastened at equal intervals. Since, as already stated, the total difference of potential is equal to 10 volts, the difference of potential between any two adjacent contact-bars will be equal to one-twentieth of the total, or $\frac{1}{2}$ volt. Connection with the separate contact-bars is effected by wires attached to the binding-posts K_1, K_2, etc., which slide on the galvanised iron strips S_1, S_2, etc., and the latter are connected with the blocks W_1, W_2, etc. The positive terminal of the dynamo is connected with the long contact-bar M_2 at the lower edge of the base-board. The cells in which the electrolytic determinations are conducted are connected between the bar M_2 and the blocks W_1, W_2, etc. The total current passed through the resistance was 60 amperes. A voltmeter (G) attached to the ends of the resistance indicates the total difference of potential.

Electrochemical analysis can often be very conveniently and satisfactorily carried out by the use of the current supplied for lighting purposes. The direct current used in the United States for incandescent lighting is usually distributed by what is known as the three-wire system. In this system the circuit consists of three wires which for the purpose of explanation will be designated as *a*, *b*, and *c*. Under normal conditions the difference of potential maintained between the wire *a* and the wire *b* is 110 volts, *a* being positive with respect to *b*. The difference of potential between *b* and *c* is also 110 volts, but *c* is negative with respect to *b*. The electrical relations between the wires may be considered as of the same nature as that between the three wires *a′*, *b′*, and *c′* (Fig. 52), where *a′* is connected with the positive pole of a galvanic element, *b′* to the negative pole of the same element, and *c′* to the negative pole of a second element connected in series with the first one.

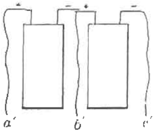


FIG. 52.

By connecting between the wires *a* and *c*, a current with a difference of potential of 220 volts can be obtained.

If, therefore, a current at a potential of 110 volts is at disposal, it is necessary to considerably reduce this before it is suitable for carrying out electroanalytical determinations. For reducing this current incandescent lamps are *extremely convenient. An ordinary 16-candle-power 110-volt* lamp has a resistance of approximately 220 ohms. Therefore when it is connected in the circuit it permits the passage of a current having the strength of 0.5 ampere.

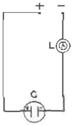


FIG. 53.

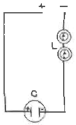


FIG. 54.

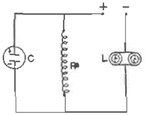


FIG. 55.

The simplest arrangement for conducting an electrolytic determination is shown in Fig. 53. In this case the electrolytic cell *C* is connected in series with a single lamp* *L*

---

* For mounting the lamps cheap porcelain sockets are very convenient.

between the terminals of a 110-volt circuit. The current through the cell will be approximately 0.5 ampere. In Fig. 54 the circuit contains two lamps (16 C. P.) in series, and the current in this case will be approximately 0.25 ampere. Two lamps in parallel will give a current of one ampere, and three lamps in series a current of approximately 0.16 ampere. By a proper arrangement of lamps in the circuit almost any desired current-strength can be obtained.

This sort of an arrangement, however, while perfectly satisfactory for depositing most metals from solutions of their salts, is not suitable when the separation of one metal from several others is to be accomplished, since the difference of potential between the electrodes in the cell is dependent on the conductivity of the solution and may therefore during the process of electrolysis increase to a value above that at which a separation can be effected.

For conducting separations of different metals the arrangement shown in Fig. 55 should be followed. Two or more lamps connected in parallel are placed in the circuit, which also contains a variable resistance *R* connected in parallel with the electrolytic vessel *c*. By properly adjusting *R* the desired difference of potential between the electrodes can be maintained throughout the electrolysis. A number of other modifications of this method are possible and will undoubtedly suggest themselves.

CHAPTER XVI.

ACCESSORY APPARATUS.

Electrodes.—The electrodes used for the purposes of electrochemical analysis are in nearly all cases composed of pure platinum or of a platinum-iridium alloy. Exceptions to this general rule are the mercury cathodes which are sometimes employed for determining metals in the form of amalgams, and the silver anodes used in the determination of the halogens.

The advantages of the platinum-iridium alloy (10% iridium) over pure platinum are that its resistance to electrolytic action is as great as that of pure platinum and its greater rigidity and elasticity make the electrodes composed of it less liable to injury. Electrodes made from platinum-iridium can be much lighter than pure platinum electrodes of the same dimensions.

The size of the electrode on which the electrolytic deposit is precipitated is of considerable importance, since when the exposed surface is large the deposit adheres more firmly to it. If a metal separates from a solution in a dense form, as in the electrolysis of double oxalates, the probability of the oxidation of the metal is not appreciably increased by enlarging the surface of the cathode. In the precipitation of lead and manganese peroxides a relatively large electrode surface is most important. It is not practical, therefore, to employ a platinum crucible for electrolytic precipitation if more than a few milligrams are to be separated; not only is the exposed surface too small, but the anode and cathode cannot be widely enough separated to facilitate the separation of the deposit in a dense form.

The nature of the surface of the electrodes is also important, since some metals separate less satisfactorily on hammered surfaces than on those which have been spun (or rolled) and polished. In some cases, as in the precipitation of certain metals and in the determination of lead as peroxide, the firm adherence of the precipitate to the electrode can only be secured by the use of a platinum electrode the surface of which has been roughened by the use of a sand-blast.

For the negative electrode (cathode) the author uses a thin platinum dish having the form shown in Fig. 56, 9 cm in diameter, 4.2 cm in depth, holding about 250 cc and weighing from 35 to 37 grams.[*]

Another form of dish electrode is shown in Fig. 57. This is the form recommended by v. Klobukow, and differs from

---

[*] Dishes of this weight must be composed of platinum-iridium to be satisfactory. The relations between the volume of the contained liquid and the available electrode surface in a dish having *exactly* the size and shape given, is shown in the following table:

Volume of Liquid, in Cubic Centimeters.	Area of Electrode Surface, in Square Centimeters.
260 (full)	160
250	155
200	130
150	114
120	100
100	90

The dish contains 150 cc when filled to within 1.7 cm of the edge, and 120 cc when filled to within 2.2 cm.

When a disk anode, 4.5 cm in diameter, is used with this dish the most uniform distribution of the current is obtained by adjusting the disk so that it is exactly in the center of the dish and about 2 cm below the edge.

that of the author chiefly by having a lip which allows liquids to be conveniently poured from it.

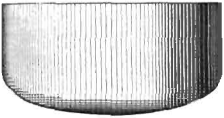


FIG. 56.

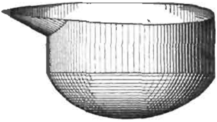


FIG. 57.

Since dishes which have become rough, scratched, or bent are not satisfactory for electrolytic determinations, it is strongly recommended that the dishes used as electrodes be reserved exclusively for their intended purpose.

FIG. 58.

As anode, the author uses a disk of moderately thick sheet platinum (Fig. 58), about 4.5 cm in diameter, which is fastened to a strong platinum wire. The disk should have a number of good-sized holes in it to promote the circulation of the liquid and allow the ready escape of the gases formed.

The author has also used an anode having the form of the platinum dish shown in Fig. 56, 50 mm in diameter and 20 mm in depth. This anode is supported by a platinum wire attached to its center and has five openings in it. It is particularly suitable for the determination of those metals which have a tendency to separate in a spongy form, *i.e.*, cadmium and bismuth.

The form of the electrodes used at the Mansfeld smelting-works chiefly for the determination of copper, is shown in

Figs. 59 to 62. The cathode* may be either a platinum

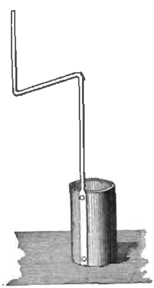


FIG. 59.

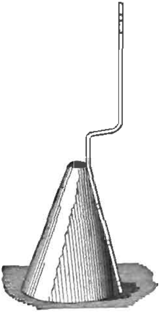


FIG. 60.

cylinder (Fig. 59) or a cone (Fig. 60). The anodes used with these are shown in Fig. 61 and Fig. 62 respectively. A vertical slit in the cathodes opposite the supporting wire, through which the wire of the anode can be passed, adds to the convenience in adjusting and removing the cathodes. The objection to this form of electrode is that the current is very unequally distributed over the surface of the cathode, the current density being particularly high on the lower edge, which often causes the deposited metal to separate there in

FIG. 61.

---

* An important advantage of this form of cathode is that it can be used in solutions containing a precipitate. When the dish electrodes are used the precipitate settles to the bottom and interferes with the deposition of the metal.

a crystalline or spongy condition. The current-density is also much lower on the outside than on the inside.

A form of electrode recommended by Winkler* is shown in Fig. 63. It is made in the form of a cylinder, 3.5 cm in diameter and 5.5 cm in height, from platinum wire gauze (wire 0.12 mm in thickness, 250 meshes per sq. cm). The top and bottom of the gauze are strengthened by a rim of sheet platinum. The weight of the electrode is from 13 to 15 grams. The surface area can be approximately calculated from the formula

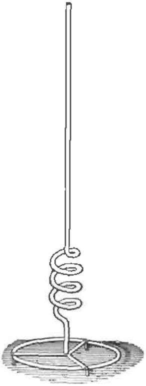


FIG. 62.

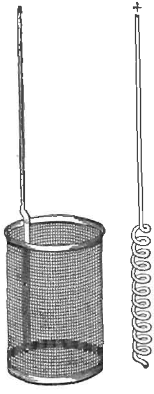


FIG. 63.

$$S = d2\pi\sqrt{nlb},$$

---

* Ber. deutsch. chem. Ges., 32, 2192 (1899).

in which d is the diameter of the wire, n the number of meshes per sq. cm, l the circumference, and b the height of the cylinder.

The advantage of this form of cathode over those composed of sheet metal is, that when the anode shown beside it is used, the current-density on the inside and outside of the cylinder is practically the same. Since, in electrolysis, the metal is deposited on the entire circumference of the separate wires, there is much less tendency for the precipitate to scale off, and as a consequence satisfactory deposits can be obtained under conditions which would not be possible with sheet-platinum electrodes. This fact permits many determinations to be carried out with much higher current-densities and consequently in a much shorter time.

Another form of electrode, designed by Oettel* is given in Fig. 64. The cathode is a sheet of platinum 8 cm high and 5.5 cm wide. The anode consists of two parallel spirals of platinum wire attached to a forked support, and is so placed that the spirals are at equal distances on either side and opposite the middle of the cathode. With this arrangement the current-density at the cathode is fairly uniform.

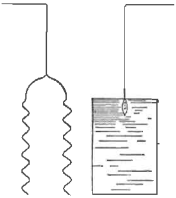


FIG 64

Stands. — For holding the electrodes the author has used a single standard (Fig. 65) having a metallic ring, to which three short contact points of platinum are riveted, which supports the platinum dish, and an insulated arm (a), which carries the anode. An objection to the use of this stand is that the brass rod to which the ring and arm are clamped is readily

---

[*] Zeit. f. Elektrochemie, 2, 102 (1895–96).

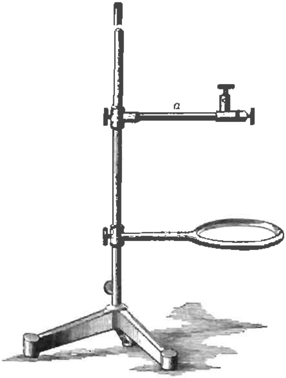


FIG 65.

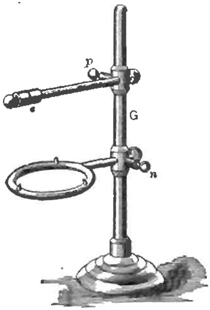


FIG 66

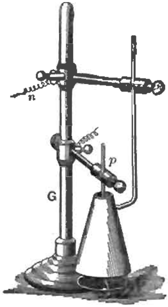


FIG 67.

corroded by the laboratory vapors, which may lead to an imperfect electrical connection. The stand shown in Fig. 66 has given good service for a long time. The ring and arm are clamped to a glass rod *G*, and *n* is connected with the negative and *p* with *the positive pole of the source of current.* The anode is clamped in position at *e*. If a cone or cylinder

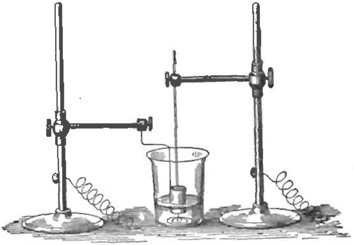


FIG. 68.

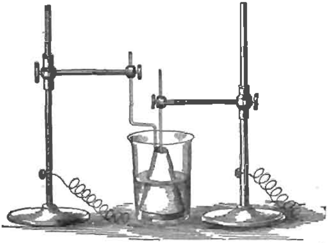


FIG. 69.

is used as the cathode, two arms are attached to the glass rod, as shown in Fig. 67. This arrangement is particularly convenient when a metal is precipitated from an acid solution, since by lifting the standard the two electrodes can be quickly removed from the electrolyte and plunged into a vessel of clean water.

Another method of supporting the electrodes is to have a separate standard for each of them (Figs. 68, 69).

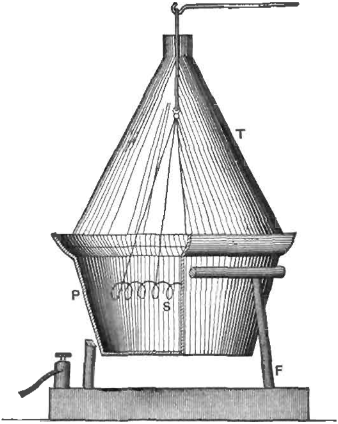


Fig. 70.

The arrangement shown in Fig. 70 has been used by Herpin. The platinum dish *P* supported by a metal tripod *F* serves as the cathode, and the anode is a spiral of platinum wire *S* (shown separately in Fig. 71). The dish is covered by a glass funnel which prevents loss of the solution by spirting.

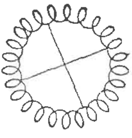


Fig. 71.

The apparatus used by Riché is shown in Fig. 72. The cathode (Fig. 73) is a cone having the shape of a crucible open at both ends and provided with a bail. It contains a number of oblong openings in the side to facilitate the circulation of the electrolyte. The cone is so placed in a platinum crucible, which serves as anode, that the distance between them is from 2 to 4 mm.

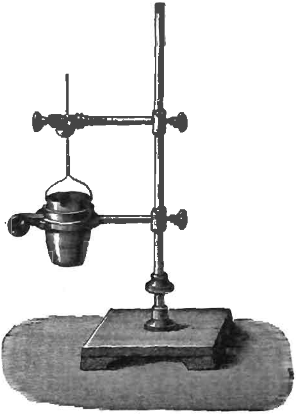


Fig. 72.

Fig. 73.

An arrangement for carrying on several similar determinations simultaneously has been described by v. Malapert.[*] It consists of a wooden frame (Fig. 74) at the top of which binding-posts for attaching the electrodes are placed. Beakers containing the solutions are supported by the shelf *B*. Arrangements of this sort are very convenient when a large number of similar determinations are carried out regularly, as is often the case in technical laboratories.

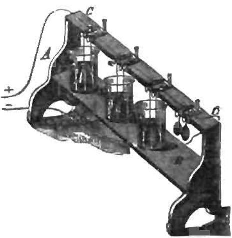


FIG. 74.

Where several similar determinations are made at the same time it is not infrequently the practice to connect the various cells in parallel with one another, and to assume *that the current distributes itself equally between them.* This assumption, however, is usually incorrect, since slight differences in the resistance of the cells, due to differences in the concentration and composition of the solution and to inequality in the distances between the electrodes, will cause marked differences in the strength of the currents passing through them. Because of this inequality, unsatisfactory results will be obtained. In such cases, therefore, the cells should always be connected *in series,* so that the exact current-strength and potential of each cell can be measured and controlled.

Many separations and determinations are promoted by heating the electrolyte. Great care should be exercised, however, that the temperature of the electrolyte is not raised

---

[*] Zts. f. anal. Ch., 26, 56 (1887).

to the boiling-point, since in this case the precipitated metal will be loosened from the electrode and its quantitative determination will become impossible. To insure a uniform heat, which is also essential, a thin asbestos board may be placed under the dish or beaker, and the source of heat can be either the burner shown in Fig. 75 or the bottom of an ordinary Bunsen burner from which the tube has been removed so that the gas burns in a small luminous flame.

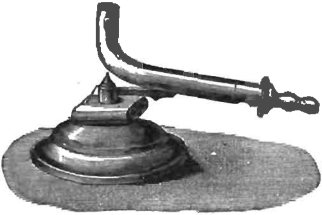


FIG. 75.

Engels,* as a result of experiments conducted in the Aachen laboratory, recommends the use of an asbestos board 2 cm below the dish and below this an ordinary Bunsen burner.

The arrangement shown in Fig. 76 can also be used. It consists of a stand made by bending a stout copper wire into two parallel circles connected by an upright. The smaller of the rings supports the dish, and the heat is furnished by the small flame from the base of

FIG. 76.

---

* Zts. f. Elektrochemie, 2, 413 (1895–96).

a Bunsen burner. The burner is covered by an asbestos chimney, which is made by moulding wet asbestos board into the form of a cylinder with openings at the upper and lower edges as indicated. The top of the cylinder is covered by a slightly concave sheet of asbestos.

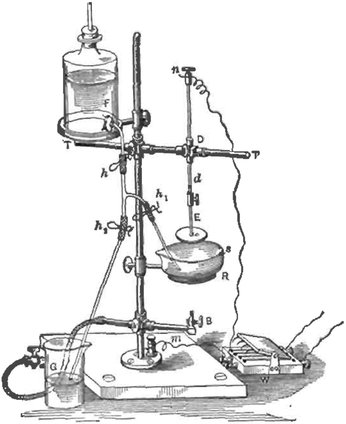


FIG. 77.

A universal stand, in which all the necessary apparatus is carried by a single vertical rod, has been described by v. Klobukow.* A sketch of this is shown in Fig. 77. *R* is the dish cathode, *E* the anode; *B* is a micro-burner for heating the solution. By a system of glass and rubber tubing pro-

---

* Journ. f. prak. Chem., (2) **34**, 539; *ibid.*, **40**, 121; *ibid.*, **33**, 473. See also Krüger, Elektrochem. Zeit., **3**, 106 ff. (1896).

vided with pinch-cocks the contents of the dish can be siphoned off into the beaker *G* and fresh water for washing can be introduced into the dish from *F*.

Another modification of v. Klobukow's apparatus is shown in Fig. 78, where an attachment is provided for imparting a slow rotary motion to the anode by means of a motor.

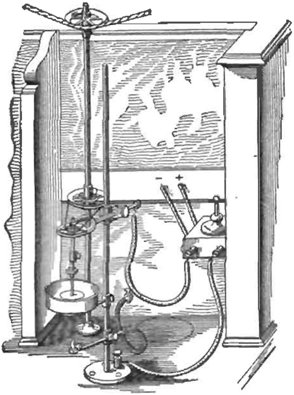


FIG. 78.

Through the courtesy of Professor F. A. Gooch of Yale University the translator is able to include a description of an extremely simple and practical arrangement for electrochemical analysis which possesses the additional advantage that it dispenses with the necessity of special platinum dishes or electrodes.* The most novel feature of this

---

* Gooch and Medway, Am. Journ. of Science, April, 1903.

arrangement, however, is that by its use the time required for conducting an electroanalytical determination is reduced to from 10 to 30 minutes.

The appliance (Fig. 79) depends upon the precipitation of the metal upon a *rapidly* rotating cathode. The cathode used is an ordinary platinum crucible (20 cc capacity), which is rotated at a speed of 600 to 800 revolutions a minute by a small electric motor. The motor is fastened so that its shaft is vertical, and to an extension of this shaft the crucible is fixed by pressing it over a rubber stopper bored centrally and fitted tightly to the end of the shaft. To secure electrical connection between crucible and shaft, a narrow strip of sheet-platinum is soldered to the shaft and then bent upward along the sides of the stopper (*A* in Fig. 79), thus bringing the shaft in electrical contact with the inside of the crucible when the latter is pressed over the stopper.

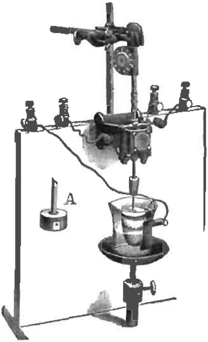


FIG 79

The solution to be electrolysed is placed in a beaker upon a small adjustable stand, so that the crucible may be dipped into the liquid to any desired depth. The crucible is connected with the source of current by attaching a wire to one of the bearings in which the shaft turns. A sheet of platinum foil suspended from the edge of the beaker serves as the other electrode.

The solution, 50 cc in volume, was placed in a beaker having a total capacity of about 150 cc, and the height of the beaker was so adjusted that the liquid covered about two-thirds of the crucible. This gave a cathode surface having an area of about 30 sq. cm.

By the use of this arrangement quantities of copper equal to about 0.25 g were satisfactorily precipitated from a sulphuric acid solution with a current of ND_{100} 10–13.3 amperes in from 15 to 20 minutes; 0.19 g of silver from a solution of the double cyanide with a current of $ND_{100}=$ 8.3–10 amperes in 10 minutes; and 0.17 g of nickel from a solution containing ammonium sulphate and an excess of ammonia with a current of $ND_{100}=11.7$–13.3 amperes in 25 minutes.

The process as described is rapid, exact, and very simple, and the special apparatus required is inexpensive. The speed with which a determination can be carried out by this method would seem to be due chiefly to the complete and constant stirring of the electrolyte, by which fresh quantities of metal ions are brought to the surface of the cathode for discharge and deposition.

It will probably be found possible to apply this method with success to most, if not all, separations and determinations.

Vessels for Electrolysis.—For the special purposes of electrolysis, in addition to the electrodes and dishes described, a large number of other forms have been suggested. These are all based more or less upon the same principle. The elbow apparatus, also originated by v. Klobukow, deserves mention. In this the gases set free at the electrodes can be separately collected and therefore quantitatively determined. The apparatus is readily understood from Fig. 80. The corks, which are paraffined, carry thick platinum wires to which the round flat plates which serve as electrodes are welded at angles of 45°. The form of the electrodes is, of course, not confined to any particular one; v. Klobukow also suggests round fluted platinum foils, wire spirals, or pointed electrodes.

In case the anode and cathode liquids are to be kept separate by a porous membrane, v. Klobukow proposes the arrangement shown in Fig. 81. The two separate arms have close-fitting ground faces, which are cemented into a brass mounting. A tight joint is obtained by a hinge and screw.

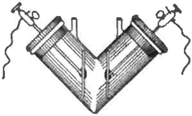


FIG. 80.

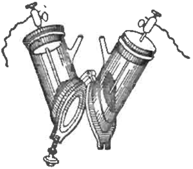


FIG. 81.

An electrolytic apparatus, depending upon another principle and serving other purposes, which nevertheless might be useful for quantitative work, is described by Hofer.* Fig. 82 shows two electrode chambers of glass provided with inlet and outlet tubes for the electrolyte, which is conducted in a continuous stream through the apparatus. There is also an escape tube for the gases generated. The two halves, between which parchment paper or other porous diaphragm is interposed, are fastened together by a firmly cemented connection provided with a screw. The electrodes have the form of spirals of platinum wire 0.8 mm in thickness, or of small platinum plates attached to wires. The connecting

---

* Ber. deutsch. chem. Ges., 27, 461 (1894).

wires pass through the gas-outlet tubes, and in case the gases are to be collected, they are carried on through T tubes placed at the top and made tight with rubber stoppers.

The liquid to be electrolysed is contained in a dropping-funnel, the tube of which is connected by rubber tubing to the lower inlet tube of one section of the apparatus. The liquid is thus continually brought to the particular electrode and is made to circulate through the cell from the bottom to the top. It flows out through the outlet tube, thence through a piece of rubber tubing provided with a screw pinch-cock for regulating the flow, and into a vessel placed at a lower level.

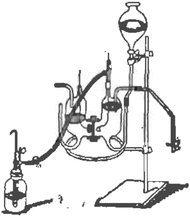


FIG. 82.

This piece of apparatus, which has hitherto been used only for the study of organic decompositions, might perhaps be suitable for the quantitative determination of gases.

CHAPTER XVII.

THE ANALYTICAL PROCESS.

THE complete process involved in the quantitative electrolytic determination of an element may be divided into a series of separate operations, as follows:

1. *Preparation of the electrodes.* These should, of course, be scrupulously clean. For scouring and polishing them sea-sand is very commonly used. This should be of good quality and free from sharp-cornered grains, or otherwise the surface of the dishes and cylinders will become scratched and worthless for many determinations.* For the removal of grease, traces of which on the cathode are extremely objectionable, the electrodes may be heated to redness, or cleaned by immersing them in a solution of chromic acid in concentrated sulphuric acid—the so-called "oxidising-mixture"—prepared by adding powdered potassium bichromate to ordinary oil of vitriol. After washing with distilled water and thoroughly drying by heating, the cathodes are allowed to stand in a desiccator for a short time before weighing. The surfaces on which the metals are to be deposited must never be touched with the fingers.

---

* The translator has observed that platinum cathodes can be very satisfactorily cleaned with a commercial product known as "Bon-Ami," which is ordinarily sold for cleaning glassware. Deeper stains can be removed successfully with "Sapolio," the surface being afterwards polished with the material first mentioned. These substances are applied with a soft cloth or small sponge, the platinum surface being rubbed gently in order to avoid the useless removal of metal.

2. *Preparation of the solution.* This is conducted according to the specific directions given for the determination to be made, and to obtain satisfactory results these directions should always be followed as closely as possible. If a dish electrode is used, the mixture of the various salts is best conducted in a beaker, and when all are in solution the liquid is transferred to the dish, where it is finally diluted to the proper volume. If the electrolysis is to be conducted at an elevated temperature, the solution should be warmed to the proper point before starting the current.

3. *Attachment of electrodes to circuit.* This is carried out in a manner dependent upon the form of electrode employed and the kind of standard used. The anode and cathode should be so adjusted that the current-density at the electrode on which the precipitation is to take place will be as uniform as possible. If the anode shown in Fig. 61 is used, it should extend to the bottom of the vessel in which the electrolysis is conducted. In general the conditions in the circuit should be such that sufficient resistance is present to prevent an abnormally high current-strength or difference of potential when the electrolysis is started, since this would lead to unsatisfactory results in many separations. It is best, therefore, to have sufficient resistance in the connected rheostat so that when the circuit with the source of current is closed, a current no greater than the maximum required for the given electrolysis will pass through the circuit.

It is also important that all metallic contacts in the circuit should be clean and rigid, since otherwise the current may become weakened or interrupted. This applies to the battery connections, to the connections between the wires and the various instruments in the circuit, and to the connections between the electrodes and the supporting standards.

4. *The electrolysis.* The circuit with the source of

current having been completed, the resistance is adjusted so that the current-strength and difference of potential between the electrodes correspond with those given in the directions. Since the relative values of these two factors are dependent on the resistance of the cell—which in turn depends upon the actual conductivity of the solution, the size and shape of the electrodes, and the distance by which they are separated—it will frequently be found that the current cannot be so regulated that the values of both of these factors will correspond with those described by some other experimenter. In such a case it is in general best to bring the potential to the desired value and allow the current-strength to adjust itself to this condition. This is especially true in the case of the electrolytic separation of a metal from others contained in the same solution, where the potential-difference is usually the factor of chief importance.

A very convenient method for determining the completion of a precipitation consists in placing a small strip of bright platinum foil in contact with the cathode. If after some time no deposit is formed on it, it is safe to assume that the electrolysis is completed. If a deposit is formed it can be quickly removed by placing the foil in contact with the anode for a few moments. This method is of course unsuited for metals which when deposited closely resemble platinum.

In order, during electrolysis, to prevent the loss of a portion of the solution in the form of small drops thrown upward by the escape of gas bubbles, the electrolytic vessel should be covered. When a dish electrode is used the cover can consist of a watch-glass cut into two equal halves by the use of a diamond, or of a watch-glass perforated by a single small opening. The hole in the watch-glass can be made with the point of a file moistened with a solution of camphor in turpentine. The cover also greatly reduces the evaporation of water from warm electrolytes.

5. *The removal of the solution, washing and drying the electrode.* Many determinations require the removal of the solution from the cathode without interrupting the current, since otherwise the deposited metal would again pass into the solution. When dish electrodes are used they can be placed on triangles of platinum wire on the bottom of good-sized beakers, and when the electrolysis is completed the solutions can be displaced by a stream of fresh water; or the solution in the dish, supported on an ordinary stand, can be siphoned off, the deposited metal being washed during the process by a stream of water from a wash-bottle. For most purposes, however, the results obtained are sufficiently accurate when the current is stopped and the contents of the dish are immediately poured out, the precipitated metal being quickly washed with pure water. When the cylindrical cathodes are used, the electrode, still attached to the stand, can be lifted quickly from the solution and plunged into a vessel of clean water. After a thorough washing with water, the electrodes are washed three times with about 5 cc of pure absolute alcohol, dried for about five minutes in an air-bath at about 70° to 90°, allowed to cool thoroughly in a desiccator, and weighed.

CHAPTER XVIII.

ARRANGEMENTS FOR ANALYSIS.

THE question as to the most suitable equipment for electroanalytical experiments does not permit of a general answer, owing to the numerous details, such as the location and construction of the building, the arrangement of rooms, etc., upon which it depends. Even if the use of accumulators in combination with a dynamo is decided upon as the most practical source of current, the details of the equipment *can be described only from a certain point of view*, according to the specific requirements. The laboratory at Aachen has followed the development of quantitative electrolysis almost from the beginning, and starting with a small and simple equipment has gradually acquired a most elaborate one.

Three equipments will therefore be described: first, a simple and practical arrangement for use where the requirements are limited; second, the former electrolytic equipment of the Aachen Institute of Technology; and third, the present equipment of the same institution.

Krüger* has published a general review on the equipment of electrolytic laboratories which contains many valuable suggestions. The arrangements of certain other laboratories have also been described by Nissenson.† The choice of special apparatus depends so much on individual

---

* Elektrochem. Zeit., 2, 73, 104, 129, 174, 207, 251; *ibid.*, 7, 76, 129.

† Zeit. Elektrochem., 6, 221.

taste, that exact directions are practically impossible. Indeed the practical advantages of the set of instruments recommended by Krüger have not been confirmed by their use in the Aachen laboratory.

Simple Arrangement for Electrolysis.

The equipment needed for carrying out a single electrolytic experiment, when a constant source of current is at hand, is an extremely simple one. A standard, a pair of electrodes and instruments for measuring the current-strength and potential-difference are all that are required. The manner in which the various pieces of apparatus are connected is shown in Fig. 83. The amperemeter (*A*) is connected in series in the circuit with the cell, and the voltmeter circuit is attached directly to points on the standard in metallic contact with the cathode and anode. The voltmeter is represented by *V*, the variable resistance for controlling the current by *R*, and the source of current by *S*.

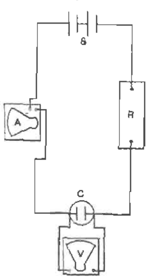


FIG. 83.

Since, however, it is often desirable to conduct several experiments simultaneously, an arrangement for accomplishing this will be described which has the advantage that it can be constructed by any one wishing to carry out electrolytic determinations.

The chief requirement is that it shall be possible at any time to measure the current-strength and potential of each separate cell, which can be accomplished, with the use of one amperemeter and one voltmeter, in the following manner:

Two blocks carrying six binding-posts each are constructed as shown in Fig. 84. These consist of a wooden block supporting a copper plate through which are drilled six holes having a diameter sufficient to permit the screws, but not the bases, of the binding-posts to pass. The binding-posts are screwed through these holes into the wooden block beneath until a close metallic contact between the posts and the copper plate is obtained. One of these blocks (Fig. 85, *A*) is connected by one of its posts with the negative, the other (*B*) with the positive pole of the source of current. Another wooden block,

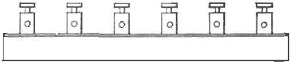


FIG. 84.

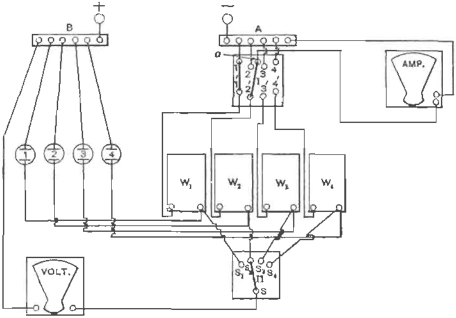


FIG. 85.

1, is placed in front of the block connected with the negative pole. This block has a number of holes bored in its upper side, and into these holes are set inverted thimbles filled with mercury. The arrangement of these holes is shown in Fig. 86, and those (*1*, *2*, *3*, and *4*) along one edge are connected with corresponding binding-posts on the block A by stout copper wires which dip into the mercury. The mercury-cups *1′*, *2′*, *3′*, *4′* are connected by wires to one terminal of the rheostats w_1, w_2, w_3, w_4, respectively, and the other terminals of the rheostats are connected by wires with posts on the block B. The cells in which the various electrolytic determinations are carried out are inserted in the circuits between the rheostats and the positive pole (C_1, C_2, C_3, C_4). The circuit through cell C_1 is completed by laying a bridge made of copper wire between the mercury-cups a and *1′*, and the current then flows from B, through C_1, through w_1, from *1′* to a, and through the amperemeter to A. The current-strength can be read from the amperemeter and regulated by the variable resistance w_1. In order to proceed with the second experiment (C_2) the cell is connected as shown, between B and W_2. A second copper-wire bridge * is now laid between mercury-cups *1* and *1′* and the first bridge between a and *1′* is removed and laid between a

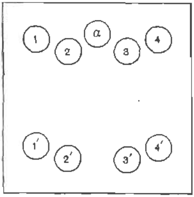


FIG. 86.

---

* When the internal resistance of the amperemeter is appreciable, which is not the case with the standard Weston instruments, the bridge used to connect the mercury-cups *1* and *1′*, *2* and *2′*, *3* and *3′*, etc., must have a resistance exactly equal to that of the amperemeter. Otherwise the current as measured with the amperemeter will be less than that which passes through the cell when the amperemeter is removed from that circuit.

and 2′. The current through C_2 now passes through the amperemeter and can be observed and regulated. In an exactly similar manner the cells C_3 and C_4 are connected with the main circuit. In order at any time to observe the current passing through any given cell the corresponding mercury-cup on the lower edge of the board *I* is connected with *a* and the bridge between the two opposite cups on *I* is removed. In this way it is possible to measure each of the separate currents without causing any interruption. All the connections in the main circuits, including the connections of the amperemeter, should be made by stout copper wires.

For measuring the differences of potential between the separate electrodes, another wooden block, Fig. 87, is prepared. This block contains four mercury-cups (S_1, S_2, S_3, S_4) arranged on the arc of a circle along one edge and one cup on the edge opposite. The cups S_1, S_2, S_3, S_4 are connected with the terminals of the rheostats w_1, w_2, w_3, w_4, as shown in Fig. 85, and the cup *S* is connected with the negative binding-post of the voltmeter, the positive post of this instrument being connected directly with one of the binding-posts on the block *B*. By placing a copper-wire bridge between the cups S–S_1, S–S_2, S–S_3, or S–S_4, the difference of potential between the electrodes in the cells C_1, C_2, C_3, or C_4, respectively, can be read with the voltmeter. The simultaneous measurement of the potential of two or more cells is of course out of the question. By increasing the number of binding-posts on the blocks *A* and *B*, and the number of mercury-cups in the blocks *I* and *II*, the number of sep-

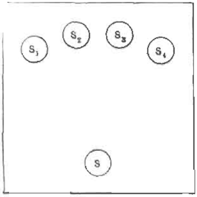


FIG. 87.

arate determinations which can be conducted at one and the same time can be increased to any reasonable number.

This simple appliance, the principles of which recur in the following pages, can be prepared by any one from the simplest materials, making it very suitable for the use of students who by working with it become acquainted with the methods of making connections and the manipulation of more elaborate apparatus.

Former Equipment of the Electrochemical Institute at Aachen.

This system was based on the employment of a dynamo which, running at a speed of 1000 revolutions per minute, furnished a current at a potential of 10 volts. The current from the dynamo was used either directly or for charging accumulators.

When the current from the dynamo was used directly for electrolytic purposes, the instrument described on p. 106 was employed for reducing and regulating the current.

In general the current from the dynamo was used to charge four accumulators, connected in series, and the current from these having a potential of 8 volts was carried by suitable conductors to the work-bench used for electrolytic experiments. The connections of the electrolytic cells to the positive conductor were effected by means of the six binding-posts marked 1, 2, 3, 4, 5, 6 (*Plate I, Fig.* 1). For connecting the electrolytic cells with the negative conductor, six wooden blocks carrying binding-posts and mercury-cups were employed.

The arrangement of the posts and cups on these blocks is diagrammatically shown in Figs. 88 and 89 (one-fourth actual size). The four mercury-cups, *1*, *2*, *3*, *4*, are in metallic contact with the four binding-posts marked K in the diagram, cups *5* and *7* are both connected with the negative conductor, and cup *6* is connected with one of the wires leading to the amperemeter. (The position of these six blocks with respect to the circuit is shown in Plate I, Fig. 1, where they are denoted by a – sign, and in Plate I, Fig. 2, where they are denoted by the letter *N*.)

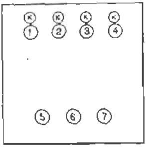


FIG. 88.

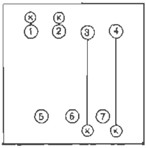


FIG. 89.

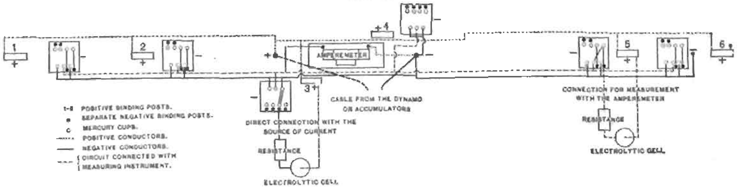
In order to carry out an electrolysis at a given current-strength a wire was carried from one of the positive binding-posts and attached to the anode of the cell, and the cathode of the cell was connected by wires to one of the binding-posts on the block connected with the negative conductor. A rheostat was inserted in the circuit between the cathode and the negative binding-post, and by means of this a moderately high resistance of, say, 60 ohms was introduced into the cell circuit. The object of introducing this high resistance at the start was to prevent the current-strength from attaining an undesirably high value when the circuit was completed. To complete the circuit it was only necessary to lay a copper bridge between the mercury-cups *4* and *6*. The current would then pass from the positive conductor, through the cell, through the rheostat, to the mercury-cup on the block, and through the amperemeter to the negative conductor. (These connections are shown in Plate I, Fig. 1, position 5.)

With a resistance of 60 ohms in the circuit the ampere-

PLATE I.

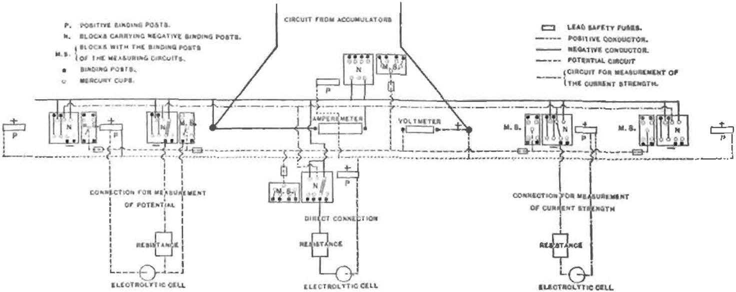
PLAN SHOWING ARRANGEMENT FOR MEASURING THE CURRENT-STRENGTH OF EACH SEPARATE ELECTROLYSIS WITH THE USE OF A SINGLE AMPEREMETER.

FIG. 1.



PLAN OF WORK-BENCH IN ELECTROCHEMICAL LABORATORY OF THE ROYAL INSTITUTE OF TECHNOLOGY AT AACHEN.

FIG. 2.



(*To face page* 138.)

meter would show only a very small current, which was increased to the desired value by reducing the resistance in the rheostat. When this was done, a bridge was inserted between the mercury-cups *4* and *7* and that between *4* and *6* was removed. By the latter operation the amperemeter was disconnected from the circuit (position 3 in the diagram). In order to observe the current-strength at any time during the electrolysis, a bridge was laid between cups *4* and *6* and the one between *4* and *7* was removed. It was, therefore, possible to measure the current-strength at any time without interrupting the current through the cell.

The amperemeter was especially constructed for the laboratory by the firm of Hartmann & Braun (Bockenheim-Frankfurt a. M.). It had two scales and two pointers (one on each side), and the scales had a radius of 16 cm. This instrument permitted the measurement of currents up to 2 amperes in decimals of 0.05 ampere, and was provided with a shunt-resistance which could be connected in parallel with it, whereby the range of measurement could be increased tenfold.

The resistance of the amperemeter was 0.32 ohm, and in order that the current-strength should remain perfectly constant when it was removed from the circuit, the bridge (Fig. 90) which was substituted for it between the mercury-cups *4* and *7* was not of simple construction, but contained

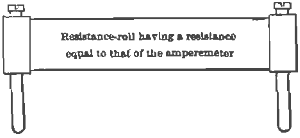


FIG. 90.

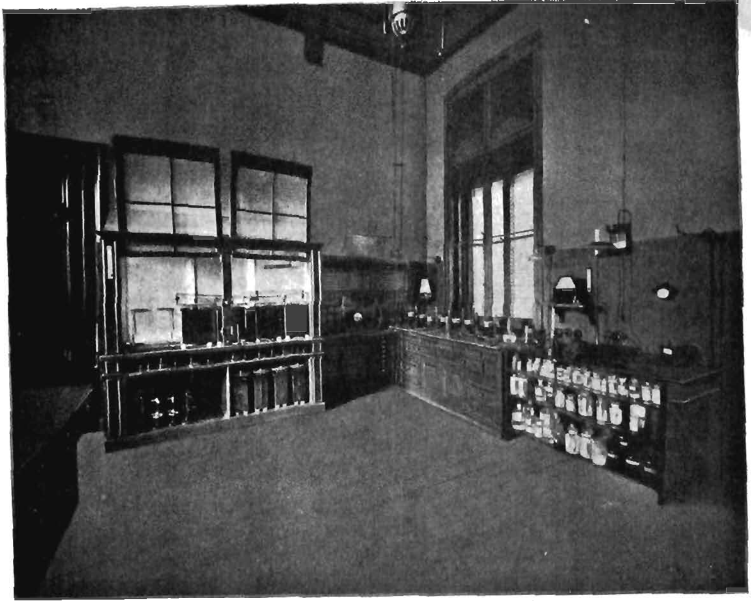
a roll having a resistance exactly equal to that of the amperemeter. Since the resistance of the bridge and amperemeter was equal, a current corresponding to the one measured flowed through the cell when the amperemeter was removed from the circuit.

For measuring the difference of potential between the electrodes of a cell a second series of blocks connected with a voltmeter was employed (M. S., Plate I, Fig. 2). These blocks contained five mercury-cups, one at the center and four others at equal distances from this. The one in the center was connected with the voltmeter circuit, the other four were each in contact with a separate binding-post. For measuring the potential a wire was connected with one of these binding-posts and the other end of the wire was attached to the stand supporting the cathode. By placing a copper bridge between the mercury-cup in contact with the given post and the cup in the center of the block the cathode was brought into electrical connection with the voltmeter, and since the voltmeter was in turn connected with the positive conductor, the potential which it registered was that existing between the electrodes in the cell. This connection is shown in Plate I, Fig. 2, to the left of the diagram.

As shown in Plate I. twenty-four separate electrolytic experiments could be conducted simultaneously.

A view of the author's private laboratory, showing the former equipment, is given in Plate II. In this laboratory special circuits were provided for supplying the direct current from the dynamo, as well as that from eight accumulators. The wire-gauze resistance described on p. 106 was used to reduce the current from the dynamo when this was employed directly or for charging the accumulators. The circuit from the dynamo and the circuit from the accumulators passed

PLATE II.



FORMER EQUIPMENT OF PRIVATE LABORATORY. See page 140.

from the private laboratory to the work-benches in the laboratory of instruction. One amperemeter showed the current which was being used in the laboratory of instruction, and another served to measure the current used in charging the accumulators.

Present Equipment of the Electrochemical Institute at Aachen.

In the former equipment of the Electrochemical Institute at Aachen the electric current was supplied by a generating plant on the premises. In designing the present equipment it was considered desirable to be as independent of such a plant as possible, since small isolated plants are uneconomical and are not always ready for use.

To avoid the maintenance of a private electric generating plant it was decided, therefore, to take the current from the cables of the municipal electric system of the city of Aachen.

The Aachen Electrical Works supply the direct current by a three-wire circuit at a potential of about 108 volts between the middle wire and an outside wire, and a potential of about 216 volts between the two outside wires. It is therefore necessary, for the purposes of electrolysis, to reduce this high potential in some suitable manner to the low potential required for experiment. This is accomplished by the use of a rotary transformer, which is efficient, practically noiseless, convenient, and compact.

It is also desirable to have the high potential current available for other purposes.

Before proceeding to the description of the plant installed by the firm of Schuckert & Co., proprietors of the Aachen Electrical Works, the nature of the different experiments carried out in the laboratory will be mentioned briefly in order that what follows may be more readily understood.

1. *Experiments with Low Potentials.*—The experiments with low potentials are confined chiefly to the electrolytic analysis of solutions of metallic salts. Experiments on the electrolytic precipitation of metals on a large scale are also carried out as an introduction to the study of electrometallurgy.

2. *Experiments with High Potentials.*—The high-potential current is employed chiefly for experiments with the electric furnace, for the decomposition of fused electrolytes, and for the decomposition of gases and other bodies having a high resistance. For producing the Davy arc a potential of about 45 volts is required.

In addition to the above, the current is also used in an electric projection lantern and for a number of arc and incandescent lights.

The distribution of the currents to the various rooms, and the control of the transformer, is effected from a central switchboard located in the author's private laboratory. By this arrangement the switchboard is placed under competent supervision and a general oversight of the entire plant is possible.

From the central switchboard circuits are carried to the following places:

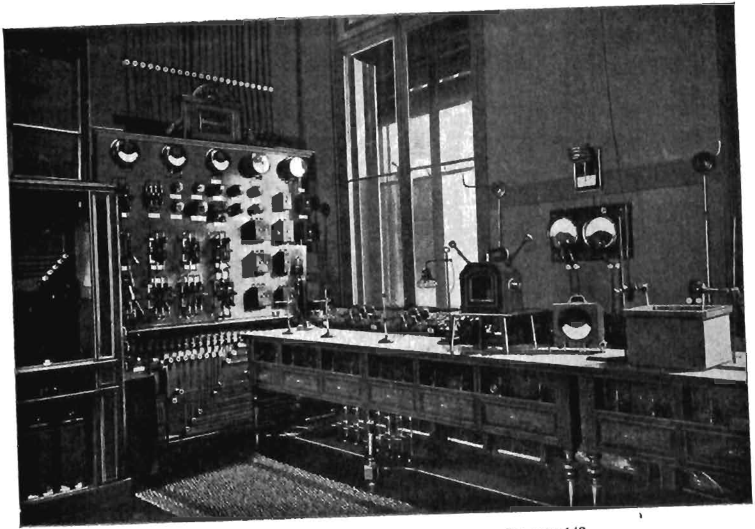
1. Private laboratory.
2. Large lecture-room.
3. Laboratory for electrochemical analysis.
4. Laboratory for experiments on a large scale with high and low potentials.

The circuits running to the different rooms are distinguished, according to the intended purposes of the current which they carry, as

a. Lighting circuits,
b. High-potential circuits,
c. Low-potential circuits,

and are entirely independent of one another.

PLATE III.



PRESENT EQUIPMENT OF PRIVATE LABORATORY. See page 143.

(To face page 142.)

The lighting circuits run to the private laboratory and to the large lecture-room.

The high-potential circuits are carried to the private laboratory, the large lecture-room, and to the laboratory for experiments with high and low potentials.

In addition to these circuits there is one for charging the accumulators and another for running the transformer.

The switches, rheostats, safety-fuses, and measuring instruments for the different circuits are placed on the central switchboard.

1. Private Laboratory.

The private laboratory contains the central switchboard and the battery of accumulators. A photographic view of the interior is given in Plate III. In the center can be seen the switchboard upon which the various instruments are mounted; to the left is the glass hood containing, in the bottom, the battery of accumulators. Along the wall on the right are two work-benches, one for electroanalytical work with low potentials and small currents, the other for experiments with high potentials and large currents.

The arrangement for electroanalysis is the following: At the back of the bench by the window is a slanting wooden frame, on the face of which are fastened the switches and binding-posts, while the connecting wires are attached to the back. There are altogether five work-places on this bench, at each of which two analyses can be performed simultaneously, so that in all ten experiments can be carried on at the same time.

The installation of these work-places, as well as those of the second work-bench, is in accordance with the scheme for current distribution shown in Plate V.

Each work-place is connected in parallel to the positive and negative conductors, which run through the work-bench.

The current for every analysis can be independently varied by means of the regulating resistance at the work-place. A *single amperemeter, which can be thrown into the circuit* of any analysis by means of a switch placed at each work-place, serves for measuring the current-strength. When the amperemeter is cut out, its place is taken by a resistance, in order that the current-strength will not be altered (see p. 135).

The measurement of the potential is carried out in a similar manner by a single voltmeter, which can at will be switched into the circuit of any analysis in progress.

A lead safety fuse is inserted in the circuit of each of the ten branches to guard against the possibility of too great current-strength.

The connections of the electrolytic apparatus to the small switchboards of the work-bench are made with very flexible rubber-insulated copper conductors, the ends of which are provided with small copper links to allow them to be more conveniently attached to the apparatus.

For conducting experiments with large currents of high or low potential, two cases furnished with locks are affixed to the second work-bench. That for low potential contains two plates which carry a number of binding-posts, thus allowing several different pieces of apparatus to be connected at the same time.

The case for high potential contains three plates, connected with the two outside conductors and the middle conductor of the three-wire system so that a maximum potential of about 216 volts is obtainable. These plates also carry several binding-posts, which permit the use of several pieces of apparatus at one time.

The two accumulator batteries contain four cells each.

One battery with the cells connected in series requires a charging current of 90 amperes; the other, similarly connected, requires 25 amperes.

The batteries are charged from the transformer.

The small battery furnishes current to the private laboratory only, while the large one supplies the rest of the plant. Each of the batteries is provided with a cell switchboard for four cells, so that by cutting out separate cells the potential of the current may be reduced and the use of high external resistances avoided.

To prevent the direction of the current becoming reversed during the process of charging, each battery circuit is provided with an automatic cut-out.

The potential of the separate cells is measured by a special voltmeter, having contact plugs which allow the potential of each cell to be independently measured at the cell switchboard.

For the measurement of the battery potential and the strength of the charging and discharging currents a special voltmeter and amperemeter are provided. Further, that the operation of charging and discharging may be more closely observed, indicators for showing the direction of the current are attached to the several circuits.

2. Large Lecture-room.

The installation of the large lecture-room is especially intended for the performance of lecture experiments which comprise the demonstration of electrolysis, the decomposition of gases and liquids by the Davy arc, and fusion experiments.

Besides this, provision is made for running an electric projecting lantern, as well as a number of incandescent and arc lamps.

3. Laboratory for the Electroanalysis of Metals.

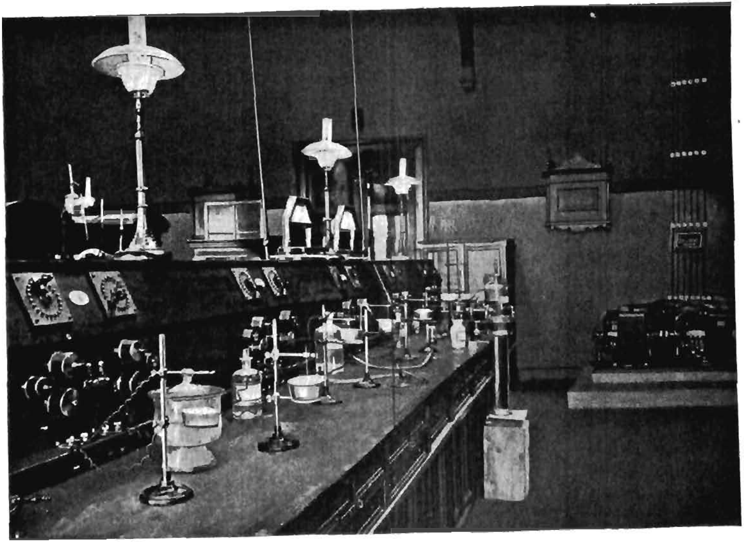
In this room the transformer is placed. It also contains a large table having ten work-places for carrying out electroanalytical experiments with low potentials. (Cf. Plate IV.)

The transformer will next be described. This consists of a combination of two direct-current dynamos with their shafts coupled directly together. One of the dynamos, arranged as a motor, is driven by the current from the two outside wires of the three-wire system by a potential, therefore, of about 216 volts. The circuit is run to the transformer from the central switchboard. The dynamo, which is coupled to the motor, and furnishes the low-potential current, is so arranged that the potential at the poles may be varied from about 4.5 to 9 volts, the corresponding current-strengths being respectively 360 and 180 amperes. The conductors carrying the low-potential current from the dynamo run to the central switchboard. The potential of 9 volts is the one generally used, the lower potential of 4.5 volts being employed for larger electrolytic experiments, such as the preparation of pure metals.

The alteration in the potential of the current is brought about by connecting the two halves of the double armature, with which the dynamo is provided, either in series or in parallel. This is done by merely changing the corresponding connections on the frame of the transformer.

Further, concerning the construction of the transformer, it should be mentioned that the machine is very solidly built and the magnets protected within the frame, so that a mechanical injury to the field-coils is out of the question. The lubrication of all parts is carried out by means of ring-lubrication, which has proved very satisfactory. Such delays as often occur when other mechanical contrivances are em-

PLATE IV.



WORK-BENCH IN LABORATORY FOR ELECTROANALYSIS. See page 147.

(*To face page* 148.)

ployed are here impossible. Owing to its construction, the transformer, which for protection is enclosed in a special covering, can run for hours without particular attention.

The action of the transformer, in spite of its speed of about 1300 revolutions per minute, is so quiet and free from any jarring or shaking, that its running can scarcely be detected even in the immediate neighborhood.

It should be stated that there is a switchboard near the transformer, by which direct currents of low potential can be taken off in this room without making use of the central switchboard. Such currents are required when experiments with high-current strength and low potential are performed; and in such cases short cables are run from this switchboard to the nearest work-bench, where the apparatus is set up.

The arrangement of the large work-bench, a photograph of which is given in Plate IV, corresponds in general to that of the table for conducting analyses in the private laboratory.

Here, on either side of the bench, there are five work-places, at each of which two analyses can be performed simultaneously, so that in all twenty experiments can be carried on at the same time.*

Plate V shows the method employed for measuring the current-strength and potential of an analysis. The amperemeter and voltmeter are above. The currents are regulated by means of the rheostats (I, II, III, and IV). These consist of slate blocks into which are fixed metal knobs attached to separate resistance spirals. By turning the lever in the direction indicated by the arrow, the resistance is cut out and the current-strength correspondingly increased.

The switches for the amperemeter $A_{(\mathrm{I, II, III, IV})}$, for the

---

* Two other work-benches have been recently added, so that there are *now twenty work-places for electroanalysis.*

electrolyses $E_{(\mathrm{I},\,\mathrm{II},\,\mathrm{III},\,\mathrm{IV})}$, and the safety-fuses $B_{(\mathrm{I},\,\mathrm{II},\,\mathrm{III},\,\mathrm{IV})}$ are covered by bronzed metal cases.

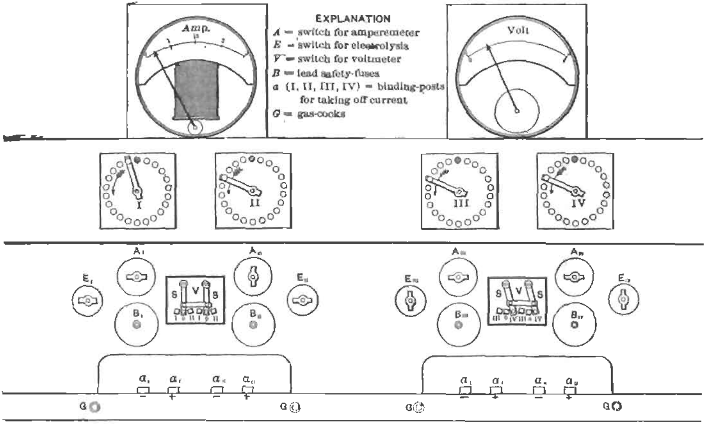
$a_{(\mathrm{I},\,\mathrm{II},\,\mathrm{III},\,\mathrm{IV})}$ are the binding-posts to which the electrolyses are connected, V is a double-pole switch used in measuring the potential. In the position *o* the voltmeter is cut out; at I, II, III, IV the corresponding electrolysis is connected with the voltmeter. As already stated, there is only one amperemeter and one voltmeter to every table with 10–20 dishes, and therefore only one electrolysis can be measured at a time. The four figures in Plate V are designed to make the explanations clearer.

In position I, where the keys A_{I} and E_{I} are horizontal, the circuit is open. In II, A_{II} is vertical; the amperemeter is connected. If the key E is now turned to the vertical position a current will flow through the circuit and the lever of the rheostat at II may be turned in the direction of the arrow until the amperemeter registers the desired current-strength. A is then brought into the position A_{III}. The current now flows no longer through the amperemeter, but through a roll of wire, the resistance of which is equal to that of the amperemeter. The current-strength remains the same as that previously shown by the amperemeter.

V serves for measuring the potential at the electrodes of the electrolytic vessel, as shown at V_{IV}. In this operation the position of A and E is the same as in III. The two metal strips (SS) are pushed to the right or left (in the figure to the right, IV), and the voltmeter then shows the potential existing at that time between the electrodes of the corresponding electrolysis. The measuring instruments are switched out of the circuit immediately after use.

PLATE V.

PLAN OF SEPARATE INSTRUMENTS ON LABORATORY WORK-BENCH.



EXPLANATION

A = switch for amperemeter
E = switch for electrolysis
V = switch for voltmeter
B = lead safety-fuses
a (I, II, III, IV) = binding-posts for taking off current
G = gas-cocks

(*To face page* 148.)

4. LABORATORY FOR PERFORMING EXPERIMENTS ON A LARGE SCALE WITH LOW AND HIGH POTENTIALS.

As already mentioned, special cases which receive their currents from separate conductors running from the central switchboard are provided for high and low potential.

Within the case for high potential there are three separate plates corresponding to the three feed-wires of the three-wire system, providing currents at potentials of 108 and 216 volts accordingly.

The case for low potential contains two connections, with possible potential at the poles up to 9 volts.

From both of the cases separate branch circuits run to the four work-benches, where they end in terminal boxes provided with locks. By this arrangement each table is provided with both high and low potential.

Each of the branches running to the tables is supplied with a safety-fuse and a switch; each table is therefore independent of the others.

In conducting experiments a set of portable measuring instruments and portable resistances for regulating the current is used.

Large and cumbersome resistances are required to produce appreciable variations in the potential. A simple appliance in use in the Aachen laboratory overcomes this difficulty in the case of experiments of short duration, where economical use of the current is not an essential feature. This scheme, originated by Löb and Kaufmann,* permits the convenient splitting up of the current of 216 or 108 volts into separate independent currents having the required lower potential.

---

* Zeit. f. Elektrochem., 2, 345 (1895–96); *ibid.*, 2, 664.

A number of lead plates are hung parallel to one another in a large porcelain trough filled with sulphuric acid (Fig. 91), in such a manner that they cut all the lines of the current. They must therefore almost touch the sides and bottom of the trough. When the current passes, these lead plates act as intermediate conductors, the sum of their separate potentials being equal to the potential of the main current.

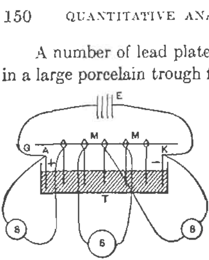


FIG. 91.

The immersed lead plates can be slid along the length of the trough on the glass rod from which they are hung. By moving the plates toward or away from the electrodes the potential is varied, and any desired potential may be obtained by making a connection between a terminal electrode and one of the plates. The arrangement is given in Fig. 91. *E* denotes the source of current; *T*, the trough filled with sulphuric acid; *A* and *K*, anode and cathode; *M*, the five plates. The wires to *S* show the removal of three separate currents of different potentials. A large number of such connections are possible. On account of the gases given off, the trough should be kept under a hood.

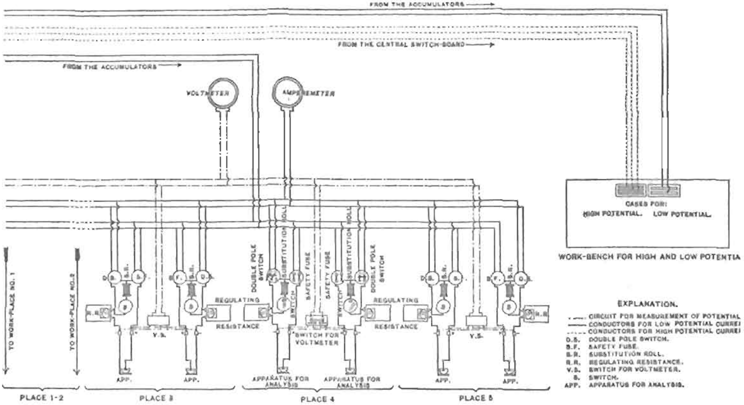
In addition to the details of the equipment which have been described, some general facts in connection with the management of the entire plant should be stated.

Since the apparatus is much used, and is not always placed in experienced hands, it was considered desirable to have all parts solidly constructed and intended for continuous use.

The switches and regulating instruments, as well as the branch-plates, are all mounted on bases of fire-proof material.

PLATE VI.

PLAN SHOWING CURRENT DISTRIBUTION ON WORK-BENCH, ELECTROCHEMICAL LABORATORY OF ROYAL TECHNOLOGICAL INSTITUTE, AACHEN.



(*To face page* 150.)

All connections are made with the best rubber-covered wire, fastened to large porcelain brackets, so that most perfect insulation of the conductors is assured.

To secure against improper use, all switch-cases are provided with safety-locks, so that currents can nowhere be taken off without the permission of the director of the laboratory.

PART SECOND.

SPECIAL.

SECTION I.

QUANTITATIVE DETERMINATION OF METALS.

IRON.

LITERATURE:

Wrightson, Zeit. f. analyt. Chem., **15**, 305 (1876).
Parodi and Mascazzini, Zeit. f. analyt. Chem., **18**, 588 (1879).
Luckow, Zeit. f. analyt. Chem., **19**, 18 (1879).
Classen and v. Reiss, Ber. deutsch. chem. Ges., **14**, 1622 (1881).
Moore, Chem. News, **53**, 209 (1886).
Smith, Amer. Chem. Jour., **10**, 330 (1888).
Brand, Zeit. f. analyt. Chem., **28**, 581 (1889).
Drown and Meckenna, J. of Analyt. and Applied Chem., **5**, 627 (1891).
Smith and Muhr, *ibid.*, **5**, 488 (1891).
Rüdorff, Zeit. f. angew. Chem., **15**, 198 (1892).
Vortmann, Monatshefte f. Chem., **14**, 542 (1893).
Classen, Zeit. f. Elektrochemie, **1**, 229 (1894).
Heidenreich, Ber. deutsch. chem. Ges., **29**, 1585 (1896).
Kollock, Journ. Am. Chem. Soc., **21**, 911 (1899).
Avery and Dales, Ber. deutsch. chem. Ges., **32**, 64 and 2233 (1899).
Verwer and Goll, *ibid.*, **32**, 806 (1899).
Verwer, Chemiker-Zeitung, **25**, No. 75 (1901); Jahrbuch Elektrochem., 6, 246.

If a solution of a ferrous salt is treated with potassium or ammonium oxalate, there is produced an intensely yellowish-red precipitate of ferrous oxalate, soluble in an excess of the reagent to a yellowish-red solution of the double salt.

The stated oxalates do not precipitate ferric salts; but, if added in sufficient quantity, a solution of the double ferric salt is produced having a more or less green color. If this solution is submitted to electrolysis, there is first produced the double ferrous salt, which is then decomposed with separation of metallic iron; the green liquid therefore becomes first red and then colorless. Because of this action, the determination of iron is more rapidly performed in solutions of ferrous than of ferric salts. Potassium iron oxalate is not adapted to electrolysis, because the potassium carbonate which is produced precipitates iron carbonate, and thus complete reduction is prevented. The electrolysis of the ammonium double salt, when ammonium oxalate is in sufficient excess, proceeds smoothly, with no separation of an iron compound. If the solution contains free hydrochloric acid, it is best to remove it by evaporation on the water-bath.

Free sulphuric acid may be neutralised with ammonia, since the ammonium sulphate thus produced only increases the conductivity of the solution. Nitrates are converted by evaporation with sulphuric acid into sulphates, or by repeated evaporation with hydrochloric acid into chlorides. The presence of phosphoric acid is not objectionable.

The determination is conducted as follows: Assuming that 1 g of iron may be present in the solution to be electrolysed, from 6 to 8 g of ammonium oxalate are dissolved by heating in as little water as possible, and with constant stirring the iron solution is gradually added.* The solution is then diluted with water to 100–150 cc and the positive

---

* It is not desirable to add ammonium oxalate solution to a ferrous solution, as difficultly soluble ferrous oxalate separates, and can be dissolved to the double salt only by long heating. With a ferric solution this precaution is unnecessary.

electrode is immersed in the liquid until it is just covered by the solution. The electrolysis is conducted according to the special directions which are given below.

CONDITIONS FOR ANALYSIS.

Metal present as sulphate.
Substance added: 6 to 8 g ammonium oxalate.
Total volume of solution: 100 to 150 cc.
Temperature: that of room, or 40° to 65°.
Current-density at cathode:
  (Room temp.) $ND_{100}=1.0$ to 1.5 amp.;
  (40° to 65°) $ND_{100}=0.5$ to 1.0 amp.
Potential-difference between electrodes:
  (Cold solutions) 3.6 to 4.3 volts;
  (Warm solutions) 2.0 to 3.5 volts.

Time required: $2\frac{1}{4}$ to $6\frac{1}{4}$ hours, depending on the temperature. For the quality of the precipitated metal, polished or roughened dishes answer equally well.

The end of the reaction is determined by taking out a small portion of the colorless solution with a capillary tube, *acidifying strongly with hydrochloric acid*, and testing with potassium sulphocyanide. When the reaction is ended the positive electrode is removed from the solution, which is poured off, and the dish washed three times with *cold* water (about 5 cc each time), and three times with absolute alcohol, dried a few moments in the air-bath at a temperature of 70° to 90°, and weighed after cooling.

The separated iron has a steel-gray color and brilliant luster, is firmly attached to the dish, and can be preserved in the air without oxidation for a full day.

EXPERIMENT 1.

Used 2.1 – 2.5 g $FeSO_4(NH_4)_2SO_4.6H_2O$ (Fe = 14.29%), 6–8 g ammonium oxalate, 120 cc of liquid.

Current-density, Amperes.	Electrode Potential, Volts.	Temp.	Time.	Found.
1 –1.5	3.85–4.3	20–40°	2 hr. 15 m.	14.21 %
1 –1.05	3.6 –4.2	36°	3 " 50 "	14.21 "
1 –1.08	3.05–3.52	65°	2 " 30 "	14.28 "
0.5–0.55	2.0 –2.3	50–52°	3 " 30 "	14.24 "

EXPERIMENT 2.

Used 2.6–2.8 g ferric potassium oxalate ($Fe_2(C_2O_4)_3.3K_2C_2O_4.6H_2O$) (Fe = 11.40%), 6–7 g ammonium oxalate.

Current-density, Amperes.	Electrode Potential, Volts.	Temp.	Time.	Found.
1.5–1.7	3.55–4.25	35–40°	2 hr. 54 m.	11.39 %
1.0–1.1	3.9 –4.0	30–40°	3 " 15 "	11.35 "
0.5–0.8	2.4 –2.8	50°	6 " 15 "	11.25 "

Edgar F. Smith has recommended the precipitation of iron from a solution of ammonium citrate to which a few drops of citric acid have been added. The author's experiments in earlier years, on the separation of iron from other metals in citric and tartaric acid solution, demonstrated that in the presence of fixed organic acids the precipitated metal always contains carbon. Heidenreich has shown, by experiments conducted in the Aachen laboratory, that iron may be quantitatively determined from such solutions under certain conditions, namely: 0.2 g ferrous ammonium sulphate, 50 cc of a 10 per cent. solution of sodium citrate, 2 cc of a saturated solution of citric acid; entire volume of liquid, 120 cc; *temperature of room*; $ND_{100} = 0.75–0.9$ amp.; potential-difference, 5 volts; time, 4–6 hours. The iron, however, always contains carbon.

COBALT.

LITERATURE:

Luckow, Dingl. Polyt. Journ., **177**, 235 (1850).
Gibbs, Zeit. f. anal. Chem., **3**, 336 (1864); **11**, *10 (1872)*; **22**, *558 (1883)*.
Merrick, Amer. Chemist, **2**, 136 (1871).
Mansfeld. O. Berg. Hüttendirektion, Zeit. f. anal. Chem., **11**, 1 (1872).
Hampe, Zeit. f. anal. Chem., **13**, 186 (1874).
Herpin, Zeit. f. anal. Chem., **15**, 535 (1876).
Wrightson, Zeit. f. anal. Chem., **15**, 300, 303, 333 (1876).
Schweder, *ibid.*, **16**, 344 (1877).
Cheney and Richards, Amer. Journ. of Science, [3] **14**, 178 (1877)
Ohl, Zeit. f. anal. Chem., **18**, 523 (1879).
Fresenius and Bergmann, Zeit. f. anal. Chem., **19**, *329 (1880)*.
Luckow, Zeit. f. anal. Chem., **19**, 314 (1880).
Classen and v. Reiss, Ber. deutsch. chem. Ges., **14**, 1622, 2771 (1881).
Riché, Zeit. f. anal. Chem., **21**, *116 (1882)*.
Schucht, Zeit. f. anal. Chem., **21**, 493 (1882).
Moore, Chem. News, **52**, 209 (1885).
Kohn and Woodgate, Journ. Soc. Chem. Indust., 8, *256 (1889)*.
Brand, Zeit. f. anal. Chemie, **28**, 588 (1889).
Le Roy, Compt. rend., **112**, 722 (1891).
Rüdorff, Zeit. f. angew. Chemie, 1892, p. 6.
Smith and Muhr, Journ. Anal. Chem., **5**, 488 (1891); *ibid.*, **7**, 189 (1893).
Vortmann, Monatsh. f. Chem., **14**, 536 (1893).
Classen, Ber. deutsch. chem. Ges., **27**, *2061 (1894)*.
Oettel, Zeit. f. Elektrochemie, **1**, 192 (1894–95).
Winkler, Zeit. f. anorg. Chem., 8, 291 (1895).
Campbell and Andrews, Journ. Am. Chem. Soc., **17**, *125 (1895)*.
Fernberger and Smith, Journ. Am. Chem. Soc., **21**, 1001 (1899).
Foster, Zeit. f. Elektrochem., 6, 160 (1899–1900).

Cobalt may be very easily precipitated from a solution f cobalt ammonium oxalate containing an excess of ammo- ium oxalate (method of the author). The metal separates apidly at the negative electrode in a compact adherent oating, showing its characteristic metallic properties. The peration is performed as in the determination of iron. 4–5 ammonium oxalate are dissolved by heating in the solution, the volume of which should be about 25 cc; it is then diluted to 100–120 cc, warmed, and electrolysed at 60–70°.

CONDITIONS FOR ANALYSIS.

Metal present as sulphate.
Substance added: 4 to 5 g ammonium oxalate.
Total volume of solution: 100 to 120 cc.
Temperature: 60° to 70°.
Current-density at cathode: $ND_{100} = 1.0$ ampere.
Potential-difference: 3.1 to 3.8 volts.
Time required: 2¼ to 3½ hours.

The state of the surface of the cathode (whether rough or smooth) has no influence on the quality of the precipitated metal.

EXPERIMENT.

Used 2.2–2.6 g $CoSO_4.K_2SO_4.6H_2O$ (Fe = 13.43%), 4–5 g ammonium oxalate, 120 cc solution.

Current-density, Amperes.	Electrode Potential, Volts.	Temp.	Time.	Found.
1 –1.1	3.1 –3.78	60–65°	2 hr. 15 m.	13.36 %
0.5–0.52	2.7 –2.95	60–65°	3 " 30 "	13.49 "
1 –1.2	3.9 –4.0	15–35°	4 " 30 "	13.43 "
0.5–0.53	3.46–3.9	15–27°	6 " 35 "	13.25 "

According to a method given by Fresenius and Bergmann, the cobalt solution, after the addition of 15–20 cc of an ammonium sulphate solution (300 g $(NH_4)_2SO_4$ to the liter) and 40 cc ammonia sp. gr. 0.96 (where more than 0.5 g cobalt is present in the solution, 50–60 cc NH_4OH) is diluted with water to 150–170 cc, and electrolysed with a current of $ND_{100} = 0.7$ as a maximum at ordinary temperatures. The presence of chlorides and nitrates is unfavorable to the reduction. Fixed organic acids (citric acid, tartaric acid) and also magesium compounds act injuriously. The presence of phoshates is not objectionable.

CONDITIONS FOR ANALYSIS.

Metal present as sulphate.

Substance added: 4.5 to 6 g ammonium sulphate and 0 to 60 cc ammonia (sp. gr. = 0.96).

Total volume of solution: 150 to 170 cc.

Temperature: that of room.

Current-density: $ND_{100} = 0.5$ to 0.7 ampere.

Potential-difference: 2.8 to 3.3 volts.

Time required: about six hours.

F. Oettel has proposed the following method for the etermination of cobalt:

The salt is dissolved in water and a quantity of ammoium chloride, equal to four times the weight of the salt taken, added. The final volume of the liquid should be 150 cc, of which is an ammonia solution (sp. gr. = 0.92). (See urther under Nickel.)

NICKEL.

LITERATURE:

Luckow, Dingl. Polyt. Journ., 177, 235 (1850).
Gibbs, Zeit. f. anal. Chem., 3, 336 (1864); 11, 10 (1872); 22, 558 (1883).
Merrick, Amer. Chemist, 2, 136 (1871).
Mansfeld. O. Berg. Hüttendirektion, Zeit. f. anal. Chem., 11, 1 (1872)
Hampe, Zeit. f. anal. Chem., 13, 186 (1874).
Herpin, Zeit. f. anal. Chem., 15, 535 (1876).
Wrightson, Zeit. f. anal. Chem., 15, 300, 303, 333 (1876).
Schweder, *ibid.*, 16, 344 (1877).
Cheney and Richards, Amer. Journ. of Science, [3] 14, 178 (1877).
Ohl, Zeit. f. anal. Chem., 18, 523 (1879).
Fresenius and Bergmann, Zeit. f. anal. Chem., 19, 329 (1880).
Luckow, Zeit. f. anal. Chem., 19, 314 (1880).

Classen and v. Reiss, Ber. deutsch. chem. Ges., 14, 1622, 2771 (1881).
Riché, Zeit. f. anal. Chem., 21, 116 (1882).
Schucht, Zeit. f. anal. Chem., 21, 493 (1882).
Moore, Chem. News, 52, 209 (1885).
Kohn and Woodgate, Journ. Soc. Chem. Indust., 8, 256 (1889).
Brand, Zeit. f. anal. Chemie, 28, 588 (1889).
Le Roy, Compt. rend., 112, 722 (1891).
Rüdorff, Zeit. f. angew. Chemie, 1892, p. 6.
Smith and Muhr, Journ. Anal. Chem., 5, 488 (1891); ibid., 7, 189 (1893).
Vortmann, Monatsh. f. Chem., 14, 536 (1893).
Classen, Ber. deutsch. chem. Ges., 27, 2061 (1894).
Oettel, Zeit. f. Elektrochemie, 1, 192 (1894–95).
Winkler, Zeit. f. anorg. Chem., 8, 291 (1895).
Campbell and Andrews, Journ. Am. Chem. Soc., 17, 125 (1895).
Fernberger and Smith, Journ. Am. Chem. Soc., 21, 1001 (1899).
Foster, Zeit. f. Elektrochem., 6, 160 (1889–1900)
Gooch and Medway, Am. Journ. of Science, April, 1903.

Nickel may be reduced under conditions similar to those for the determination of cobalt; the metal is precipitated from a solution of double oxalates, containing ammonium oxalate in excess, as a bright adherent coating on the negative electrode.

CONDITIONS FOR ANALYSIS.

Metal present as sulphate.
Substance added: 6 to 8 g ammonium oxalate.
Total volume of solution: 120 cc.
Temperature: 60° to 70°.
Current-density at cathode: $ND_{100} = 1.0$ ampere.
Potential-difference: 3 to 4 volts.
Time required: about 3 hours.

The question of the complete precipitation of the nickel can be settled by adding a small quantity of ammonium sulphide to the solution and concentrating the solution by evaporation, when any nickel remaining will be precipitated as sulphide. If the quantity of this is appreciable it can be determined by adding bromine to dissolve the sulphide and again electrolysing the solution after the addition of an excess of ammonia.

According to Fresenius and Bergmann, nickel can be completely precipitated from a solution containing ammonium sulphate and free ammonia (see Cobalt).

Oettel has demonstrated that nickel may also be determined in solutions containing the chloride. Since the presence of nitric acid is very objectionable, however, this must be entirely removed if present. Oettel effected this by evaporating the nitric acid solution to complete dryness and then boiling the residue several times with concentrated hydrochloric acid in a long-necked flask, until the reaction of nitric acid with diphenylamine was no longer obtained. Small quantities of nickel nitrate can be precipitated as hydroxide, washed and dissolved in hydrochloric acid. Large quantities are most conveniently converted into sulphate and determined by one of the methods mentioned above.

To the solution of the chloride so much ammonia (sp. gr. =0.92) is added that 10% by volume of free ammonia is present (when less is present black oxide of nickel separates on the anode). About 10 g ammonium chloride per gram of metal to be precipitated is added, and the electrolysis is conducted with currents of $ND_{100}=0.4$ ampere. The time required is from 7 to 8 hours, and the method permits large quantities of nickel (as much as 2 grams) to be precipitated in white, strongly adherent deposits. A uniform current-density on all portions of the surface of the cathode is important to the success of this method.*

E. F. Smith † recommends the precipitation of nickel and cobalt from a solution containing an alkali cyanide

---

* Classen, Ausgewählte Methoden, p. 410.

† Electro-Chemical Analysis, 1902, p. 94.

under the following conditions: Enough potassium cyanide is added to the solution of the metal salt to redissolve the precipitate at first formed and to provide an excess of 0.1 gram of the cyanide; 2 grams of ammonium carbonate are then added, the solution is diluted to 150 cc, warmed to 60°, and electrolysed with a current of $ND_{100} = 1.5$ ampere and a potential-difference of 6 to 6.5 volts. The time required for complete precipitation is about three and one-half hours.

According to Fernberger and Smith the determination of nickel may also be conducted in a solution containing phosphates. They mention the following experiment:

To a solution of the nickel salt (containing 0.1360 g of Ni) 45 cc of a disodium hydrogen phosphate solution (sp. gr. = 1.0358) and enough phosphoric acid to dissolve the precipitate formed and to have a few drops in excess were added. The solution was then diluted to 250 cc, warmed to 65°, and electrolysed for three and one-half hours with a current of $ND_{100} = 0.53$ ampere and a potential-difference of 7 volts.

Campbell and Andrews dissolve nickel hydroxide in 30 cc of a 10 per cent. solution of disodium hydrogen phosphate, to which 30 cc of a concentrated ammonia solution are added, and, with a distance of 5 mm between the electrodes, separate the nickel by the use of a current of $ND_{100} = 0.14$ amp.

Gooch and Medway have used the apparatus described on p. 124 for the determination of nickel. Nickel ammonium sulphate was dissolved in 25 cc of water and 20 cc of strong ammonia were added. In this solution about 1 g of ammonium sulphate was dissolved and the electrolysis was conducted with currents of from 1.5 to 4 amperes (equivalent to $ND_{100} = 5 - 13.3$ amperes). The time required for the complete precipitation of the nickel (0.0954 – 0.1738 g) was from 20 to 30 minutes.

ZINC.

LITERATURE:

Wrightson, Zeit. f. anal. Chem., **15**, 303 (1876).
Parodi and Mascazzini, Ber. deutsch, chem. Ges., **10**, 1098 (1877); Zeit. f. anal. Chem., **18**, 588 (1879).
Riché, Zeit. f. anal. Chem., **17**, 216 (1878).
Beilstein and Jawein, Ber. deutsch, chem. Ges., **12**, 446 (1879); Zeit. f. anal. Chem., **18**, 588 (1879).
Reinhardt and Ihle, Journ. f. prakt. Chem., **24**, 193 (1881).
Classen and v. Reiss, Ber. deutsch. chem. Ges., **14**, 1622 (1881).
Riché, Zeit. f. anal. Chem., **21**, 119 (1882).
Millot, Bull. de la Soc. chim., **37**, 339 (1882).
Gibbs, Zeit. f. anal. Chem., **22**, 558 (1883).
Moore, Chem. News, **52**, 209 (1885).
Luckow, Zeit. f. anal. Chem., **25**, 113 (1886).
v. Malapert, Zeit. f. anal. Chem., **26**, 56 (1887).
Herrick, Journ. Anal. Chem., **2**, 167 (1888).
Brand, Zeit. f. anal. Chem., **28**, 581 (1889).
Vortmann, Ber. deutsch. chem. Ges., **24**, 2753 (1891).
Warwick, Zeit. f. anorg. Chem., **1**, 290 (1892).
Rüdorff, Zeit. f. angew. Chem., 1892, p. 197.
Vortmann, Monatsh. f. Chemie, **14**, 536 (1893).
Classen, Ber. deutsch. chem. Ges., **27**, 2060 (1894).
Jordis, Zeit. f. Elektrochemie, **2**, 138, 565, 655 (1895–96).
Nicholson and Avery, Journ. Am. Chem. Soc., **18**, 659 (1896).
Paweck, Zeit. f. Berg-u. Hüttenwesen, **46**, 570 (1898).
Riderer, Journ. Am. Chem. Soc., **21**, 789 (1899).
Smith, Journ. Am. Chem. Soc., **24**, 1073 (1902).

The metal may be easily and quickly separated from the double salts of zinc ammonium oxalate and zinc potassium oxalate (method of the author).*

The reduced metal has a bluish-white color, and under proper conditions adheres firmly to the negative electrode.

---

* The reduction of zinc from a solution of zinc ammonium oxalate is very often credited to Reinhardt and Ihle. The author, however, described this method in Fehling's "Handwörterbuch" before the publication of the article by Reinhardt and Ihle in the Journal für praktische Chemie, to the editor of which, Kolbe, the author especially stated the facts at the time.

Indeed, the metallic zinc often adheres so firmly to the platinum dish that, after being cleaned with water and alcohol and dried, it is with difficulty dissolved by warming with acids. Generally, after this operation, a dark coating of platinum-black remains which can only be removed by igniting the dish and again treating with acids. It is therefore desirable, before weighing the dish, to precipitate upon it a thin coating of copper, tin, or, better, silver. In laboratories where many zinc determinations are performed, silver dishes may be advantageously employed.

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 70–80°, 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 Silver).

In determining zinc by this method, the zinc salt is dissolved in a little water by warming, about 4 g of potassium oxalate or an equal amount of ammonium oxalate is added and the whole is brought into solution by warming and, if necessary, by the addition of small quantities of water.* The liquid is now *transferred to a platinum dish coated with* copper or silver and electrolysed. The author has demonstrated by experiments that the separation of the zinc in a dense, metallic form is possible if the solution be kept acid during the process of analysis.

---

* If the alkali oxalate be added to a dilute solution of a zinc salt, there first forms a precipitate of zinc oxalate which is not completely converted into the soluble zinc double salt if the solution of the alkali oxalate is too dilute.

For acidifying the solution, a cold saturated solution of oxalic acid, or, better, a solution of tartaric acid (3 : 50) is employed. At the start the solution is electrolysed for about 3–5 minutes without addition of acid, and then the acid is permitted to flow in drops (about 10 drops per minute) from a burette with a fine outlet, upon the watch-glass covering the dish. The acid flows through the holes in the watch-glass into the dish itself. After the reduction is completed (this is determined with potassium ferrocyanide), the metal must be washed without interrupting the current.

CONDITIONS FOR ANALYSIS.

Metal present as sulphate.

Substance added: 4 g potassium or ammonium oxalate.

Total volume of solution: 120 cc.

Temperature: 50° to 60°.

Current-density at cathode:

$ND_{100} = 0.5$ to 0.1 ampere.

Potential-difference: 3.5 to 4.8 volts.

Time required: about 2 hours.

Roughened or polished dishes answer equally well, but they should be copper or silver plated before use.

EXPERIMENT.

Used 1.8–2 g zinc ammonium sulphate (Zn = 19.29%), 4 g potassium oxalate, 120 cc solution.

Current-density. Amperes.	Electrode Potential, Volts.	Temp.	Time.	Found.
0.5–0.55	3.5–4.0	55–60°	2 hr.	16.44 %
0.9–1	4.7–4.8	60°	1 " 50 m.	16.42 "

According to v. Miller and Kiliani, 4 g potassium oxalate and 3 g potassium sulphate are dissolved in water, the neutralised zinc solution (sulphate or nitrate containing not more than 0.3 g Zn) carefully added, and electrolysis effected without heat, by a current of $ND_{100} = 0.3–0.5$ ampere. The reaction is complete in 2 to 3 hours.

N. Eisenberg * obtained the following results by the preceding method:

Subst. Taken.	Current-density, Amperes.	Electrode Potential, Volts.	Temp.	Time.	Found.	Condition of Metal.
1.8312	0.4 –0.35	3.9–4.0	25–26°	4 hr.	16.35 %	partly spongy
1.8312	0.40–0.35	4.1–4.2	28–30°	4 "	16.01 "	spongy

Remark: (1) Roughened dish; (2) Polished dish.

The constant mixing of the liquid by means of a stirring appliance is recommended for this method.

According to Jordis, zinc, when present in the form of *sulphate, chloride, or nitrate, may be separated from a lactic acid solution.* The ease with which this method can be carried out appears from the directions of the author, which read as follows: "2 g ammonium sulphate and 5–7 g ammonium lactate are added to the neutral solution containing not less than 0.3–0.5 g zinc, which is then acidified with a few drops of lactic acid. A stirring attachment is employed, and the solution is electrolysed with a current of $ND_{100} = 1.0 - 1.5$ amp. After 40–60 minutes the electrolyte is poured into a second dish and the separation completed in this. With a current of the above density this requires 20–25 minutes. A somewhat concentrated solution of about 120–150 cc is advantageous."

"Since the lactic acid is but very slowly decomposed during the electrolysis, its regeneration resulting from the action of the sulphuric acid formed upon the ammonium lactate, the electrolyte remains acid until the end and requires no further attention."

---

* Inaugural-Dissert. Heidelberg, 1895.

Luckow, Beilstein and Jawein, and Millot have described *the precipitation of zinc from solutions containing potassium* cyanide. To a neutral solution of the zinc salt, or a solution made slightly alkaline with sodium hydroxide, just enough of a solution of pure potassium cyanide is added in small portions to dissolve the precipitate of zinc cyanide at first formed, and the solution is diluted to 150 cc. The current-density can be from 0.5 to 0.1 ampere, and the electrolysis may be conducted at ordinary temperatures, or from 50° to 60°. In the latter case the difference of potential between the electrodes will be from 5 to 8 volts and the time required from two to two and one-half hours. If the determination is to be carried out over night weaker currents can be used at room temperature and a good deposit will be obtained. The completion of the precipitation can be determined by decomposing a small quantity of the solution with hydrochloric acid and adding potassium ferrocyanide.

A method previously suggested by Vortmann depended *on the addition of a known weight of a mercury salt to the* zinc solution, and the precipitation of the mercury and zinc by electrolysis in the form of an amalgam. Paweck has substituted a direct method for this, and precipitates the zinc on an amalgamated cathode.

For this purpose two circular disks 6 cm in diameter are cut from ordinary brass-wire gauze, and after thorough cleansing by scouring and by treatment with acids are attached to a brass wire 10 cm long and 1 mm thick, pointed at the lower end, in such a manner that the wire extends about 2 mm beyond the lower disk, and the two disks are parallel and about 12 mm apart. After washing with water, alcohol, and ether, and drying, this electrode is immersed in a solution of 0.6 g mercuric chloride, 5 cc concentrated nitric acid, 200 cc water, and electrolysed for ¾ to 1 hour with a current of 0.1 to 0.2 ampere. By this treatment the electrode is evenly amalgamated, and it is then washed with hydrochloric acid, water, alcohol, and ether, and dried at a gentle heat, as is obtained by holding it a short distance from a hot asbestos plate. It is then placed on a watch-glass in a desiccator, and accurately weighed before using for an analysis.

The solution, which may contain as much as 0.5 g of zinc as sulphate, is prepared by adding 10 g of sodium-potassium tartrate and 7 to 8 g of pure sodium or potassium hydroxide dissolved in water, and is diluted to a final volume of 200 cc. The electrolysis is conducted with a current-strength of 0.1 to 0.5 ampere and a potential-difference of from 2.6 to 3.6 volts. The operation requires from 3 to 4 hours, and the end of the precipitation can be determined with hydrogen sulphide. When completed, the cathode is removed quickly, washed with water, alcohol, and ether, dried as before, and allowed to stand in a desiccator for 15 minutes before weighing. For a second experiment the cathode can be cleaned by treating with almost concentrated hydrochloric acid, and is washed with water, etc., as in the first case.

Paweck *also succeeded in precipitating the zinc quantitatively* on unamalgamated brass-wire gauze cathodes. The solution in this case consisted of the zinc salt as sulphate, 14 g sodium or potassium sulphate and three drops of concentrated sulphuric acid. The circuit was so adjusted that the current began to pass as soon as the cathode was introduced into the solution, and the washing at the end was carried out without interrupting the current. A potential-difference of 3.6 volts was employed.

Smith has determined the following conditions as suitable for the determination of zinc by the method originally proposed by Riché.

To the solution of the zinc salt (potassium zinc sulphate equal to 0.2002 g Zn) 1 g of sodium acetate and 0.3 cc of acetic acid (99%) were added. The volume of the final solution was 150 cc and the electrolysis was conducted at a temperature of 65° in silvered dishes, with a current of $ND_{100}=0.36$ to 0.70 ampere and a potential-difference of 4 to 5 volts. The time required was two hours, and towards the end of the operation, when the solution appeared to be filled with small gas bubbles, it was neutralised with ammonia.

For the electrolytic determination of zinc Smith* states that he prefers the method suggested by Parodi and Mascazzini, which he describes as follows: To a solution of the element (0.1–0.25 g Zn) as sulphate add 4 cc of a solution of ammonium acetate (ordinary laboratory strength, presumably!), 20 cc of citric acid, and dilute to 200 cc with water. The electrodes are then introduced into the liquid, their distance apart being not more than a few millimeters. A platinum cone is used as cathode and the current should be 0.5 ampere and 5.9–6.3 volts at ordinary temperatures, or 0.5 ampere and 4.8 to 5.2 volts when the solution is warmed to 50–60°.

According to Vortmann, zinc can be quantitatively precipitated from alkaline (NaOH) solutions containing sodium potassium tartrate by currents of $ND_{100}=0.3$ to 0.6 ampere. This behavior of zinc is important chiefly in separations (see Cobalt-Zinc, Zinc-Nickel).

---

* Electro-Chemical Analysis (1902), p. 84.

MANGANESE.

LITERATURE:

Luckow, Zeit. f. anal. Chem., 8, 24 (1869).
Riché, Ann. d. Chim. et Phys., [5], 13 508 (1878).
Luckow, Zeit. f. anal. Chem., 19, 17 (1880).
Schucht, *ibid.*, 22, 493 (1883).
Classen and v. Reiss, Ber. deutsch. chem. Ges., 14, 1622 (1881).
Moore, Chem. News, 53, 209 (1886).
Smith and Frankel, Journ. Anal. Chem., 3, 385 (1889);
Chem. News, 60, 262 (1889).
Brand, Zeit. f. anal. Chem., 28, 581 (1889).
Rüdorff, Zeit. f. angew. Chem., 15, 6 (1892).
Warwick, Zeit. f. anorg. Chem., 1, 285 (1892).
Classen, Ber. deutsch. chem. Ges., 27, 2060 (1894).
Gröger, Zeit. f. angew. Chem., p. 253 (1895).
Engels, Zeit. f. Elektrochemie, 413 (1895–96); 286, 305 (1896–97).
Kaeppel, Zeit. f. anorg. Chem., 16, 268 (1898).

From the results of experience in the Aachen laboratory, none of the methods long in use are applicable for the direct quantitative determination of this metal as peroxide. It is generally assumed that the peroxide when dried at about 68° has the composition $MnO_2.H_2O$, an assumption which the author cannot confirm. If the attempt be made to convert the hydrated peroxide into anhydrous peroxide by prolonged drying at a higher temperature, a strongly hygroscopic substance results which rapidly increases in weight during the process of weighing. It is therefore necessary to convert the dried peroxide into mangano-manganic oxide by *ignition, an operation conducted with ease and safety.* After determining the necessary conditions for the separation of large quantities of lead peroxide, the author was induced to assume that manganese behaved similarly to lead. Investigation proved, however, that strong inorganic acids interfere with complete precipitation, and even make it impossible. Of the organic acids, acetic acid alone is suitable, although the precipitation of large quantities, even when roughened dishes are used, cannot be successfully carried out, since it is impossible to obtain firmly adhering precipitates.

If a salt other than the acetate is at hand, it is best to precipitate the manganese as dioxide with ammoniacal hydrogen peroxide. The precipitate is washed thoroughly and dissolved in 5 cc acetic acid, 5 cc hydrogen peroxide (4–5%), and 25 cc water. This is especially necessary when the manganese is present as chloride or when the solution contains other chlorides. Permanganic acid is first reduced to a manganous salt. In acetic acid solutions, even when roughened dishes are used, the maximum quantity of manganese which can be satisfactorily determined as peroxide is only about 0.08 gram.

CONDITIONS FOR ANALYSIS.

Metal present as acetate or sulphate.
Substance added: 25 cc acetic acid (sp. gr. = 1.069).
Total volume of solution: 75 cc.
Temperature: 50° to 70°.
Current-density at anode: $ND_{100} = 0.3$ to 0.35 ampere.
Potential-difference: 4.3 to 4.9 volts.
Time required: 3 hours.
Roughened dishes should be used.

A rapid and complete separation was secured by Engels, as a result of investigations conducted in the Aachen laboratory. The method is as follows: 1–2 g of the manganese salt is dissolved in about 125 cc of water, and 10 g ammonium acetate and 1.5–2 g chrome alum are also added. The clear solution is then electrolysed. Chlorides must not be present, since the evolution of chlorine interferes with the separation of the manganese. If they are present, the manganese is converted into acetate as described above.

CONDITIONS FOR ANALYSIS.

Metal present as acetate or sulphate.

Substance added: 10 g ammonium acetate and 1.5 to 2 g chrome alum.

Total volume of solution: 125 cc.

Temperature: 80°.

Current-density at anode: $ND_{100} = 0.6$ to 1.0 ampere.

Potential-difference between electrodes: 2.8 to 4.0 volts.

Time required: about 1¼ hour.

Roughened dishes *must* be used.

EXPERIMENT.

In the determinations given below. 10 g ammonium acetate and 1.5–2 g chrome alum were added to the solution.

$Mn(NH_4)_2(SO_4)_2.6H_2O$, 19.52% Mn.	Current-density ND_{100}, Amp.	Electrode Potential, *Volts.*	Temp	Time.	Found Mn_3O_4, *g.*	Found Mn_3O_4, *Per Cent.*
1.1522 g	0.6–0.5	2.8–3.1	80°	$\frac{5}{4}$ hr.	0.2235	19.39
1.2554 "	0.6–0.5	2.8–3.1	80°	" "	0.2436	19.40
1.2994 "	0 6	3.	83°	" "	0 2520	19.39
1.8099 "	1.1	3.7–4.1	80°	" "	0.3513	19.40

In the determination of manganese in the salts of permanganic acid, the solution of the latter is decomposed, according to Engels, with 5 cc acetic acid and enough hydrogen peroxide to completely decolorise it. Since the presence of even small quantities of hydrogen peroxide prevents the separation and the firm adherence of the precipitate, the excess of hydrogen peroxide must be removed. This may be most easily accomplished by the addition of small quantities of chromic acid, until further addition no longer causes the evolution of gas; generally 0.3–0.5 g is sufficient.

EXPERIMENT.

50 cc of a potassium permanganate solution were decomposed with 5 cc acetic acid and 10 cc of a weak solution o hydrogen peroxide. The excess of H_2O_2 was removed witl CrO_3.

	Current-density ND_{100}.	Potential.	Time.	Temp.	Mn_3O_4.
I.	1.5 amp.	2.8 volts	1 hr.	85°	0.1217 g
II.	1.65 "	3.15 "	1 "	85°	0.1220 "
III.	1.78 "	3.4 "	1 "	80°	0.1220 "

The current-strength available varies between comparatively wide limits. Weak currents also give rapid and satisfactory results.

EXPERIMENT.

Three dishes, each containing manganese sulphate solution, 10 g ammonium acetate, and 1 g chrome alum, were connected in parallel, and the current from a thermopile passe through. The potential at the electrodes at the beginnin of the electrolysis was 3.2 volts, the entire current-strengt 1.5 amp., so that each dish received about 0.4 amp. Th manganese salt used contained 20.45% Mn_3O_4.

$Mn(NH_4)_2(SO_4)_2.6H_2O$. Gram.	Current-density ND_{100}. Amp.	Potential, Volts.	*Temp.*	*Time.*	*Found.*
1.1955	0.22	3.2	80°	2 hrs. 30 min.	20.45 %
0.9009	0.22	3.2	80°	2 " " "	20.44 "
1.2012	0.22	3.2	80°	2 " " "	20.40 "

Since manganese separates as peroxide from a cold solutio to which *ammonium* acetate has been added, at 1.25 volt and when warmed to 80° as low as 1–1.1 volts, the electrolysis may therefore be conducted with low electromotive force The constancy of the latter may be assured by connecting i shunt (page 103). The lower the potential, the longer th time required for the separation. With the maximum potential of 1.8 volts it takes from 4 to 5 hours. For the firm adherence of the precipitate a temperature of 80° is essential.

In those cases (*i.e.*, in the presence of silver) where the chrome alum produces a precipitate in the solutions, it may be replaced by 10 cc of alcohol, which in general is not as satisfactory as the chrome alum in separating the manganese peroxide.

When alcohol is used, the electrolysis is conducted at a temperature of 75–80°, with a maximum potential of 2 volts, which gives a current-density ND_{100} = about 0.15 amp. Time required for the electrolysis, about 5 hours.

Kaeppel has stated that by the addition of acetone to solutions of manganese sulphate he was able to deposit quantities of manganese dioxide as great as 1.6 g on roughened anodes. He employed solutions containing manganese equivalent to 0.15 to 1.6 gram of manganese dioxide in 150 cc, and added from 1.5 to 10 cc of acetone, depending on the amount of manganese sulphate present. The electrolysis was conducted at a temperature of from 50° to 60° and required from 2 to 5½ hours. As source of current he states that he used accumulators and Cupron elements, giving a potential-difference of 4 to 4.25 volts and currents of from 0.7 to 1.2 ampere, directions which are insufficient to permit a repetition of his experiments. His method has not given satisfactory results when tried in the author's laboratory.*

ALUMINIUM, URANIUM, CHROMIUM, BERYLLIUM.

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 car-

---

* Classen, Ausgewählte Methoden, p. 370.

bonate, 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.

Uranium is acted on in the same way as aluminium.

Chromium ammonium oxalate is oxidised by the current with formation of ammonium chromate. To determine the chromic acid, the ammonium carbonate is decomposed by boiling, the solution acidified with acetic acid, and the chromic acid determined as lead or barium chromate.

When beryllium ammonium oxalate is subjected to electrolysis, *the beryllium is kept in solution by the hydrogen* ammonium carbonate produced, provided the solution is cold.

The behavior of aluminium, chromium, uranium, and beryllium can be made use of, as explained later, to separate them from each other and from all metals which separate from their double oxalates in the metallic state at the negative electrode.

URANIUM.

LITERATURE:

Smith, Am. Chem. Journ., 1, 329 (1879).
Luckow, Zeit. f. anal. Chem., 19, 18 (1880).
Smith and Wallace, Journ. Am. Chem. Soc., 20, 279 (1898).
Kollock and Smith, Journ. Am. Chem. Soc., 23, 607 (1901).
Kern, Journ. Am. Chem. Soc., 23, 685 (1901).

According to Smith and Wallace uranium can be determined by the electrolysis of a solution containing free acetic acid. The uranium separates on the cathode as yellow uranic hydroxide, which, on the continued action of the current *is converted into black hydrated protosesquioxide.* When the solution had become colorless, the current was interrupted, the precipitate was washed with dilute acetic acid and boiling water, dried, ignited to protosesquioxide, and weighed.

To a solution containing urano-uranic oxide (Ur_3O_8 = 0.1185 g in 10 cc), 0.5 cc of concentrated acetic acid was added and, after diluting to 40 cc, the solution was electrolysed at 70° with a current of ND_{100} = 0.18 ampere and a potential-difference of 3 volts. The precipitation was complete in 5 hours.

Kollock and Smith recommend the following conditions: uranium acetate (U_3O_8 = 0.0986–0.2295 g), 0.2 cc acetic acid (29%), total volume of solution = 125 cc, temperature 65–70°, ND_{100} = 0.05–0.55, potential-difference = 4.0–16.2 volts, time 4–6 hours.

For uranyl nitrate solutions, the same authors recommend the following conditions: 0.1222–0.1320 g U_3O_8, volume of solution = 125 cc, temp. = 65–75°, ND_{100} = 0.02–0.04 ampere, potential-difference = 2.0–4.6 volts, time 5–8 hours.

COPPER.

LITERATURE:

Gibbs, Zeit. f. anal. Chem., 3, 334 (1864).
Hampe, Berg- u. Hüttenm. Ztg., 21, 220 (1862); *ibid.*, 25, 113 (1866).
Luckow, Journ. f. prak. Chem., 96, 259 (1865).
Boisbaudran, Bull. Soc. Chim., 7, 468 (1867).
Luckow, Zeit. f. anal. Chem., 8, 23 (1869).
Mansfeld. O. Berg- u. H. Direktion, Zeit. f. anal. Chem., 8, 23 (1869).
Merrick, Amer. Chemist, 2, 136 (1871).
Mansfeld. O. Berg- u. H. Direktion, Zeit. f. anal. Chem., 11, 1 (1872).
Classen and v. Reiss, Zeit. f. anal. Chem., 14, 246 (1875).
Wrightson, Zeit. f. anal. Chem., 15, 299 (1876).
Herpin, Zeit. f. anal. Chem., 15, 335 (1876).
Schweder, Berg- u. Hüttenm. Ztg., 36, 11, 21 (1877);
Zeit. f. anal. Chem., 16, 345 (1877).
Fresenius, Zeit. f. anal. Chem., 16, 339 (1877).
Ohl, Zeit. f. anal. Chem., 18, 523 (1879).
Luckow, Zeit. f. anal. Chem., 19, 1 (1880).

Classen, Ber. deutsch. chem. Ges., **14**, 1622, 1627 (1881).
Mackintosh, Am. Chem. Journ., **3**, 354 (1881).
Riché, Zeit. f. anal. Chem., **21**, 116 (1882).
Foote, Am. Chem. Journ., **6**, 333 (1884).
Moore, Chem. News, **53**, 209 (1886).
Rüdorff, Ber. deutsch. chem. Ges., **21**, 1888 (1888).
Classen, Ber. deutsch. chem. Ges., **21**, 2898 (1888).
Oettel, Zeit. f. anal. Chem., **27**, 15 (1888).
Smith, Am. Chem. Journ., **12**, 329 (1890).
Croasdale, Journ. Anal. Chem., **5**, 133 (1891).
Regelsberger, Zeit. f. angew. Chemie, **2**, 473 (1891).
Meeker, Journ. Anal. Chem., **6**, 267 (1892).
Rüdorff, Zeit. f. angew. Chem., p. 5 (1892).
Warwick, Zeit. f. anorg. Chem., **1**, 285 (1892).
Schmucker, Journ. Anal. Chem., **7**, 252 (1893).
Smith and Moyer, Zeit. f. anorg. Chem., **4**, 267 (1893).
Classen, Ber. deutsch. chem. Ges., **27**, 2060 (1894).
*Oettel, Chemiker-Zeitung, **18**, 47, 879 (1894).*
Wagner, Zeit. f. Elektrochemie, **2**, 613 (1895–96).
Heidenreich, Ber. deutsch. chem. Ges., **29**, 1585 (1896).
Hollard, Compt. rend., **123**, 1003 (1896).
Forster and Seidel, Zeit. f. anorg. Chem., **14**, 106 (1897).
Revay, Zeit. f. Elektrochem., **4**, 313 (1897–98).
Head, Trans. Am. Inst. Mining Engineers (1898).
Ullmann, Chem. Ztg., **22**, 808 (1898).
Kollock, Journ. Am. Chem. Soc., **21**, 911 (1899).
Fernberger and Smith, Journ. Am. Chem. Soc., **21**, 1001 (1899).
Gooch and Medway, Am. Journ. of Science, April, 1903.

If copper be reduced from a solution containing an excess of ammonium oxalate, it is not always possible to obtain the *metal in a compact form.* For this reason the author, as long ago as 1888,* began experiments on the determination of this metal from a solution of the acid double oxalate. Further experiments in this direction have shown that coherent, bright-red copper precipitates can be obtained when copper is reduced from such solutions at a temperature of about 80°. The solution containing the copper is treated with a cold saturated solution of ammonium oxalate, heated

---

* Ber. deutsch. chem. Ges., **21**, 2898 (1888).

as directed, and at first electrolysed for a few minutes without the addition of oxalic acid. A cold saturated oxalic acid solution is then run in from a burette. The method of procedure here is similar to that described under Zinc (p. 165).

In the analysis of substances low in copper, the solution may be made acid at the start; in concentrated solutions, on the contrary, the electrolysis must be conducted in solutions which are as nearly neutral as possible, since otherwise difficultly soluble oxalate of copper will separate out, owing to the free oxalic acid present. The end of the reaction is determined by testing with potassium ferrocyanide a small portion of the solution strongly acidified with hydrochloric acid. The precipitate must be washed without stopping the current. The metal is dried in an air-bath after treating with water and alcohol.

The precipitated copper has a bright-red color, adheres firmly to the dish, and has little resemblance to the copper precipitated from nitric acid solutions (see below). The chief advantage of this method is the rapidity with which it may be conducted.

CONDITIONS FOR ANALYSIS.

Metal present as sulphate.

Substance added: 4 g ammonium oxalate, oxalic acid as described above.

Total volume of solution: 120 cc.

Temperature: 80°.

Current-density at cathode: $ND_{100} = 1.0$ ampere.

Potential-difference: 2.5 to 3.2 volts.

Time required: 2 hours.

EXPERIMENT.

Used 1 g copper sulphate, 4 g ammonium oxalate, oxalic acid as described above, 120 cc solution.

Current-density, ND_{100} = Amperes.	Electrode Potential, Volts.	Temp.	Time.	Taken.	Found.
1.0 – 0.8	2.8–3.2	80°	2 hr.	0.2529 g	0.2531 g
0.45–0.35	2.5–2.8	80°	2½ "	0.2529 "	0.2528 "

Copper precipitate bright red.

As has been observed by Luckow, copper may also be precipitated from a solution to which nitric acid has been added.

The reduction of copper from a nitric acid solution depends upon the presence of a certain quantity of nitric acid and the absence of chlorides. To about 200 cc of solution, containing the copper as sulphate, 20 cc of nitric acid * (sp. gr. = 1.21) are added and the liquid is subjected to electrolysis. The end of the reaction is determined with ammonia.

The presence of chlorides is to be avoided. In the presence of antimony, arsenic, mercury, silver, tin, and bismuth, traces of these metals come down with the copper, especially when strong current-densities are employed. In the presence of these elements it is best to conduct the electrolysis with currents of from 0.2 to 0.3 ampere, the maximum quantity of 10% by volume of concentrated nitric acid being present in the solution. Iron, cobalt, nickel, cadmium, manganese, and zinc can be separated readily from copper by this method.

According to the researches of Schröder large quantities of iron are detrimental, since a secondary reaction may take place between the ferric salt formed and the precipitated copper, which causes the copper to redissolve.

Copper separates in a crystalline form from solutions

---

* Such a large quantity of nitric acid is required only when the copper is to be separated from other metals present in the same solution. When no other metal is present 2 to 3 per cent. by volume of concentrated acid is sufficient.

warmed to 50–60°; it is moreover impossible to separate *the last traces of copper at this temperature.*

CONDITIONS FOR ANALYSIS.

Metal present as nitrate or sulphate.

Substance added: 5% by volume dilute nitric acid.

Total volume of solution: 120 to 150 cc.

Temperature: 20° to 30°.

Current-density at cathode: $ND_{100}=0.5$ to 1.0 ampere (the latter only when no other metal than copper is present in the solution).

Potential-difference between electrodes: 2.2 to 2.5 volts.

Time required: 4 to 5 hours. By continuously stirring the solution the operation is hastened.

EXPERIMENT.

Used about 1 g copper sulphate and 5% by volume nitric acid. Entire volume of liquid 120 cc.

Current-density ND_{100}, Amperes.	Electrode Potential, Volts.	Temp.	Time	Taken.	Found.
1.1–1.0	2.2 –2.5	25–30°	5 hr.	0.2495 g Cu	0.2490 g. Cu
1.0–0.95	2.25–2.3	30–32°	5 "	0.2510 " "	0.2505 " "

A solution containing free nitric acid may also be used for separating such metals as are not reduced in the presence of this acid, or which are set free at the positive electrode in the form of peroxides. In such cases, however, it must be kept in mind that the nitric acid is gradually converted into ammonia, on account of which, after the current has acted for some time, nitric acid must be occasionally added.

For the determination of copper, employing the apparatus described on p. 124, Gooch and Medway used a solution containing 0.0651–0.2548 g of copper as sulphate, to which 6–7 drops of dilute sulphuric acid (1 : 4) were added. The total volume of the solution was about 50 cc, and the electrolysis was conducted with a current of from 0.8 to 4 amperes (equivalent to $ND_{100}=2.7–13.3$ amperes). The time required for the complete precipitation of the copper was from 10 to 25 minutes.

The same investigators also used a solution containing 0.0651 g of copper to which from 6 to 9 drops of dilute nitric acid (1 : 4) had been added. The volume of the solution was 50 cc and the precipitation of the copper was conducted with a current of 0.8–1.8 ampere, equal to $ND_{100}=2.7–6$ amperes. The time required was from 20 to 35 minutes. From tests of this method made by the translator it would appear that the precipitation of copper from a nitric acid solution is more satisfactory and equally rapid when the quantity of dilute nitric acid (1 : 1) added to the solution is equal to about 5% of the final volume. Under these conditions the conductivity of the solution is so high that the temperature of the electrolyte remains low throughout the electrolysis. As stated elsewhere in the text, the separation of copper from a nitric acid solution proceeds most satisfactorily when the solution is cold.

Copper may be separated from a solution containing ammonium oxalate or one containing free nitric acid, in the presence of small quantities of antimony and arsenic. If, however, the amounts of the latter are considerable, then, after continued action of the current, antimony and arsenic are deposited upon the copper, causing the negative electrode to appear more or less dark-colored. In order to determine the copper in such cases, the dried electrode is ignited for a short time, as a result of which the copper is oxidised and the antimony and arsenic are driven off. The residue of oxide is dissolved in nitric acid and again submitted to electrolysis.*

In general the presence of chlorides causes the copper to separate in a spongy condition. To avert this action and to secure an adherent precipitate, Rüdorff adds 2–3 g ammonium nitrate and 20 cc ammonia (sp. gr. 0.96), dilutes with water to 100 cc, and electrolyses this solution. At the close of the reduction the solution is acidified with dilute acetic acid, the dish filled to overflowing with water, emptied, shaken to remove the last drops of water, and dried at 100° in the air-bath.

In the laboratory of the Munich Polytechnic Institute the preceding method is carried out under the following conditions: Ammonia is added in slight excess until the precipitate which at first appears is redissolved. Then 20–25 cc ammonia, sp. gr. 0.96, are added, in case not more than 0.5 g copper is present.† In this solution 3–5 g ammonium nitrate are dissolved, it is diluted to 100 cc, and the electrolysis is conducted with a current of $ND_{100} = 2$ amperes. The precipitate must be washed without interrupting the current.

Oettel, who also carried out experiments on the quantitative determination of copper from ammoniacal solutions, found that, by the addition of ammonium nitrate, 0.2–0.25 g of copper sulphate was quantitatively reduced in 6–8 hours at ordinary temperatures. The results of his investigation are:

"1. That copper can be separated in a compact form from weakly ammoniacal solutions containing ammonium nitrate, by currents of $ND_{100} = 0.07–0.27$ ampere. With too little ammonium nitrate, as well as in the presence of large

---

* Mansfeld'sche Hüttendirektion.

† If as much as 1 g Cu is present, the quantity of ammonia is increased to 30–35 cc.

quantities of free ammonia, the precipitate shows a tendency to a spongy structure.

"2. The highest concentration of the solution is 0.8 g copper per 100 sq. cm electrode surface, with the employment of a wire-shaped positive electrode.

"3. The presence of chlorine, zinc, arsenic, and small quantities of antimony is without detrimental action; when the solution contains lead, bismuth, mercury, cadmium, or nickel, the results of the determinations are somewhat too high."

E. F. Smith has proposed the determination of copper in solutions containing hydrogen disodium phosphate and free phosphoric acid. The proper conditions, according to Fernberger and Smith, are the following:

Metal present as sulphate (=1293 g Cu); substance added: 20 cc of a solution of hydrogen disodium phosphate (sp. gr. = 1.0358) and 5 cc phosphoric acid (sp. gr. = 1.347); temperature: 54–64°; total volume: 225 cc; $ND_{100} =$ 0.035–0.068 amperes; potential-difference: 2.2–2.6 volts; time: 6–7 hours.

A rapid and accurate method for the determination of copper has been worked out by Carl Engels in the Aachen laboratory. This method has the advantage over the use of nitric acid solutions that it can be more rapidly performed, and that, in separations, it also dispenses with the tedious conversion of the nitrates into sulphates. This method is based upon the addition of urea.

The separation of copper from solutions containing sulphuric acid is possible also if hydroxylamine is added. The method is as follows:

If the separation is to be carried out with weak currents, say during the night, the addition of 2 cc concentrated sulphuric acid and about ½ g hydroxylamine sulphate is recommended. A fine crystalline precipitate and absolutely accurate results are obtained with a current-strength of $ND_{100} =$ 0.08–0.18 *ampere*. The *potential at the poles of a shunt circuit* was 1.8–2.2 volts; after connecting the dish the potential sank to 1.1–1.3 volts, with a current of 0.1–0.2 amp.

EXPERIMENT.

Taken $CuSO_4.5H_2O$.	*Current-density* ND_{100}.	*Potential.* Volts.	Time.	*Found.* Cu.	Per Cent.*
1.0130 g	0.1 amp.	1.1	Night.	0.2574	25.41
1.7065 "	0.12 "	1.3	"	0.4335	25.40
1.1893 "	0.1 "	1.2	"	0.3021	25.41

If stronger currents are used, the amount of sulphuric acid must be increased. 10–15 cc of conc. sulphuric acid are poured into the solution of the salt, it is diluted to 150 cc, and 1 g hydroxylamine sulphate is added. If 0.3–0.5 g Cu is present, with a current-strength of $ND_{100} = 1$ amp., the separation is finished in 1½ to 2 hours. The condition of the precipitated copper is much better and much more suited for quantitative determination than the copper obtained under similar conditions without the addition of hydroxylamine.

Urea exerts a far more satisfactory action than hydroxylamine upon the separation of copper from solutions containing sulphuric acid. With a current-strength of $ND_{100} = 1$ ampere, not the slightest tendency toward a spongy separation is exhibited, but a bright-red, crystalline coating is obtained on the negative electrode. The analysis, with the *stated current-density, is completed in 1¼ hours.*

10–15 cc concentrated sulphuric acid and 1 g urea are added to the solution of the copper, which is then diluted to 150 cc.

---

* [Theory 25.33% Cu.]

CONDITIONS FOR EXPERIMENT.

Temperature of liquid: Most suitable, 60–70°.
Potential-difference: 2.7–3.1 volts.
Current-density: $ND_{100} = 0.8–1$ amp.
Time: 1½ hours.

EXPERIMENT.

Used copper sulphate containing 28.08% Cu.

Quant. Subst., g	Current-density ND_{100}, Amp.	Potential, Volts.	Temp.	Time.	Found.
1.1364	1.05	3.1	25°	1 hr. 15 m.	25.09 %
0.9671	1.2	3.1	55°	1 " 15 "	25.09 "
1.3972	0.75	2.7	65°	1 " 45 "	25.09 "

The current may be interrupted in washing the precipitate. The separated copper contains traces of carbon, and also platinum which dissolves from the anode. These admixtures can be determined by dissolving the copper in dilute nitric acid (1 : 10). A thin dark coating remains on the dish, which may be washed with water, but not with alcohol, without becoming loosened. The weight of the dish, determined after washing and drying in the air-bath, is used as a basis for calculating the weight of the separated copper.

With weaker currents the length of time required is of course greater. With a current-density of $ND_{100} = 0.2$ ampere, the precipitation of from 0.3 to 0.4 g Cu is completed in 3½–4 hours. It is desirable in this case to add less sulphuric acid to the solution; 5 cc conc. H_2SO_4 to each 150 cc, is the proper proportion.

Four dishes were connected in parallel, and for every 150 cc of solution of the copper salt which they contained 1 g urea and 5 cc conc. H_2SO_4 were added. The four electrolyses were then conducted in the cold, with the current from a thermopile. The entire current-strength was $ND_{100} = 0.8$

ampere, so that each dish received a current of $ND_{100} = 0.2$ ampere. The analyses were completed in 4 hours. The per cent. of copper in the salt used was 25.08.

Used $CuSO_4.5H_2O$.	Found Cu.	Found %.
1.0101 g.	0.2533 g.	25.07
1.0815 "	0.2709 "	25.05
1.0320 "	0.2589 "	25.08
1.0111 "	0.2535 "	25.07

BISMUTH.

LITERATURE.

Luckow, Zeit. f. anal. Chem., **19**, 16 (1880).
Classen and v. Reiss, Ber. deutsch. chem. Ges., **14**, 1622 (1881).
Thomas and Smith, Am. Chem. Journ., **5**, 114 (1883).
Schucht, Zeit. f. anal. Chem., **22**, 492 (1883).
Wieland, Ber. deutsch. chem. Ges., **17**, 1612 (1884).
Moore, Chem. News, **53**, 209 (1886).
Smith and Knerr, Am. Chem. Journ., **8**, 206 (1886).
Eliasberg, Ber. deutsch. chem. Ges., **19**, 326 (1888).
Brand, Zeit. f. anal. Chem., **28**, 596 (1889).
Vortmann, Ber. deutsch. chem. Ges., **24**, 2749 (1891).
Smith and Frankel, Am. Chem. Journ., **12**, 428 (1891).
Rüdorff, Zeit. f. angew. Chem., p. 199 (1892).
Smith and Saltar, Zeit. f. anorg. Chem., **3**, 418 (1893).
Smith and Moyer, Journ. of the Am. Chem. Soc., **15**, 28, 101 (1893).
Schmucker, Zeit. f. anorg. Chem., **5**, 199 (1894).
Kollock, Journ. Am. Chem. Soc., **21**, 911 (1899).
Balachowsky, Compt. rend., **131**, 179 (1900).
Wimmenauer, Zeit. f. anorg. Chem., **27**, 1 (1901).
Brunck, Ber. deutsch. chem. Ges., **35**, 1871 (1902).
Kammerer, Journ. Am. Chem. Soc., **25**, 83 (1903).

Until recently it has been found impossible to quantitatively precipitate bismuth in a compact, metallic form, since it has a strong tendency to separate in a more or less spongy state from all of its compounds.

In an article published in 1903, Kammerer (*loc. cit.*) states that this element can be satisfactorily determined under the following conditions:

Metal: 0.10 to 0.15 g Bi dissolved in 1 cc nitric acid (sp. gr. = 1.42).

Substance added: 2 cc sulphuric acid (sp. gr. 1.84)., 1 g potassium sulphate.

Total volume: 150 cc.

Temperature: 45° to 50°.

Current-strength: $ND_{100} = 0.02$ ampere.

Potential-difference: 1.8 volt.

Time: 8 to 9 hours.

The end of the precipitation is determined with ammonium sulphide, or by adding water to the contents of the dish and observing whether a dark ring appears above the deposited metal. During the electrolysis the electrolytic vessel should be tightly covered to prevent evaporation. The precipitate should be washed without interrupting the current, first with hot water, then with a mixture of 1 part alcohol and 2 parts ether, and finally with pure anhydrous ether.

CADMIUM.

LITERATURE:

Wrightson, Zeit. f. anal. Chem., 15, 303 (1876).
Smith, Pr. Am. Phil. Soc. (1878).
Clarke, Zeit. f. anal. Chem., 18, 104 (1879).
Beilstein and Jawein, Ber. deutsch. chem. Ges., 12, 759 (1879).
Smith, Am. Chem. Journ., 2, 43 (1880).
Luckow, Zeit. f. anal. Chem., 19, 16 (1880).
Classen and v. Reiss, Ber. deutsch. chem. Ges., 14, 1028 (1881).
Moore, Chem. News, 53, 209 (1886).
Brand, Zeit. f. anal. Chem., 28, 581 (1889).
Smith, Am. Chem. Journ., 12, 329 (1890).
Vortmann, Ber. deutsch. chem. Ges., 24, 2749 (1891).
Rüdorff, Zeit. f. angew. Chem., p. 197 (1892).
Smith and Wallace, Ber. deutsch. chem. Ges., 25, 779 (1892).
Warwick, Zeit. f. anorg. Chem., 1, 258, 291 (1892).
Smith and Muhr, Journ. Anal. Chem., 7, 189 (1893).

Classen, Ber. deutsch. chem. Ges., 27, 2060 (1894).
Heidenreich, *ibid.*, 29, 1586 (1896).
Hardin, Journ. Am. Chem. Soc., 18, 990 (1896).
Avery and Dales, Journ. Am. Chem. Soc., 19, 380 (1897).
Wallace and Smith, Journ. Am. Chem. Soc., 19, 870 (1897).
Rimbach, Zeit. f. anal. Chem., 37, 284 (1898).
Smith and Wallace, Journ. Am. Chem. Soc., 20, 279 (1898).
Kollock, Journ. Am. Chem. Soc., 21, 911 (1899).
Balachowsky, Compt. rend., 131, 384 (1900).
Miller and Page, Chem. News, 84, 312 (1901).

The separation of this metal in a compact form, with a bright metallic luster, can be accomplished * by the electrolysis of a solution of the double oxalate which is kept acid by the addition of a cold saturated solution of oxalic acid during the progress of the operation (see under Zinc).

To prepare the double salt, the cadmium compound is dissolved in 20–25 cc water by warming in a platinum dish; a hot solution, which should be previously filtered, of 10 g ammonium oxalate in 80–100 cc water is added and the solution is electrolysed. As soon as the action of the current has begun, several cubic centimeters of oxalic acid are poured upon the watch-glass covering the dish and the liquid is kept weakly acid during the electrolysis.

CONDITIONS FOR ANALYSIS.

Metal present as sulphate.

Substance added: 10 g ammonium oxalate, oxalic acid as described above.

Total volume of solution: 120 cc.

Temperature: 70° to 75°.

Current-density at cathode: $ND_{100} = 0.5$ to 1.0 ampere.

Potential-difference: 3.0 to 3.4 volts.

---

* The condition of the precipitated cadmium, when the directions are closely followed, depends upon the absolute cleanliness of the surface of the cathode.

Time required: about 3 hours. The maximum quantity of metal which can be precipitated is about 0.15 g. Polished dishes give the best results.

The end of the reaction is determined with hydrogen sulphide, by testing a small portion of the solution acidified with hydrochloric acid. The metal must be washed without interrupting the current. (Method of the author.)

Smith and Luckow recommend the precipitation of cadmium from a solution of the chloride or sulphate, which has been saturated with sodium acetate. Eliasberg, who tested this method in the Aachen laboratory, found that the reduction took place readily when the solution, of about 100 cc volume, was treated with about 3 g sodium acetate and a few drops of acetic acid, and the electrolysis was carried out at a temperature of 40–50°.

In the laboratory of the Munich Polytechnic Institute the foregoing method is practiced as follows: The solution, neutralised if necessary, containing not more than 0.5 g cadmium, is treated with 3 g sodium acetate and made weakly acid with acetic acid. The solution is warmed to 45° and electrolysed with a current of $ND_{100} = 0.02–0.07$ ampere. The metal is washed without interrupting the current, and quickly dried at 100°.

During the electrolysis the solution should *not* be warmed above 50°, on account of the formation of basic salts. Cadmium is only partly precipitated from solutions strongly acidified with acetic acid. By this method 0.2 g of cadmium may be separated in about five hours. The presence of nitrates is detrimental.

According to Beilstein and Jawein, the determination of cadmium may be conducted from a solution of the double salt with potassium cyanide. A solution of potassium cyanide is added to the solution of the cadmium salt until the precipitate at first formed is redissolved and a slight excess of potassium cyanide is present. This solution is diluted to 150 cc, and electrolysed at ordinary temperatures with a current of $ND_{100}=0.5$ ampere and a potential-difference of 4.7–5 volts. Time required 6–7 hours. The completion of the precipitation of the cadmium is determined by removing a small quantity of the solution, adding a slight excess of sulphuric acid, boiling to expel the hydrocyanic acid, and testing with hydrogen sulphide. (Classen, Ausgewählte Methoden, p. 112.)

The precipitation of cadmium from a potassium cyanide solution is described by Kollock as follows:

Ten cubic centimeters of a solution of cadmium sulphate, containing 0.1659 g of Cd, was used. and to this 1 g of potassium cyanide was added. The solution was diluted to a volume of 125 cc, and electrolysed at 60° with a current of $ND_{100}=0.04$ to 0.06 ampere and a potential-difference of from 2.9 to 3.2 volts. The cadmium was completely precipitated in about 5 hours.

Vortmann has suggested the determination of cadmium by a method similar to that used for the determination of bismuth and zinc, by precipitation from a solution of the ammonium double salt in the form of amalgam.

A method of determination proposed by E. F. Smith has been described by Wallace and Smith as follows:

0.1329 g of cadmium oxide was dissolved in acetic acid, the solution was evaporated to dryness, and the residue was dissolved in 30 cc of water. This solution was warmed to 50° and electrolysed with a current of $ND_{100}=0.06$ ampere and a potential-difference of 3.5 volts. The metal was completely precipitated in four hours. By adding 1 g of ammonium acetate after the electrolysis had proceeded for about 1 hour the time required for complete precipitation was shortened. The deposit should be washed without interrupting the current.

The same authors also describe the following experiment: 0.1270 g of cadmium oxide was dissolved in 2 cc of sulphuric acid (sp. gr. 1.09), the solution was diluted to 30 cc, and electrolysed for a period of 4½ hours at 50° with a current of $ND_{100} = 0.15$ ampere and a potential-difference of 2.5 volts. The deposited cadmium was washed without interrupting the current, and was in the form of an adherent coating which gave excellent results.

Another method has been proposed by Smith which depends upon the precipitation of cadmium from a solution containing phosphates and free phosphoric acid. It is best illustrated by the following experiment described by Smith and Wallace:

To ten cubic centimeters of a solution of cadmium sulphate, containing 0.1656 g cadmium, 30 cc of a solution of disodium hydrogen phosphate (sp. gr. 1.0358) and 1.5 cc of phosphoric acid (sp. gr. 1.347) were added, the solution was diluted to 100 cc, warmed to 50° and electrolysed with a current of $ND_{100} = 0.06$ ampere and a potential-difference of 3 volts. At the expiration of 4 hours the current was increased to 0.35 ampere and a potential of 7 volts. The metal was completely precipitated at the end of 7 hours, and was bright and adherent.

LEAD.

LITERATURE:

Becquerel, Compt. rend., No. 26 (1854).
Luckow, Dingl. Polyt. Journ., p. 177 (1865).
May, Am. Journ. Science, [3] 6, 255 (1873).
Hampe, *Zeit. f. anal. Chem.*, *13*, 183 (1874).
Parodi and Mascazzini, Ber. deutsch. chem. Ges., *10*, 1098 (1877).

Parodi and Mascazzini, Zeit. f. anal. Chem., 16, 469 (1877);
ibid., 18, 588 (1879).
Riché, Zeit. f. anal. Chem., 17, 219 (1878);
Ann. d. Chim. et Phys., 13, 508 (1878).
Luckow, Zeit. f. anal. Chem., 19, 215 (1880).
Classen, Zeit. f. anal. Chem., 21, 257 (1882).
Schucht, Zeit. f. anal. Chem., 21, 488 (1882).
Riché, Zeit. f. anal. Chem., 21, 117 (1882).
Kiliani, Berg- u. Hüttenm. Zeitung, p. 253 (1883).
Tenny, A. Chem. Journ., 5, 413 (1884).
Smith, Pr. Am. Phil. Soc., 24, 428 (1886).
Brand, Zeit. f. anal. Chem., 28, 581 (1889).
Vortmann, Ber. deutsch. chem. Ges., 24, 2749 (1891).
Rüdorff, Zeit. f. angew. Chem., p. 198 (1892).
Warwick, Zeit. f. anorg. Chem., 1, 258 (1892).
Medicus, Ber. deutsch. chem. Ges., 25, 2490 (1892).
Nissenson, Zeit. f. angew. Chem., p. 646 (1893).
Nissenson and Rüst, Zeit. f. anal. Chem., 32, 424 (1893).
Classen, Ber. deutsch. chem. Ges., 27, 2060 (1894);
Ber. deutsch. chem. Ges., 27, 163 (1894).
Kreichgauer, Ber. deutsch. chem. Ges., 27, 315 (1894);
Zeit. f. anorg. Chem., 9, 89 (1895).
Nissenson and Neumann, Chem. Ztg., 19, 177, 1143 (1895).
Neumann, Chem. Ztg., p. 381 (1896).
Hollard, Bull. Soc. Chim., 19, 911 (1898).
Nissenson, Chem. Ztg., 23, 868 (1900).
Marie, Chem. Ztg., 24, 314, 480 (1900).
Linn, Journ. Am. Chem. Soc., 24, 435 (1902).

If a solution of a lead salt containing an excess of ammonium oxalate be electrolysed warm, the lead separates at the negative electrode, adheres firmly, and shows its characteristic metallic properties; but it oxidises partially on washing with water and alcohol, so that the results are always too high. The precipitation of lead as amalgam presents some difficulties, inasmuch as some lead peroxide separates at the positive electrode and must be dissolved. According to G. Vortmann, the aqueous solution of the lead salt, containing sufficient mercuric chloride to produce the amalgam, is treated with 3–5 g sodium acetate and a few cubic centimeters of concentrated potassium nitrite solution. The precipitate produced by the latter reagent (which is added to prevent the formation of peroxide) is dissolved in acetic acid, and the clear yellow solution diluted and electrolysed. If lead peroxide appears on the positive electrode during the reaction, more potassium nitrite is added. The end of the reaction is determined by testing with ammonium sulphide. As lead amalgam oxidises rather readily when moist, it is *quickly washed with water, alcohol, and ether, dried by the* warmth of the hand and by blowing upon it, and finally in the desiccator.

The amalgam may also be separated from an aqueous solution acidified with nitric acid. However, as free nitric acid favors the formation of lead peroxide, more frequent addition of potassium nitrite is necessary, and complete precipitation is thereby seriously hindered.

In a solution containing free nitric acid, lead is acted on like manganese; it is oxidised, and separates as hydrated peroxide at the positive electrode. If there is no other metal in the solution, it must contain at least 10 per cent. free nitric acid, according to Luckow; in the presence of other metals *(mercury, copper, etc.), the oxidation is complete even in* the presence of little nitric acid.

In the Munich laboratory experiments have been conducted as to the quantity of nitric acid (sp. gr. 1.36), and have demonstrated that this depends on the temperature and the current-density which is used. The current-density depends in turn on the condition of the surface of the positive electrode. If this is very smooth, a current of $ND_{100}=0.05$ is sufficient, otherwise one of $ND_{100}=0.5$ is needed to produce an adherent precipitate. When $ND_{100}=0.05$ ampere, 2 per cent. by volume of nitric acid should be added when the solution is heated, and 10 per cent. by volume at ordinary temperatures. When $ND_{100} = 0.5$ the volume-percentages are, respectively, 7 and 20 for heated and cool solutions.

Heating the solution to about 50° materially assists the separation. The precipitate may be washed without loss, after the current is interrupted.

Chlorine compounds must not be present in the solution for electrolysis.

Even when the stated conditions are observed, the quantity of lead which can be precipitated as peroxide in an adherent form is relatively small.* The rapid separation of large quantities of lead peroxide, firmly adherent like a metal, may only be carried out without difficulty, as the author's researches have shown, when the inside of the platinum dish serving as anode is roughened with a sand-blast.† By the use of such dishes it is possible, with a current of 1.5 ampere, to precipitate in a few hours as much as 4 g of lead peroxide on 100 sq. cm of surface.

For conducting the determination of lead, after the solution of the lead salt has been accomplished, 20 cc nitric acid (sp. gr. 1.35–1.38) are added, the solution is diluted to about 100 cc, warmed to 60–65°, and electrolysed with a current of $ND_{100} = 1.5$–1.7 amperes. If the warming is continued during the electrolysis, the precipitation of quantities up to 1.5 g lead peroxide is completed in about 3 hours; with larger quantities in about 4–5 hours. Complete precipitation is

---

* From experience in the Aachen laboratory, the greatest possible quantity is 0.15 g PbO_2 per 100 sq. cm surface, while according to the statements of Dr. Cohen (Chem. Ztg., 1893, No. 98) as much as 0.3 g can be precipitated.

† The platinum refinery of G. Siebert in Hanau has faultlessly carried out the roughening in the desired manner at the request of the author. Such roughened dishes are of course applicable to all other electrolytic determinations.

insured by adding about 20 cc of water and observing whether the freshly wetted surface of the electrode becomes darker. In case no blackening is observed at the end of 10–15 minutes, the current is stopped and the precipitate is washed with water and alcohol and dried at 180–190°. The residue is anhydrous peroxide.

CONDITIONS FOR ANALYSIS.

Metal present as acetate or nitrate.

Substance added: at least 10% (by volume) of nitric acid (sp. gr. 1.35).

Total volume of solution: 120 cc.

Temperature: 60° to 70°.

Current-density at anode: $ND_{100} = 1.0$ to 2.0 amperes.

Potential-difference between electrodes: 2.3 to 2.7 volts.

Time required: 3 to 5 hours.

Where the quantity *of peroxide to be separated* is at all considerable, roughened dishes must be used.

EXPERIMENT.

Used lead nitrate (Pb = 72.21%) dissolved in 100 cc water, with the addition of 20 cc nitric acid (sp. gr. 1.35–1.38).

Current-density, Amperes.	Electrode Potential, Volts.	Temp.	Time.	Found.
1.55–1.45	2.43–2.4	60–65°	1 hr. 5 m.	72.20 %
1.6 –1.58	2.48–2.43	60–65°	1 " 10 "	72.10 "
1.6 –1.65	2.41–2.36	60–65°	1 " 5 "	72.20 "

Under these conditions lead can be separated from zinc, iron, cobalt, nickel, aluminium, and magnesium, which remain in solution, and also from copper, antimony, gold, mercury, and cadmium, which are wholly or partially precipitated on the cathode. Silver and bismuth, which separate partly as metals on the cathode and partly as oxides on the anode, interfere with the determination; but if 20% *of nitric acid is contained in the solution these latter ele-*

ments do not interfere with the results unless present in considerable quantity.

The presence of arsenic is very objectionable, and when enough (0.05 g) is present no lead is deposited as peroxide, but instead it is precipitated as metal mixed with arsenic on the cathode. If the electrolysis is continued for some time the arsenic is gradually eliminated from the solution as arseniuretted hydrogen and the precipitated metals again pass into the solution. If the electrolysis is conducted for a sufficiently long period, all of the lead will ultimately be precipitated as peroxide on the anode. The effect of selenium is similar to that of arsenic. In conducting separations, the solution should always contain 20% of nitric acid.

In the analysis of substances containing lead and sulphur, especially when, as is often necessary, these are decomposed with nitric acid, a precipitate of insoluble lead sulphate is frequently obtained. Lead sulphate can be brought readily into solution under conditions suitable for the electrolytic determination of the lead by the following treatment: A slight excess of ammonia is added and the mixture is warmed for a short time; this converts the lead sulphate into porous lead hydroxide. With constant stirring, the mixture is now poured, little by little, into a platinum dish containing about 20 cc of warm nitric acid, and the lead sulphate which reappears either dissolves immediately or, if the quantity is large, the greater part goes at once into solution and the remainder dissolves slowly on warming the solution for a short time. The vessel in which the decomposition of the lead sulphate has been conducted is first washed with a little nitric acid and then with water, the washings being added to the solution in the platinum dish.

THALLIUM.

LITERATURE:

Schucht, Zeit. f. anal. Chem., **22**, 241, 490 (1883).
Neumann, Ber. *deutsch. chem.* Ges., **21**, 356 (1888).

This metal can be completely precipitated from an ammonium oxalate solution.

The properties of thallium, however, are similar to those of lead; its determination, therefore, requires special consideration.

G. Neumann, in connection with a research on certain double salts of thallium in the Aachen laboratory, has also investigated the quantitative determination of the metal. As his method is of value in the investigation of thallium compounds, it is here described. The process is based on precipitation of the thallium as metal, and determination of the volume of hydrogen set free by its solution in hydrochloric acid.

The apparatus shown in Fig. 92 is used for the process. *k* is a flask of about 100 cc capacity, containing platinum-foil electrodes of 9 sq. cm surface, terminating in contact-wires fused into the glass. The thallium salt and about 5 g ammonium oxalate are dissolved in this flask and electrolysed, after dilution, with a current of 0.1 ampere. The completion of the reaction is ascertained by testing with am-

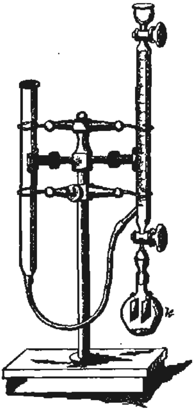


FIG. 92.

monium sulphide. As the ammonium oxalate is converted into carbonate by the current, and the measuring-tube would be insufficient to contain the liberated carbon dioxide, the solution remaining in the flask is removed after the reaction. This may readily be done by the use of two siphons. Neumann's automatic arrangement for this purpose is shown in Fig. 93; it is very convenient where many determinations are to be performed, and its operation is easily seen from the figure. The washing is conducted without interrupting the current. To remove the gas bubbles clinging to the electrode it is desirable to heat the flask a short time after the washing is complete. The flask is then connected to the measuring-tube, the thallium dissolved, and the hydrogen collected and measured in the usual way.

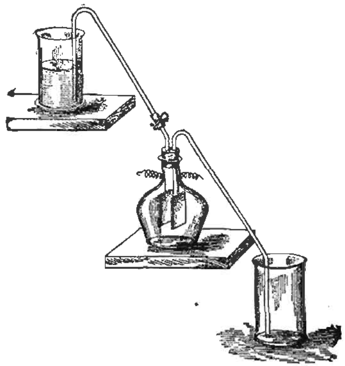


FIG. 93.

SILVER.

LITERATURE:

Luckow, Dingl. Polyt. Journ., 178, 43 (1880);
Zeit. f. anal. Chem., 19, 15 (1880).
Fresenius and Bergmann, Zeit. f. anal. Chem., 19, 342 (1880).
Schucht, Zeit. f. anal. Chem., 19, 316 (1880).
Krutwig, Ber. deutsch. chem. Ges., 15, 1267 (1882).
Kinnicutt, Am. Chem. Journ., 4, 22 (1882).
Schucht, Zeit. f. anal. Chem., 22, 417 (1883).
Smith, Journ. Anal. Chem., 3, 254, 385 (1889).
Frankel, Am. Chem. Journ., 11, 264, 352 (1890).
Smith, Am. Chem. Journ., 12, 335 (1891).
Rüdorff, Zeit. f. angew. Chem., p. 5 (1892).
Smith and Spencer, Elektrochem. Zeit., 1, 542 (1894).
Eisenberg, *Dissertation*, Heidelberg (1895).
Hardin, Journ. Am. Chem. Soc., 18, 990 (1896).
Kollock, Journ. Am. Chem. Soc., 21, 911 (1899).
Fulweiler and Smith, Journ. Am. Chem. Soc., 23, 582 (1901).
Gooch and Medway, Am. Journ. of Science, April, 1903.

Of the methods proposed for the determination of silver the one suggested by Luckow (separation of the silver from the potassium double cyanide) is probably the most suitable If insoluble silver compounds (silver chloride, silver oxalate are to be analysed, they are dissolved in potassium cyanide solution. For conducting the method, 3 g potassium cyanide are added to the solution, which is then diluted to 100–120 cc Eisenberg, who tested the method in the Aachen laboratory was convinced that its successful performance, as well as the metallic condition of the precipitated silver, depends upon the purity of the potassium cyanide used. Even the so-called "purissimum" potassium cyanide of commerce is unsuited It is therefore desirable to prepare pure potassium cyanide by passing hydrocyanic acid gas into an alcoholic solution of potassium hydroxide.

CONDITIONS FOR ANALYSIS.

Metal present as nitrate or sulphate.

Substance added: 3 g of *pure* potassium cyanide.

Total volume of solution: 100 to 120 cc.

Temperature: 20° to 30°.

Current-density at cathode: $ND_{100}=0.2$ to 0.5 ampere.

Potential-difference: 3.7 to 4.8 volts.

Time required: 1½ to 5 hours.

For this determination roughened dishes give best results.

J. Krutwig treats the solution of the silver salt with ammonia in slight excess, adds ammonium sulphate, and electrolyses.

In the Munich laboratory the following conditions have been determined for the preceding process. The solution, which must not contain more than 0.5 g silver, is treated with 20 per cent. by volume of ammonia (sp. gr. 0.96) and 5% ammonium sulphate solution (1 : 10), warmed, and electrolysed with a current of $ND_{100}=0.02$–0.05 ampere. After the current is stopped the precipitate must be very thoroughly washed to completely remove the ammonium sulphate.

Fresenius and Bergmann have found that silver can also be precipitated in a dense form from a solution containing nitric acid: 20 cc of nitric acid (sp. gr. 1.2) are added to the silver solution, which is then diluted with water to about 200 cc and electrolysed.

According to results in the Munich laboratory, it is desirable to add to the solution, which may contain as much as 0.4 g silver, 3 per cent. by volume of nitric acid, sp. gr. 1.36, and to electrolyse the heated solution with a current of $ND_{100}=$ 0.04–0.05 ampere. The silver must be carefully washed without interrupting the current, to prevent loss. An insuf-

ficient quantity of nitric acid may lead to the formation of peroxide.

Silver can be obtained as a white strongly adhering deposit on roughened dishes by electrolysing a solution containing 1 to 2 cc of nitric acid (sp. gr. 1.4) and 5 cc of alcohol, if the potential-difference between the electrodes is carefully regulated so as to be within the limits 1.35–1.38 volt. The time required for precipitation is from 6 to 8 hours, and depends but little on the amount of silver contained in the solution. A quantity of from 0.1 to 0.5 gram of silver is convenient, but the quantity may be as great as 2 grams. The chief factor of importance is the potential-difference, which must be kept within the limits specified, since an increase to even 1.4 volt causes the silver to separate in a spongy form, which is useless for quantitative determination.*

Kollock describes an experiment under the following conditions: 0.1270 g of silver, present as nitrate, 0.5 to 1 g of potassium cyanide, temperature 65°, total volume 100 cc, $ND_{100}=0.04$ to 0.07, potential-difference 2.5 to 3.2 volts, time required 3 to 5 hours.

A further experiment is described by Fulweiler and Smith as follows: 0.2133 g silver present, 2 g potassium cyanide added, total volume 125 cc, temperature 60–65°, $ND_{100}=0.03$–0.04, potential-difference 2.5–2.7 volts, time required for complete precipitation of the silver 3–4 hours.

For the determination of silver by precipitation on a rapidly rotating cathode (p. 124), Gooch and Medway used a solution prepared by adding to 50 cc of a silver nitrate solution enough potassium cyanide to dissolve the silver cyanide at first formed. Three cubic centimeters of dilute sulphuric acid were then run in, and enough ammonia was

---

* Classen, Ausgewählte Methoden, p. 3.

added to make the solution strongly alkaline. The weight of silver taken varied from 0.0968 to 0.1898 g, and the electrolysis was conducted with a current of 1.8–3 amperes (equivalent to $ND_{100}=6–10$ amperes). The time required for the complete precipitation of the silver was from 8 to 15 minutes.

MERCURY.

LITERATURE:

Clarke, Am. Journ. Science, 16, 400 (1878);
Ber. deutsch. chem. Ges., 11, 1140 (1878).
Luckow, Zeit. f. anal. Chem., 19, 14 (1880).
Classen and Ludwig, Ber. deutsch. chem. Ges., 19, 323 (1886).
Hoskinson, Am. Chem. Journ., 8, 209 (1886).
Smith and Kneer, Am. Chem. Journ., 8, 206 (1886).
Smith and Frankel, Am. Chem. Journ., 11, 264 (1889).
Smith, Journ. Anal. Chem., 5, 202 (1891).
Smith and Cauley, Am. Chem. Journ., 12, 428 (1891);
Journ. Anal. Chem., 5, 489 (1891).
Vortmann, Ber. deutsch. chem. Ges., 24, 2749 (1891).
Frankel, Journ. Franklin Inst., 131, 144 (1891).
Brand, Zeit. f. angew. Chem., p. 202 (1891).
Freudenberg, Zeit. f. phys. Chem., 12, 110 (1891).
Rüdorff, Zeit. f. angew. Chem., p. 5 (1892).
Smith and Moyer, Journ. Anal. Chem., 7, 252 (1893).
Smith and Wallace, Journ. Anal. Chem., 7, 189 (1893).
Schmucker, Journ. Am. Chem. Soc., 15, 204 (1893).
François, Journ. Pharm. et Chim., [5] 30, 240 (1894).
Eisenberg, Dissertation, Heidelberg (1895).
Rising and Lehner, Berg- u. Hüttenm. Ztg., 55, 175 (1896).
Wallace and Smith, Journ. Am. Chem. Soc., 18, 169 (1896).
Hardin, Journ. Am. Chem. Soc., 18, 990 (1896).
Schmucker, Zeit. f. anorg. Chem., 5, 206 (1896).
Fernberger and Smith, Journ. Am. Chem. Soc., 21, 1001 (1899).
Kollock, Journ. Am. Chem. Soc., 21, 911 (1899).
Bindschedler, Zeit. f. Elektrochem., 8, 329 (1902).
Glaser, Zeit. f. Elektrochem., 9, 11 (1903).

The metal can be readily separated from solutions of the *mercuric* salts to which 4–5 g *ammonium oxalate* have been added (method of the author). If the mercury is present as chloride in the solution, the electrolysis is continued until mercurous chloride disappears from the positive electrode.

CONDITIONS FOR ANALYSIS.

Substance added: 4 to 5 g ammonium oxalate.
Total volume of solution: 120 to 150 cc.
Temperature: 16° to 40°.
Current-density at cathode: $ND_{100} = 1.0$ ampere.
Potential-difference: 5.5 volts.
Time required: 2 hours.

Roughened dishes are preferable to polished, on account of the more uniform distribution and firmer adherence of the mercury to the cathode. On polished dishes the mercury separates in the form of small globules.

EXPERIMENT.

Subst. Used. $HgCl_2$, g.	Current-density, Amperes. ND_{100}	Electrode Potential, Volts.	Temp.	Time, hrs.	m.	Found. %	Remark.
0.4068	0.2 –0.15	2.6 –3.35	30–23°	5	15	73.74	Roughened Dish.
0.4073	1.02–0.93	4.05–4.75	29–37°	1	30	73.63	
0.4076	1.08–0.92	4.42–4.88	25–40°	2	5	73.77	
0.4080	1.15–1.09	4.97–5.05	18–40.5°	2	5	73.87	
0.4080	1.12–0.93	4.95–4.85	18–38°	2	5	73.84	
0.4080	1.52–0.48	3.65–4.65	16–27°	3	55	73.67	
0.4070	0.2 –0.23	2.89–3.75	28–24°	5	15	73.80	Polished Dish.
0.4073	1.06–0.95	4.45–5.00	30–39.5°	1	30	73.29	
0.4076	1.16–1.09	5.32–5.53	23–40°	2	5	73.93	
0.4080	1.20–0.99	4.70–4.90	18–43°	3	—	73.55	
0.4075	1.51–0.48	3.87–4.50	16–30°	3	55	73.85	

Theory 73.85% Hg.

Mercury may also be quantitatively precipitated from a *solution containing nitric, sulphuric, or hydrochloric acid.* If no other metal than mercury is present, 1–2 per cent. by volume of nitric acid is sufficient; while in the presence of other metals, which are not precipitated from solutions containing free acid, 5 per cent. by volume is required. In the latter case a current-density not greater than 0.5 ampere is employed; in the former the current-density may be raised to 1 ampere. Time, about 2 hours.

The precipitation of mercury from a nitric acid solution is described by Kollock as follows: 0.1403 g of mercury was dissolved in 3 cc of concentrated nitric acid, the solution was diluted to 125 cc and electrolysed, at 70°, with a current of $ND_{100}=0.06$ *ampere and a potential-difference of 2 volts.* The mercury was completely precipitated in 2 hours.

The same author describes the precipitation of mercury from a sulphuric acid solution under the following conditions: To a solution containing mercuric chloride equivalent to 0.1403 g of Hg, 1 cc of concentrated sulphuric acid was added, and the solution, after dilution to 125 cc, was electrolysed at 65° with a current of $ND_{100}=0.4$–0.6 ampere and a potential-difference of 3.5 volts. The precipitation of the mercury was complete in 1 hour.

If hydrochloric acid is used, only a few drops are added, since larger quantities have a detrimental action on the separation of the metal. *Large quantities of chlorides have an* action similar to that of large quantities of hydrochloric acid.

Insoluble mercury compounds may be easily electrolysed by suspending them in water slightly acidified with hydrochloric acid, or in a dilute solution of sodium chloride (about 10 per cent.). This process, originated by the author, is used at Almadèn for determining the amount of mercury contained in cinnabar.

François has shown that in a similar manner the iodide, iodate, chloride, and bromide can be electrolysed in the solid state. 0.5 g of the solid iodide was introduced into a platinum crucible, which served as cathode, and 20 cc of a solution of 20 g of ammonium nitrate in 100 cc ammonia was added. The anode was a platinum wire 1 mm in diameter, which dipped for a distance of only 1 mm into the liquid. The contents of the crucible were stirred from time to time with a glass rod. The washing was conducted first with ammonia and then with water, the liquids being allowed to stand in contact with the precipitated mercury for some time. Finally the cathode was washed with alcohol and ether and dried at a low temperature. For exact results the anode should be weighed before and after the electrolysis to determine any loss of platinum from this.*

Edgar F. Smith has described the determination of mercury by the electrolysis of a solution containing potassium cyanide. The solution of the mercuric salt, which may contain about 0.2 g mercury, is treated with 0.25–2 g of potassium cyanide, diluted with water to 175 cc, and submitted to electrolysis.

Heidenreich, working in the Aachen laboratory, has determined the following conditions for this method.

CONDITIONS FOR ANALYSIS.

Metal present as mercuric salt.
Substance added: 2 to 3 g potassium cyanide.
Total volume of solution: 175 cc.
Temperature: that of room.
Current-density: $ND_{100} = 0.03$ to 0.08 ampere.
Potential-difference: 1.65 to 1.75 volt.
Time: about 5 hours.

---

* Classen, Ausgewählte Methoden, p. 50.

The metal reduced by this method must be washed with water only, and not with alcohol, since when the latter is used, small quantities of mercury will become loosened and will be carried away.

The following experiment has been described by Kollock: Mercuric chloride equivalent to 0.1439 g mercury, 0.5 g potassium cyanide, total volume 100 cc, temperature 65°, current-density $ND_{100}=0.02-0.07$ ampere, potential-difference 1.6–3.2 volts, time required 3–6 hours. The mercury was completely precipitated.

Smith and Wallace describe the precipitation of mercury from a sodium sulphide solution under the following conditions: To a solution containing 0.1913 gram of mercury as chloride there was added 20 cc of a sodium sulphide solution (sp. gr. 1.22). The total volume of the solution was 125 cc. The electrolysis was carried out at a temperature of 65° with a current of $ND_{100}=0.13$ ampere. The mercury was completely precipitated in 3 hours.

GOLD.

LITERATURE:

Persoz, *Annal. Chim. Pharm.*, 65, 164 (1848).
Luckow, Zeit. f. anal. Chem., 19, 14 (1880).
Bruhnatelli, Phil. Mag., 21, 187 (1886).
Smith and Muhr, Ber. deutsch. chem. Ges., 23, 2175 (1890).
Smith, Journ. Anal. Chem., 5, 204 (1891).
Frankel, Journ. Franklin Inst., 1891.
Smith and Wallace, Ber. deutsch. chem. Ges., 25, 779 (1892).
Smith, Am. Chem. Journ., 13, 206 (1892).
Smith and Muhr, Am. Chem. Journ., 13, 417 (1892).
Rüdorff, Zeit. f. angew. Chem., p. 695, (1892).
Kollock, Journ. Am. Chem. Soc., 21, 911 (1899).

Gold may be separated in a compact form from solutions of gold salts containing potassium cyanide. To form the double cyanide, about 3 g of potassium cyanide are added. The solution is then electrolysed at ordinary temperatures or at temperatures between 50° and 60°. Since it is generally supposed that the gold can be removed from the platinum dish with *aqua regia* only (an operation by which the platinum is also dissolved), platinum dishes coated with a thin deposit of silver have previously been used for this determination. According to a private communication from D. W. Dupré, of Stassfurt, the gold may be readily removed from the platinum dishes by warming with a solution of chromic anhydride in saturated sodium chloride solution. The author can confirm this statement; in this operation gold only, and no platinum, goes into solution. According to Smith, the deposited gold can be removed from the cathode by allowing it to stand in contact with dilute potassium cyanide solution, the electrode being connected as anode with a source of feeble current.

Since the conditions for the separation of gold from double cyanides had not been previously determined, they were ascertained by Dr. v. Wirkner at the suggestion of the author.

CONDITIONS FOR ANALYSIS.

Substance added: 3 g potassium cyanide.

Total volume of solution: 120 cc.

Temperature: 50° to 60°; the electrolysis can also be conducted at room temperature, but this is undesirable, since a brownish decomposition product of potassium cyanide often separates.

Current-density at cathode: ND_{100} = 0.3 to 0.8 ampere.

Potential-difference: 2.7 to 4 volts.

Time required: for warm solutions 1½ hour, for cold solutions from 4 to 5 hours.

EXPERIMENT.

A solution of chloride of gold of unknown strength was used. The electrolyses were carried out in roughened platinum-iridium dishes without a coating of silver. Used 3 g potassium cyanide, 120 cc liquid.

Taken, cc. Gold Chloride Sol.	Current-density. Amperes.	Electrode Potential. Volts.	Temperature.	Time. hr. m.	Found. g.
15	0.3	3.5–3.9	20–27°	5 —	0.0545
15	0.35	3.9–4.0	22–28°	14 (overnight)	0.0548
30	0.37	3.6–3.9	20–28°	4 15	0.1090
15	0.38	2.7–3.8	52–55°	1 30	0.0544
15	0.38	2.7–3.4	53–54°	1 20	0.0546
15	0.39	2.7–3.8	52–56°	1 30	0.0545
15	0.85	4.0–4.1	52–56°	1 30	0.0544

Smith states * that gold can be satisfactorily precipitated from a solution containing sodium sulphide (sp. gr. 1.18) by a current of 0.1–0.2 ampere when the total volume is about 125 cc.

ANTIMONY.

LITERATURE:

Böttcher, Journ. f. prak. Chem., 73, 484 (1858).
Gore, Chem. Gazette, 16, 59 (1858).
Wrightson, Zeit. f. anal. Chem., 15, 300 (1876).
Parodi and Mascazzini, *ibid.*, 18, 588 (1879).
Luckow, *ibid.*, 19, 13 (1880).
Chittenden and Blake, Trans. Conn. Acad. Science, 7, 276 (1880).
Classen and v. Reiss, Ber. deutsch. chem. Ges., 14, 1622 (1881); *ibid.*, 17, 2467 (1884).
Classen and Ludwig, Ber. deutsch. chem. Ges., 18, 1104 (1885).
Lecrenier, Chemiker Zeitung, 13, 1219 (1888).
Vortmann, Ber. deutsch. chem. Ges., 24, 2762 (1891).
Sanderson, Ber. deutsch. chem. Ges. (Ref.) p. 340 (1891).
Smith and Muhr, Journ. Anal. Chem., 5, 448 (1891); Journ. Anal. Chem., 7, 189 (1893).

---

* Electro-Chemical Analysis (1902), p. 111.

Rüdorff, Zeit. f. angew. Chem., p. 199 (1892).
Classen, Ber. deutsch. chem. Ges., 27, 2060 (1894).
Hollard, Ecl. électr., 26, 165 (1900).
Ost and Klapproth, Zeit. f. angew. Chem., p. 827 (1900); Zeit. f. Electrochem., 7, 376 (1900).

Antimony is precipitated from a hydrochloric acid solution, but not in an adherent form. If potassium oxalate is added to the solution of the trichloride, antimony is easily reduced, but adheres even less firmly than in the former case. *An adherent metallic deposit can be obtained by adding potassium tartrate,* but the separation is then too slow.

The precipitation of antimony from the solutions of its sulpho-salts is complete and satisfactory. *If ammonium sulphide is used to produce a double salt, it must contain* neither free ammonia nor polysulphides. Ammonium hydrosulphide, therefore, is convenient for the determination; it should be kept in small tightly corked bottles.

When a solution of antimony containing ammonium sulphide is electrolysed, there is formed over the metal a coating of sulphur which cannot be washed off with water. When the metal is washed afterward with alcohol, the thin coating of sulphur can be removed by rubbing with the finger or a handkerchief moistened with alcohol, without danger of loss.

The use of ammonium sulphide has the disadvantage that, when several determinations are made together, the odor becomes unbearable. For this reason the author has made a series of experiments with potassium and sodium monosulphide and hydrosulphide, the results of which show that the precipitation of antimony from double salts with these compounds proceeds satisfactorily. As sodium sulphide (Na_2S) is one of the salts named which is most desirable for facilitating the separation of antimony from tin and arsenic, the following particulars relate exclusively to the use of this salt[*] for the determination of antimony.

The following equations probably represent the reactions which take place in the electrolysis of the antimony sulpho-salt.

At the cathode:

$$Sb_2S_3 + 3Na_2S + 6H = 2Sb + 6NaHS.$$

At the anode:

$$6\,NaHS + 3O = 3Na_2S_2 + 3H_2O.$$

The reduction of antimony from the prepared sulpho-salts can be carried out as well at ordinary as at higher temperatures. *In the first case the determination requires* 17–18 hours, in the latter about 2 hours. If the separation is conducted in polished dishes, only relatively small quantities of the metal can be made to adhere firmly to the dish, and the employment of weak currents is necessary. In recent experiments roughened dishes have been used, and the precipitation has been conducted from hot solutions and with stronger currents.

To carry out the analysis, 80–100 cc of a solution of sodium monosulphide (sp. gr. about 1.14) are added to the antimony solution, which is diluted with water to 120 cc and *electrolysed. If the metal is precipitated from a warm* solution, it must be washed without interrupting the current. The end of the reaction can only be determined with certainty by the use of another electrode which is dipped into the liquid and brought into contact with the dish, *i.e.*, the cathode.[†]

---

[*] For the preparation of this salt, see section on Reagents.

[†] See page 130

The dish with the separated antimony is treated in the usual way with water and perfectly pure absolute alcohol, dried for a short time in the air-bath at 80–90°, and weighed.

CONDITIONS FOR ANALYSIS.

Composition and volume of the solution as described above:

A.

Temperature: ordinary room temperature.
Current-density at cathode: $ND_{100} = 0.3$ to 0.35 ampere.
Potential-difference: 1.0 to 1.8 volts.
Time required: 17½ hours.

B.

Temperature: 55° to 70°.
Current-density at cathode: $ND_{100} = 1.0$ to 1.5 amperes.
Potential-difference: 1 to 2 volts.
Time required: 2½ hours.

The method of determining antimony in solutions of the polysulphides of the alkalies is very simple. The solution containing polysulphides is treated with an excess of ammoniacal hydrogen peroxide and heated till it becomes colorless. If a great excess of hydrogen peroxide is used, it may happen that the alkali sulphide is entirely decomposed and antimony sulphide precipitated. If the solution is entirely colorless, or if a precipitate of antimony sulphide has already appeared, the solution is cooled, 80 cc of a solution of sodium monosulphide are added, the whole is diluted with water to about 120–150 cc and electrolysed as above directed.

According to Lecrenier, the presence of polysulphides can be counteracted by adding 50 cc to 75 cc of a solution *of sodium sulphite (20%) and heating until* the liquid is colorless. This reaction depends upon the formation of sodium thiosulphate from the sulphite, sulphide, and sulphur of the polysulphides.

TIN.

LITERATURE:

Luckow, Zeit. f. anal. Chem., 19, 13 (1880).
Gibbs, Chem. News, 42, 291 (1880).
Classen and v. Reiss, Ber. deutsch. chem. Ges., 14, 1622 (1881).
Classen, Ber. deutsch. chem. Ges., 17, 2467 (1886); 18, 1104 (1887).
Bongartz and Classen, *ibid.*, 21, 2900 (1888).
Freudenberg, Zeit. f. phys. Chem., 12, 121 (1891).
Rüdorff, Zeit. f. angew. Chem., p. 196 (1892).
Classen, Ber. deutsch. chem. Ges., 27, 2060 (1894).
Engels, Zeit. f. Elektrochemie, 2, 418 (1895–96).
Heidenreich, Ber. deutsch. chem. Ges., 28, 1586 (1895).
Campbell and Champion, Journ. Am. Chem. Soc., 20, 687 (1898).
Ost and Klapproth, Zeit. f. angew. Chem., p. 817 (1901).

Tin separates completely from a solution containing the ammonium double oxalate, or from an ammonium sulphide solution. Sodium and potassium sulphides cannot be used, *as tin separates only partially from a dilute solution of the* corresponding sulpho-salt, and not at all from a concentrated solution.

If tin is precipitated from the ammonium double oxalate, a separation of stannic acid readily occurs, especially when much tin is present, which must be redissolved by addition of oxalic acid. The reduction of tin may be carried out without difficulty, however, if *acid* ammonium oxalate is used instead of the neutral oxalate. The results obtained by this process are so accurate that the author has found it adapted *to the determination of the atomic weight of tin.*

The solution of tin is treated with a cold saturated solution of acid ammonium oxalate in the proportion of 20 cc to

0.1 g tin. The solution is diluted to about 150 cc and electrolysed. The tin is completely precipitated as a closely adherent, shining, silver-white metal, even when as much as 6 g is present. The current is interrupted and the metal washed as usual with water and alcohol, and dried at 80–90°.

CONDITIONS FOR ANALYSIS.

Composition and volume of the solution as described above.
Temperature: ordinary room temperature.
Current-density at cathode: 0.2 to 0.6 ampere.
Potential-difference: 2.7 to 3.8 volts.
Time required: 8 to 10 hours.

EXPERIMENT.

Used 0.9–1 g $SnCl_4.2NH_4Cl$ [32.10% Sn], 120 cc of a saturated solution of acid ammonium oxalate.

Current-density, Amperes.	Electrode Potential, Volts.	Temp.	Time.	Found.
0.2–0.3*	2.7–3.8	25°	8 hr. 5 m.	32.06%
0.3–0.6	2.8–3.8	30–35°	9 " 45 "	32.00 "

If larger quantities of the tin salt are used, it is necessary to add acid ammonium oxalate from time to time, on account of the decomposition of the acid ammonium oxalate, which causes the solution to react alkaline. According to recent investigations, the determination of tin may be carried out by treating the solution of the tin salt with neutral ammonium oxalate to form the double salt, acidifying with oxalic acid and electrolysing warm.

Heidenreich, who tested this method in the Aachen laboratory, found that the determination of tin can be completed in 4–4½ hours. 4 g ammonium oxalate to every 0.3 g tin present are added to the solution, which is then acidified with 9–10 g oxalic acid, warmed to 60–65°, and electro-

---

* Finally increased to 0.5 ampere.

lysed with a current of $ND_{100} = 1$–1.5 amperes. The precipitate *must be washed without interrupting the current.*

Instead of oxalic acid, acetic acid may be used; it possesses, however, no advantages. 100 cc of a saturated solution of ammonium oxalate are added to the solution of the tin salt, which is then acidified with 25 cc acetic acid (sp. gr. 1.0615; about 50%). The metal is precipitated in the form of radiated crystals, in contrast to the precipitate from acid ammonium oxalate solutions. *Tin adheres better to roughened than to polished dishes.*

The following experiments were conducted by the acetic acid method:

Current-density, Ampere.	Electrode Potential, Volts.	Temp.	Time.	Found.
0.3 increased to 0.5	3.2–3.8	25°	6 hr. 15 m.	32.00%
0.5 " " 1.0	3.6–4.2	25–30°	5 " 45 "	32.01 "

In these experiments the tin in the polished dishes appeared brilliantly crystalline, and in the roughened dishes silver-white.

Since tin, like zinc, is dissolved with difficulty from the platinum dishes by acids, it is necessary to use fused acid potassium sulphate to remove it.* It is therefore best to precipitate the tin in coppered dishes (see Zinc).

Engels worked out the following method in the Aachen laboratory: The tin salt is dissolved in water containing a few cubic centimeters of oxalic acid, and 0.3–0.5 g hydroxylamine, 2 g ammonium acetate, and 2 g tartaric acid are added for every 0.5–1.2 g tin salt taken. The solution is then diluted to 150 cc, warmed to 60–70°, and electrolysed with a current

---

* The removal of the deposited tin from the electrode can usually be effected without difficulty by warming with a mixture of 5 g tartaric acid, 8 cc water, and 2 cc of concentrated nitric acid.

of $ND_{100} = 0.7$ to 1.0 ampere and a potential-difference of 4 to 5 volts. Under these conditions the time required for complete precipitation of the tin is 3 to 5 hours.

EXPERIMENT.

$SnCl_4 \cdot 2NH_4Cl$, g.	Current-density, Amp.	Electrode Potential, Volts.	Temp.	Time.	Found.		Calculated.
					g.	Per Cent.	
0.9175	1–0.8	5.2–5.6	70°	3 hr.	0.2970	32.37	32.37%
0 9859	1–0.8	4.8–5.3	63°	3 "	0.3195	32.40	"
0.9050	1–0.9	5.0–5 6	65°	3 "	0.2931	32.30	"
1.1879	0.5	5.1–6.0	45°	6 "	0.3847	32.38	"
1.0026	0.7	3.4	60°	3 "	0.3238	32.36	"
0.9940	0.7	4.0	60°	3½ "	0.3219	32.38	"
1.0024	0.8	4.6	60°	3 "	0.3250	32.42	"
1.0022	0.8	4.2–4.4	60°	3 "	0.3252	32.44	"

In the solution of the ammonium sulpho-salt tin behaves like antimony. The tin solution (if necessary after neutralisation with ammonia) is treated with ammonium sulphide free from ammonia (no more is added than is needed to form the sulpho-salt), diluted to 150–175 cc, warmed to 50–60°, and electrolysed with a current of 1–2 amperes, at a potential-difference of 3.5–4 volts. Under these conditions 0.3–0.4 g of tin can be reduced in an hour. Sometimes a deposit of sulphur adheres so strongly to the tin at the edge of the dish that it cannot be washed off with water; it may, however, be easily removed, after washing with alcohol, by gentle rubbing with a linen cloth.

In gravimetric analysis tin is often separated from other metals by sodium sulphide instead of ammonium sulphide. In order to determine the tin electrolytically in such cases, the sodium sulphide must be converted into ammonium sulphide.* To accomplish this, the solution is treated with about 23 g pure ammonium sulphate free from iron, and

---

* Sodium sulphide cannot be replaced by potassium sulphide in the separation from other metals, because the latter produces difficultly soluble potassium sulphate when ammonium sulphide is formed.

heated very carefully, with the dish covered, till the hydrogen sulphide has all escaped; the solution is then kept in gentle ebullition for about fifteen minutes. Complete conversion into ammonium sulphide is shown by the greenish-yellow color of the solution. If the heating is continued too long, tin sulphide may separate; it can be dissolved in ammonium sulphide. After the solution is completely cool, any sodium sulphate that may have separated is dissolved by addition of water and the solution electrolysed.

The determination of the tin is much more simply and easily accomplished by converting the solution of tin sulphide in sodium sulphide into the acid oxalate. This conversion may be accomplished in two ways: either the sulpho-salt is decomposed with dilute sulphuric acid to remove the greater part of the sulphur as hydrogen sulphide, and the separated tin sulphide oxidised with hydrogen peroxide* until the stannic acid which is produced appears pure white, or the heated alkaline solution is treated directly with hydrogen peroxide (of which a great quantity is needed), then acidified with sulphuric acid to precipitate stannic acid, neutralised with ammonia, and treated with more hydrogen peroxide. In either case the solution is heated to decompose the excess of hydrogen peroxide, and the stannic acid allowed to settle and then filtered off. The precipitate is washed with the oxalate solution from the filter into a beaker, the filter washed with hot oxalic acid solution, and the stannic acid in the beaker dissolved by heating. Sometimes there is a residue of sulphur, which is removed by filtration. The filtrate is collected in the weighed platinum dish to be used for the electrolysis, and the sulphur is washed with a cold saturated solution of ammonium oxalate or acid ammonium oxalate. The solution for electrolysis must contain at least 4 g of the oxalate.

---

* Classen and Bauer, Ber. d. ch. Ges., **16**, 1062 (1883).

ARSENIC.

LITERATURE:

Luckow, Zeit. f. anal. Chem., 19, 14 (1880).
Classen and v. Reiss, Ber. deutsch. chem. Ges., 14, 1622 (1881).
Moore, *Chem. News*, 53, 209 (1886).
Vortmann, Ber. deutsch. chem. Ges., 24, 2704 (1891).
Ducru, Compt. rend., 131, 886 (1900).

Arsenic cannot be quantitatively separated either from aqueous solutions or from solutions containing hydrochloric acid, ammonium oxalate, or alkali sulphides. From aqueous *as from oxalic acid solutions a part of the metal is reduced*, while from hydrochloric acid solutions, if the current is allowed to act for a sufficient length of time, all of the arsenic passes off in the form of arseniuretted hydrogen.

The behavior of arsenic (present as arsenic acid) in a concentrated solution of sodium sulphide permits the separation of arsenic from antimony, as will be shown later.

PLATINUM.

LITERATURE:

Luckow, Zeit. f. anal. Chem., 19, 13 (1880).
Classen, Ber. deutsch. chem. Ges., 17, 2467 (1884).
Smith, Am. Chem. Journ., 13, 206 (1891).
Rüdorff, *Zeit. f. angew. Chem.*, p. 698 (1892).

Platinum is very readily precipitated from its solutions by the electric current. According to the *determinations* made by Dr. W. Göbbels in the Aachen laboratory, if a solution of a platinum salt containing 2–3 per cent. by volume of sulphuric acid is used and is electrolysed with a current of $ND_{100} = 0.1–0.2$ ampere, all the platinum separates in a short time in the form of platinum-black. If, however, a solution heated to 60–65° is electrolysed with a current of $ND_{100} = 0.05$ amp. and a potential-difference of 1.2 volts the platinum separates quantitatively and in a very compact form. The reduced metal is so dense that it cannot be distinguished from hammered platinum. The operation requires a period of from 4 to 5 hours. *If it is desired to remove the deposited platinum, the cathode should be first plated with a coating of copper or silver (see Zinc).*

According to the method employed in the Munich laboratory, if the quantity of platinum present is about 0.4 g, 2 per cent. by volume of dilute sulphuric acid (1 : 5) is added to the solution of the platinum salt, the liquid is heated to about 65°, and electrolysed with a current of $ND_{100} = 0.01$ to 0.03 ampere. The potential-difference when the current-density is 0.03 ampere is at first about 0.05 volt, but rises toward the end of the reaction to 1.7 volts. Although the odor of chlorine escaping at the anode can be detected throughout the entire operation, no evidence has been obtained that any platinum passes into solution from the anode. The precipitation is complete in about 5 hours.

Iridium is not reduced from its solutions by a current of $ND_{100} = 0.05$ amp. and 1.2 volts potential: this property may be used for the quantitative separation of platinum from iridium (Classen).

PALLADIUM.

LITERATURE:

Wöhler, Lieb. Ann., 133, 357 (1865).
Schucht, Zeit. f anal. Chem., 22, 242 (1883).
Smith and Keller, Am. Chem. Journ., 12, 252 (1890).
Smith, *ibid.*, 13, 206 (1891); 14, 435 (1892);
Zeit. f. anorg. Chem., 3, 476 (1893).
Joly and Leidié, Compt. end., 116, 146 (1893).

Palladium is determined in the same way as platinum. If the current of $ND_{100} = 0.05$ ampere, with a potential-difference of 1.2 volts, is used for the reduction, the palladium is obtained in an excellent metallic condition.

MOLYBDENUM.

LITERATURE:

Smith, Am. Chem. Journ., 1, 329 (1879).
Hoskinson and Smith, Am. Chem. Journ., 7, 90 (1885).
Kollock and Smith, Journ. Am. Chem. Soc., 23, 669 (1901).

According to Kollock and Smith the quantitative determination of this element by electrolysis is possible under the following conditions:

To 125 cc of a solution of ammonium molybdate (containing the equivalent of 0.1302 g of molybdenum trioxide) two drops of concentrated sulphuric acid were added, and the solution was electrolysed at 75° with a current-density of $ND_{100} = 0.04$ *ampere and a potential-difference of 2.2 volts. The molybdenum separated as black hydrated sesquioxide on the cathode.* The precipitation was complete in about 3 hours. The deposit was washed without interrupting the current, and while still moist was dissolved in dilute nitric acid, the solution evaporated to dryness, and the residue gently heated on an iron plate to expel the last traces of the nitric acid. White molybdic acid remained. If blue spots appeared in the mass, they were removed by a second treatment with nitric acid. The analytical results showed a close agreement with theory.

The authors state that the method is accurate, is easy of execution, and requires comparatively little time.

POTASSIUM, AMMONIUM. (NITROGEN.)

Potassium and ammonium may be determined, as is well known, by converting them into potassium or ammonium platinchloride, and weighing the precipitate, dried at 110°, on a tared filter. This method, which is almost universally employed in the separation of potassium from sodium, has many disadvantages. It is preferable, after precipitating and washing the platinum salt as usual, to dissolve it in water, and determine the platinum as directed on p. 218.

SECTION II.

DETERMINATION OF NITRIC ACID IN NITRATES.

LITERATURE:

Luckow, Zeit. f. analyt. Chem., 19, 11 (1880).
Vortmann, Ber. deutsch. chem. Ges., 23, 2798 (1890).
Ulsch, Zeit. f. Elektrochem., 3, 546 (1896–97).

As is well known, nitric acid is often converted into ammonia, and the latter determined. The action of the electric current converts nitric acid into ammonia, as explained in the Introduction (p. 38). If the solution of an alkali nitrate, acidified with dilute sulphuric acid, is acted on by the current, no ammonia is formed.

Luckow discovered that the reduction of the nitric acid always takes place when a salt from which the metal is precipitated by the current is also present in the solution. Copper salts are best adapted for this purpose. G. Vortmann has determined in the Aachen laboratory the conditions for the quantitative determination of nitric acid in nitrates. The solution of the nitrate is treated with a sufficient quantity of copper sulphate (in the analysis of potassium nitrate, half as much crystallised copper sulphate as potassium nitrate), acidified with dilute sulphuric acid, and electrolysed cold. When the reaction is complete the solution is poured off, sodium hydroxide solution is added, and the ammonia distilled off and determined volumetrically in the usual way. For this purpose one-fifth normal solutions of ammonia and sulphuric acid are used. To standardise the sulphuric acid, a weighed quantity (0.5 g) of crystallised copper sulphate is decomposed by electrolysis, and the resulting free acid titrated with ammonia. Vortmann decomposed 0.4876 g $CuSO_4.5H_2O$, and used, for the neutralisation of the acid set free, 19.6 cc of ammonia of a strength equal to the one-fifth normal sulphuric acid. 1 cc of the latter corresponds therefore to 0.0028017 g of nitrogen in the form of ammonia.

The method described by Ulsch is based on the reduction *of the nitric acid, set free by adding sulphuric acid* to a solution of nitrates, when the electrolysis is conducted with a copper cathode. For further details consult the original article.

SECTION III.

DETERMINATION OF THE HALOGENS.

Chlorine, Bromine, Iodine.

LITERATURE:

Vortmann, *Monatshefte* f. Chem., *15*, 280 (1894); *16*, 674 (1895); Elektrochem. Zeit., *1*, 137 (1894).
Whitefield, Am. Chem. Journ., 8, 421 (1897).
Specketer, Zeit. f. Elektrochem., 4, 539 (1897–98).
Müller, Ber. deutsch. chem. Ges., *35*, 950 (1902).

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 ion 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 replacing the original silver anode by a second weighed silver anode and noting its increase in weight.

For an experimental test of the method, a weighed quantity of iodide is dissolved in water, 6–10 cc of a 10% solution of sodium hydroxide added, and the solution diluted to 100–150 cc. The silver anode, having the form of a watch-glass 6 cm in diameter, is fixed about 5 mm from the bottom of the copper dish which serves as cathode.

The cold solution is electrolysed with a current-strength of 0.03–0.07 ampere and a difference of potential of 2 volts. After 4–5 hours the greater part of the iodine will be converted into silver iodide, and the remainder may be separated on a fresh silver anode, after the addition of sodium potassium tartrate to the solution. The liquid is warmed to 50–70° and electrolysed with a current having a difference of potential of 1.2–1.3 volts and a current-strength of 0.01–0.02 ampere.

SECTION IV.

SEPARATION OF METALS.

IRON.

Iron—Cobalt.

LITERATURE:

Classen, Ber. deutsch. chem. Ges., 27, 2060 (1894).
Engels, Compt. rend., 15, 5, 20 (1896).
Ducru, Bull. Soc. Chim., 17, 881 (1897).
Neumann, Chem. Ztg., 22, 731 (1898).

The two metals may be determined by electrolysing the solution of the double oxalates, as directed under Iron (p. 155), weighing the iron and cobalt together, and determining the former volumetrically.

After weighing the iron and cobalt, the deposit is dissolved in dilute sulphuric acid (dilute sulphuric acid is poured over the metals, and concentrated acid gradually added, so that the solution becomes heated), and the iron is titrated in the platinum dish with potassium permanganate. To overcome the red color of cobalt sulphate, a sufficient amount of nickel sulphate is added before the titration. The end of the reaction is easily recognised.

The residue of cobalt and iron may also be dissolved in hydrochloric acid, the iron oxidised with hydrogen peroxide, and titrated with stannous chloride, after removing the excess of hydrogen peroxide by boiling.

EXPERIMENT.

Used 1 g each of $CoSO_4.K_2SO_4.6H_2O$ and $Fe_2(C_2O_4)_3.3K_2C_2O_4.6H_2O$, and 8 g ammonium oxalate. Volume of liquid, 120 cc.

Current-density, Amperes.	Electrode Potential, Volts.	Temp.	Time. hr.	m.	Found, Fe+Co. g	Calculated.	Titrated.
2.0–1.6	3.0–3.6	65–70°	1	40	0.2658	0.1141 g Fe[*] 0.1517 " Co 0.2658 g	0.1140 g Fe
1.55–1.4	3.2–3.6	62–65°	1	20	0.2650	0.1138 g Fe 0.1517 " Co 0.2655 g	0.1140 " "
1.0–0.85	2.85–3.1	60–65°	2	30	0.2585	0.1137 g Fe 0.1451 " Co 0.2586 g	0.1140 " "
0.5–0.4	2.0–2.7	60–67°	4	—	0.2593	0.1136 g Fe 0.1452 " Co 0.2588 g	0.1133 " "
0.5–0.45	2.35–2.7	58–62°	4	—	0.2617	0.1139 g Fe 0.1477 " Co 0.2616 g	0.1141 " "

Iron—Nickel.

LITERATURE:

Vortmann, Monatshefte f. Chem., 14, 536 (1893);
Elektrochem. Zeit., p. 6 (1894).
Classen, Ber. deutsch. chem. Ges., 27, 2060 (1894).
Engels, Compt. rend., 15, 5, 20 (1896).
Ducru, Bull. Soc. Chim., 17, 881 (1897).
Neumann, Chem. Ztg., 22, 731 (1898).

The method of determination is exactly like the preceding. Iron and nickel separate in the form of a beautiful white alloy scarcely distinguishable from platinum. This alloy re-

---

[*] The numbers placed under the heading "Calculated" are the quantities of iron and cobalt in the two salts taken, which were separately determined by electrolysis.

sists strongly the action of acids, and is only very slowly attacked by dilute sulphuric or hydrochloric acid.

Since the precipitation of the last trace of nickel takes place very slowly, the use of a current of at least $ND_{100} = 1$ ampere is to be recommended. Toward the end of the operation the current-strength should be increased.

To determine the iron, the precipitate in the dish must be heated with concentrated hydrochloric acid; and if the iron is to be titrated with permanganate, the solution must be reduced by nascent hydrogen. It is more simple to oxidise with hydrogen peroxide, and, after removing the excess, titrate the ferric chloride with stannous chloride.

EXPERIMENT.

Used 1 g each of $NiSO_4.(NH_4)_2SO_4.6H_2O$ and $Fe_2(C_2O_4)_3.3K_2C_2O_4.6H_2O$, and 8 g ammonium oxalate. Volume of liquid, 120 cc.

Current-density, Amperes.	Electrode Potential, Volts.	Temp.	Time. hr. m.	Found, Fe+Ni.	Calculated.
2.2–1.75	3.45–4.0	70–65°	2 —	0.2760 g	0.1135 g Fe[*] 0.1622 " Ni 0.2757 g
2.0–1.75	3.35–3.9	69–67°	2 —	0.2654 "	0.1135 g Fe 0.1527 " Ni 0.2662 g
1.1–0.7	2.6–3.1	65–71°	4 30	0.2675 "	0.1135 g Fe 0.1550 " Ni 0.2683 g
0.5–0.4	2.6–3.0	68–71°	5 —	0.2664 "	0.2664 g

Vortmann adds 4–6 g sodium potassium tartrate and an excess of sodium hydroxide to the solution, warms, and pre-

---

[*] The numbers placed under the heading "Calculated" are the quantities of iron and cobalt in the two salts taken, which were separately determined by electrolysis.

cipitates the iron with a current of $ND_{100} = 0.3–0.5$ ampere in three to four hours, the nickel remaining in solution.

Iron—Zinc.

LITERATURE:

Vortmann, Monatshefte f. Chem., 14, 536 (1893).

If the double oxalates of iron and zinc are submitted to electrolysis, the two metals do not separate as an alloy, but zinc, with a little iron, is first precipitated on the negative electrode. The electrolysis proceeds very satisfactorily, and the united weight of the two metals may readily be determined if there is less than one-third as much zinc as iron in the solution. If the proportion of zinc is greater, the zinc dissolves with the evolution of gas as the action proceeds, and a precipitate of oxide of iron is formed.

Vortmann proposes the following method: 4–6 grams of potassium sodium tartrate and an excess of a 10–20% solution of sodium hydroxide are added to the solution of the metals, and the liquid is electrolysed at a potential-difference of 2 volts, with a current-strength of $ND_{100} = 0.07–0.1$ ampere. It is best to raise the temperature at the close of the operation to 50–60°. After several hours the iron will be precipitated, the zinc remaining in solution. The zinc can then be quantitatively precipitated by electrolysing with a potential-difference of 4 volts.

Iron—Manganese.

LITERATURE:

Classen, Ber deutsch. chem. Ges., 18, 1787 (1885).
Engels, Compt. rend., pp. 5, 40 (1896).
Kaeppel, Zeit. f. anorg. Chem., 16, 268 (1898).

As stated in the Introduction, a solution of ammonium oxalate is decomposed by electrolysis, mainly into hydrogen and hydrogen ammonium carbonate. The latter is partly decomposed into ammonia, most of which remains in solution, and carbon dioxide. In the electrolysis of a *hot* solution of ammonium oxalate, the ammonium carbonate produced by the current is partly neutralised as a result of dissociation of ammonium oxalate; carbon dioxide is rapidly liberated at the positive electrode.

If a solution of the double oxalates of iron and manganese is subjected to electrolysis without the previous addition of a great excess of ammonium oxalate, the characteristic color of permanganic acid appears immediately at the anode. Manganese dixode gradually separates at the positive electrode, and iron at the negative. If the electrolysis is conducted under these conditions, it is impossible to obtain a quantitative separation of the two metals, since the manganese dioxide carries down with it considerable quantities of ferric hydroxide. The complete separation of the metals is possible only when the separation of the manganese dioxide is delayed till most of the iron is precipitated. If a solution of the double oxalates of iron and manganese, which contains a great excess of ammonium oxalate, is electrolysed *in the cold,* the greater part of the manganese dioxide is precipitated only after most of the ammonium oxalate is decomposed. In this case, however, the separation of the manganese dioxide is incomplete, because by the action of the current a considerable quantity of ammonium carbonate or ammonia is produced which acts on the manganese double salt, causing a portion of the precipitate (a mixture of dioxide and a lower oxide) to pass into solution.

The rapid decomposition of ammonium oxalate when heated gives a simple means of delaying, or entirely preventing, the formation of a manganese precipitate during electrolysis.

The double oxalate is prepared by the method given under

Iron, with the difference only that 8 to 10 g ammonium oxalate are dissolved in the liquid, which is warmed to 80–90°, and *electrolysed with a current of $ND_{100}=0.5$ amp.*

When the reduction is complete, the solution is poured off, the dish washed repeatedly with water, and this, together with traces of the dioxide precipitate, removed by alcohol; it is sometimes necessary to rub the dish gently with the finger.

The preceding method gives satisfactory results when the percentage of manganese is not too high. For the analysis of manganiferous iron (ferro-manganese, for example) this method has no practical value, since the percentage of manganese is here required, while by this method the iron is determined directly and the manganese must be determined in the liquid from which the iron has been separated.

To obtain a complete separation, the solution, containing suspended manganese dioxide, is heated with a solution of pure potassium or sodium hydroxide in a porcelain dish, till the ammonium carbonate produced by electrolysis is decomposed and the solution no longer has the odor of ammonia; and then sodium carbonate and a *small* quantity of sodium hypochlorite, or, better, hydrogen peroxide, are added. The manganese dioxide quickly falls to the bottom, and can be filtered off. The precipitate is best washed with hot water to which a little ammonium-nitrate has been added, and is either converted into mangano-manganic oxide (Mn_2O_4) by ignition, or, better, into manganese sulphate ($MnSO_4$).

The conversion into manganese sulphate is accomplished by moistening the precipitate in the crucible with a little pure concentrated sulphuric acid, and igniting very gently, so that the bottom of the crucible is heated to a low red heat.

If it is desired to determine the manganese as manganese sulphide, the solution is boiled till the ammonium carbonate is decomposed, the remaining ammonia is neutralised with nitric acid, and ammonium sulphide added till the precipitation is complete. The manganese sulphide is either determined as such by ignition in a stream of hydrogen, or, more simply, converted into manganese sulphate by heating with a few drops of sulphuric acid.

Kaeppel conducts the separation of iron from manganese in a solution of the double salts of pyrophosphoric acid. A solution of ferric ammonium sulphate (0.1 to 0.15 g Fe) and manganous ammonium sulphate (0.035 to 0.11 g Mn) was added with constant stirring to a boiling solution containing 12 g sodium pyrophosphate, and when the solution had become clear five drops of phosphoric acid were added. If the phosphoric acid produced turbidity, this was removed by adding a few drops of sodium pyrophosphate solution. The total volume of the solution was 230–250 cc, and the electrolysis was conducted in a platinum dish which served as anode with a current of 1.8 to 2.5 ampere (*sic.*), at a potential-difference of 4 volts. The temperature of the electrolyte was 30–40°, and the time required was 8 to 10 hours; the iron being precipitated. For the iron fairly accurate results were obtained, but the manganese remaining in the solution could not be determined by electrolytic methods. The deposited iron was washed without interrupting the current.

Iron—Aluminium.

LITERATURE:

Classen, Ber. deutsch. chem. Ges., *18*, 1795 (1885); *27*, 2060 (1894).
Engels, Compt. rend., *15*, 5, 20 (1896).

When a solution containing the above metals and a great excess of ammonium oxalate is electrolysed *in the cold*, iron is deposited on the negative electrode, while the aluminium remains in solution as long as ammonium oxalate is present in the solution in greater proportion than the ammonium carbonate formed from it. If a precipitate of aluminium hydroxide finally appears, it is only when the solution is almost free from iron. A small portion withdrawn by a capillary tube is tested, from time to time, with ammonium sulphide or another reagent already mentioned, and the current is stopped as soon as no reaction is obtained.

The process is as follows: The aqueous or weakly acid solution (in the latter case neutralised with ammonia) of the sulphates (the chlorides are not as well adapted to the process) is treated with ammonium oxalate in excess, and enough solid ammonium oxalate added (with gentle warming if necessary) to give the proportion of 2–3 g ammonium oxalate to 0.1 g of the metals. The entire volume of the solution should be 150–175 cc. If the temperature of the solution is not over 40°, it may be submitted to electrolysis at once, since it gradually cools under the action of a current of the given strength.

It is not best to continue the action of the current longer than is necessary to reduce the iron; for, otherwise, a large part of the aluminium is precipitated as hydroxide, and clings so closely to the negative electrode that it cannot be removed.

In such a case it is necessary to bring the aluminium hydroxide into solution by acidifying with oxalic acid, and, in case too much acid has been added, to pass the current till the last traces of the redissolved iron have been again precipitated.

The oxalic acid is poured gradually down the glass which covers the platinum dish, without interrupting the current, till there is no more ebullition, and the aluminium precipitate is dissolved.

If the quantity of the aluminium is not greater than that of the iron, the method gives good results without further treatment. In other cases the precipitate of aluminium hydroxide is dissolved, without interrupting the current, by careful addition of oxalic acid, and the electrolysis repeated until the iron is completely precipitated. To determine the aluminium in the solution poured off from the iron, it is heated in a porcelain dish till the ammonia is driven off, filtered, and the aluminium hydroxide converted, by ignition, into Al_2O_3.

EXPERIMENT.

Used 1 g each of $Fe_2(C_2O_4)_3.3K_2C_2O_4.6H_2O$ and $Al_2(SO_4)_3.K_2SO_4.24H_2O$, and 8 g ammonium oxalate. Volume of liquid, 120 cc.

Current-density, Amperes.	Electrode Potential, Volts.	Temp.	Time, hr. m.	Taken, g.	Found, g.
1.95–1.6	4.3 –4.4	31–42°	2 35	0.1135 Fe	0.1143 Fe
1.65–1.35	3.8 –4.1	30–48°	3 —	0.1150 "	0.1159 "
1.00–0.84	3.55–3.8	31–36°	4 30	0.1135 "	0.1138 "
0.50–0.42	2.75–3.1	30–32°	5 40	0.1135 "	0.1139 "

In order to avoid the separation of aluminium hydroxide (small quantities of which often adhere to the iron) strong currents, which raise the temperature of the solution, should not be used.

The effect of strong currents and high temperatures is illustrated in the above experiment.

Iron—Chromium.

LITERATURE:

Classen, Ber. deutsch. chem. Ges., 27, 2060 (1894).
Engels, Compt. rend., 15, 5, 20 (1896).

If a solution which contains an excess of ammonium oxalate, and chromium as sesquioxide, that is, as chromium ammonium oxalate, be submitted to electrolysis, all of the chromium is converted into a chromate. If iron is also present, it is precipitated in the metallic state on the negative electrode; the metal has a peculiarly characteristic luster.

When the precipitation is complete, the liquid is poured off from the precipitated metal and is boiled to decompose ammonium carbonate, and the chromic acid reduced by boiling with hydrochloric acid and alcohol. The chromium is then precipitated as hydroxide with ammonia.

The hydroxide is converted into Cr_2O_3 in the usual manner, and weighed.

EXPERIMENT.

A. Used 1 gram of $Fe_2(C_2O_4)_3.3K_2C_2O_4.6H_2$, 1 gram of $3K_2C_2O_4.Cr_2(C_2O_4)_3.6H_2O$, and 8 grams ammonium oxalate. Solution diluted to 120 cc.

Current-density, Amperes.	Electrode Potential, Volts.	Temp.	Time, hr. m.	Taken, Fe.	Found, Fe.
2.00–1.60	3.4–3.6	62–68°	4 —	0.1120 g	0.1123 g
1.60–0.95	3.2–3.8	66–68°	5 —	0.1135 "	0.1135 "
1.95–1.50	3.3–3.7	62–65°	3 —	0.1135 "	0.1130 "

B. Used 2 g chrome alum, 1.5890 g ferrous ammonium sulphate, and 8 g ammonium oxalate.

Current-density, Amperes.	Electrode Potential, Volts.	Temp.	Time, hr. m.	Taken, Fe.	Found, Fe.
1.5	3	65°	4 —	14.28%	14.19%

C. Used 2 g chrome alum, 1 g $Fe_2(C_2O_4)_3.3K_2C_2O_4.6H_2O$, and 8 g ammonium oxalate.

Current-density, Amperes.	Electrode Potential, Volts.	Temp.	Time, hr. m.	Taken, Fe.	Found, Fe.
1.50–1.60	3.0–3.2	65°	4 —	11.40%	11.35%

Iron—Uranium.

The separation of iron from uranium depends upon the same principle as the separation of iron from aluminium. It is necessary to have a great excess (8 g) of ammonium oxalate present in the solution, in order to retain the uranium in the form of the double salt until all of the other metal is precipitated.

The process is conducted in the same manner as the separation of aluminium from iron. When a strong current is employed, especially when there is an insufficient quantity of ammonium oxalate present, it may happen that, as a result of the decomposition of the hydrogen ammonium carbonate by the heat produced, the uranium is precipitated as hydroxide.

The uranium solution, after the other metal has been separated, is freed from oxalic acid by further electrolysis, and finally the ammonium carbonate is decomposed by heating.

To bring the finely divided precipitate of uranium hydroxide into suitable condition for filtration, nitric acid is added, the solution is heated till the precipitate is wholly dissolved, and ammonia is added to reprecipitate the hydroxide. The precipitate is converted into uranium oxide by ignition in a stream of hydrogen.

Iron—Aluminium—Chromium.

LITERATURE:

Classen, Ber. deutsch. chem. Ges., 14, 2771 (1881).

The separation is performed as above. To separate the aluminium from chromium, the solution poured off from the precipitated metals is boiled till it has only a weak odor of ammonia, the aluminium hydroxide filtered off, and the chromium precipitated as above.

Iron—Chromium—Uranium.

LITERATURE

Classen, Ber. deutsch. chem. Ges., 14, 2771 (1881);
ibid. 17, 2483 (1884).

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. Uranium is separated as hydroxide, while chromium remains in solution as ammonium chromate. To accomplish the quantitative separation of chromium from uranium the electrolysis must be continued till the oxalic acid is completely oxidised.

The solution is boiled to decompose the resulting ammonium carbonate, and allowed to stand six hours. The chromium is determined, as above, in the filtrate from the uranium.

Iron—Beryllium.

LITERATURE:

Classen, Ber. deutsch. chem. Ges., 14, 2771 (1881).

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. The iron is precipitated according to the directions given under the separation of aluminium from iron.

Strong currents are not advisable lest the solution become heated, and thus the ammonium carbonate, which holds the beryllium in solution, be decomposed. The beryllium hydroxide *may, in any case, begin to precipitate before the iron* is fully deposited. The determination of beryllium in the solution poured off from the iron is very simple; the solution is boiled to decompose the hydrogen ammonium carbonate, and the heating continued till the solution has only a weak odor of ammonia. The beryllium hydroxide is filtered, washed with hot water, and converted into BeO by ignition in a platinum crucible.

Iron—Beryllium—Aluminium.

LITERATURE:

Classen, Ber. deutsch. chem. Ges., 14, 2771 (1881).

The process is precisely like the foregoing. When the iron is reduced the solution is poured into a second platinum dish, and the action of the current is continued till all the oxalic acid is decomposed, and the aluminium is precipitated as hydroxide. The beryllium is precipitated from the filtrate as hydroxide by boiling.

It is advisable to redissolve the aluminium hydroxide, to convert it again into the double oxalate, and to repeat the electrolysis.

Iron—Copper.

LITERATURE:

Schweder, Berg- u. Hüttenm. Ztg., 36, 5, 11, 31 (1877).
Vortmann, Monatshefte f. Chem., 14, 536 (1893).
Classen, Ber. deutsch. chem. Ges., 27, 2060 (1894).
Fernberger and Smith, Journ. Am. Chem. Soc., 21, 1001 (1899).

The separation may be accomplished according to the method given by Luckow (p. 179), if the operation is conducted at ordinary temperatures. To determine the iron in the solution from which the copper has been removed it is evaporated to dryness with the addition of sufficient sulphuric acid to convert the iron into sulphate, and the double oxalate is prepared by the method given on page 154.

EXPERIMENT.

Used about 1 g each of copper sulphate and ferrous ammonium sulphate and 5 cc nitric acid (sp. gr. 1.35). Volume of liquid, 120 cc.

Current-density, Amperes.	Electrode Potential, Volts.	Temp.	Time, hr. m.	Taken Cu.	Found Cu.
1.0–0.9	3.0–3.3	19–32°	4 —	0.2528 g	0.2518 g
1.1–1.0	2.6–3.2	18–32°	3 30	0.2450 "	0.2430 "

The free sulphuric acid in the decanted liquid was neutralised with ammonium hydroxide, and 8 g ammonium oxalate were added.

Current-density, Amperes.	Electrode Potential, Volts.	Temp.	Time, hr. m.	Taken Fe.	Found Fe.
1.30–0.8	2.7–4.5	31–42°	3 —	0.1406 g	0.1416 g
1.45–1.1	3.0–3.5	60°	3 30	0.1435 "	0.1438 "

A similar separation may also be carried out in the presence of sulphuric acid instead of nitric acid. Three cubic centimeters of the concentrated acid are used, the other conditions being the same.

Current-density, Amperes.	Electrode Potential, Volts.	Temp.	Time, hr. m.	Taken Cu.	Found Cu.
1.05–1.20	3.0–2.85	22–30°	2 10	0.2539 g	0.2534 g
1.00–0.95	2.5–2.45	56–59°	2 —	0.2510 "	0.2504 "

The determination of the iron was conducted as before.

Current-density, Amperes.	Electrode Potential, Volts.	Temp.	Time, hr. m.	Taken Fe.	Found Fe.
1.55–1.32	3.4–3.8	33–40°	4 —	0.1421 g	0.1419 g
1.60–1.40	3.0–3.5	61–64°	3 —	0.1675 "	0.1625 "

The separation of iron and copper may be effected if the copper is precipitated *from a hot solution of the double* oxalate containing free oxalic, tartaric, or acetic acid. A saturated solution of oxalic acid is used, and one of tartaric acid which contains 6 g acid in every 100 cc.

EXPERIMENT.

Used about 1 g each of copper sulphate and ferric salt, 6 g ammonium oxalate. The copper must be washed without interrupting the current.

Current-density, Amperes.	Electrode Potential. Volts.	Temp.	Time.	Taken Cu.	Found Cu.
1.1–1.0	2.95–3.5	51–62°	3 hr.	0.2528 g	0.2525 g
0.7–0.7	3.20–2.85	62°	3 "	0.2530 "	0.2532 "

The iron was determined in the solution which was poured *off from the copper*, the free acid being first neutralised with ammonium hydroxide.

Current-density, Amperes.	Electrode Potential. Volts.	Temp.	Time.	Taken Fe.	Found Fe.
1.4–1.3	3.0–3.2	68–70°	2¼ hr.	0.1435 g	0.1431 g
1.0–0.9	3.1–3.3	30–40°	3 "	0.1429 "	0.1425 "

Vortmann dissolves the oxides of both metals in an ammoniacal solution, to which are added several grams of ammonium sulphate, and electrolyses with a current of $ND_{100} =$ 0.1–0.6 ampere. Only copper is precipitated, the ferric hydroxide remaining unaltered in solution.

According to Fernberger and Smith, copper can be separated from iron under the conditions given in the following experiment:

60 cc of a solution of disodium-hydrogen phosphate (sp. gr. 1.0358) were added to a mixture of 25 cc of a copper sulphate solution (=0.1239 g Cu) and 50 cc of a solution of ferric ammonium alum (=0.2002 g Fe). The precipitate which formed was dissolved in 10 cc phosphoric acid (sp. gr. 1.347), and the solution diluted to a total volume of 225 cc was electrolysed at 53° with a current of $ND_{100} = 0.04$ ampere and a potential-difference of 2.4 volts. The copper was completely precipitated in about 7 hours.

Iron—Lead.

This separation is effected by precipitating the lead as peroxide from a solution containing free nitric acid (p. 195). To determine the iron remaining in the solution add sulphuric acid, evaporate to dryness to expel the nitric acid, and determine the iron by electrolysis in an oxalic acid solution as described under Iron-Copper.

Iron—Bismuth.

LITERATURE:

Kammerer, Journ. Am. Chem. Soc., 25, 83 (1903).

According to Kammerer the iron should be present as ferrous sulphate, and the solution having a volume of 150 cc should contain 1 cc nitric acid (sp. gr. 1.43), 1 g potassium sulphate, and 2 cc sulphuric acid (sp. gr. 1.84). The electrolysis is conducted at 45° with a current of $ND_{100}=0.025$ ampere and a potential-difference between the electrodes of 2 volts. About 8 hours are required for the complete separation of the bismuth.

Iron—Cadmium.

LITERATURE:

Stortenbeker, Zeit. f. Elektrochem., 4, 409 (1897–98).

The following method for separating these two elements is given by Stortenbeker: Cadmium and ferrous sulphates are dissolved in 100 cc of water slightly acidified with a few drops of dilute sulphuric acid, and to this solution 2 to 3 grams of potassium cyanide are added. The mixture is then warmed until perfectly clear, and if it does not become yellow immediately a few drops of a solution of potassium hydroxide are added. The solution is diluted to 200 cc and electrolysed with a current of $ND_{100}=0.05$ to 0.10 ampere, at the room temperature. Cadmium will be deposited.

Iron—Silver.

LITERATURE:

Kollock, Journ. Am. Chem. Soc., 21, 911 (1899).

The following experiment is described by Kollock: To a solution containing 0.1 g silver as nitrate and 0.1 g of iron as ferrous ammonium sulphate, 2.5–4 g potassium cyanide were added and the solution was diluted to 125 cc. The electrolysis was carried out at 65–75° with a current of $ND_{100}=$ 0.02–0.04 ampere and a potential-difference of 1.8–2.2 volts. The silver was completely precipitated in from 3 to 4 hours.

COBALT.

Cobalt—Nickel.

LITERATURE:

Vortmann, Monatsh. f. Chemie, 14, 536 (1893).
Cohen, Zeit. f. Elektrochem., 4, 501 (1897–98).
Balachowsky, Compt. rend., 132, 1492 (1901).
Rosenheim and Huldschinsky, Pharm. Centralbl., 42, 393 (1901).

The following method for separating these two elements is described by Balachowsky: To an acetic acid solution containing 0.3 g of the metals, 3 g ammonium sulpho-cyanide, 1 g urea, and enough ammonia to neutralise the free acetic acid, are added. The solution is diluted to a convenient volume and electrolysed at 70–80° in a platinum dish-electrode with a maximum potential-difference between the electrodes of 1.0 volt and a current of $ND_{100} = 0.8$ ampere. The *precipitation of the nickel is complete in 1½ hour, but* the deposited metal contains sulphur and should therefore be dissolved in nitric acid, the sulphur filtered off, and the nickel again precipitated by one of the standard methods (p. 160). The cobalt remaining in the first solution is determined by destroying the ammonium sulphocyanide by boiling with nitric acid, filtering off any sulphur which appears, and precipitating the cobalt by one of the regular methods.

The method proposed by Vortmann depends upon the electrolysis of a solution containing sodium potassium tartrate made strongly alkaline with sodium hydroxide. Vortmann states that with a current-density of $ND_{100} = 0.3$ to 0.06 ampere the nickel remains in the solution while the cobalt is precipitated. The essential data for repeating these experiments are lacking.

Cobalt—Zinc.

LITERATURE:

Vortmann, Monatsch. f. Chemie, 14, 536 (1893);
Elektrochem. Zeit., 1, 6 (1894).
Smith and Wallace, Journ. of Anal. Chem., 7, 183 (1893).
Waller, Zeit. f. Elektrochem., 4, 241 (1897–98).

According to Vortmann an excess of a 10–20% solution of sodium hydroxide is added to the solution containing the metals. Several grams of sodium potassium tartrate are then added and the electrolysis is conducted with a current of $ND_{100} = 0.07–0.1$ ampere and an electrode tension of 2 volts. The cobalt is precipitated, but the addition of potassium iodide is necessary in order to prevent the separation of cobaltic oxide at the anode.

According to Waller, who conducted his researches in the laboratory of the author at Aachen, satisfactory results can be obtained under the following conditions:

6 grams of sodium potassium tartrate and from 1.0 to 1.5 g of potassium iodide were dissolved in the solution containing the metals as sulphates, which was then made alkaline with 10 cc of a solution of sodium hydroxide containing 2 to 3 grams of NaOH. The solution was diluted to 150 cc, and was electrolysed at 60–65° with a current of $ND_{100} =$ 0.05 to 0.1 ampere and a potential-difference of 2 volts. Since a little oxide of cobalt is always deposited on the anode it is important that the latter should be weighed both before and after the electrolysis, in order to determine the weight of cobalt thus separated. This seldom amounts to more than 1% of the entire quantity present.

The zinc is afterwards separated from the solution by electrolysing with a potential-difference of 4 volts.

Cobalt—Aluminium.

The method is carried out similarly to that of iron from aluminium.

Cobalt—Uranium; Cobalt—Chromium; Cobalt—Uranium—Chromium.

The methods employed are similar to those of the corresponding separations from iron (p. 234).

Cobalt—Copper.

LITERATURE:

Warwick, Zeit. f. anorg. Chem., 1, 299 (1892).
Classen, Ber. deutsch. chem. Ges., 27, 2060 (1894).
Rüdorff, Zeit. f. angew. Chem., p. 388 (1894).
Fernberger and Smith, Jour. Am. Chem. Soc., 21, 1001 (1899).

The separation of these two elements can be satisfactorily *conducted by the electrolysis of a solution containing* ammonium oxalate, at a temperature of 50–60°, if the difference of potential between the electrodes is so regulated as *to be kept between 1.1 and 1.3 volt.* Under these conditions only copper will be precipitated.

EXPERIMENT.

Used 1 g copper sulphate (25.33% Cu), 1 g cobalt ammonium sulphate, and 6 g ammonium oxalate.

Electrode Potential, Volts.	Temp.	Time, hr.	Time, m.	Found g Cu.	Found % Cu.
1.24–1.30	50–60°	3	50	0.2602	25.36
1.20–1.35	50–60°	3	30	0.2531	25.29
1.20–1.29	50–60°	4	—	0.2522	25.28

These elements may also be separated in a solution containing free nitric acid (p. 179).

For effecting the separation in a solution containing phosphates we are indebted to Fernberger and Smith for the following particulars: To a solution containing 0.1329 g Cu and 0.1 g Co in the form of sulphates, 60 cc disodium hydrogen phosphate (sp. gr. 1.0358) and 10 cc phosphoric acid (sp. gr. 1.347) were added, and the mixture was diluted to a volume of 225 cc. The electrolysis was conducted at 62° with a current of $ND_{100} = 0.035$ ampere and a potential-difference of 1.5 volt. The copper was completely deposited in 6 hours.

Cobalt—Bismuth.

LITERATURE:

Smith and Wallace, Journ. of Anal. Chem., 7, 183 (1893).
Smith and Moyer, Zeit. f. anorg. Chem., 4, 268 (1893).
Kammerer, Journ. Am. Chem. Ges., 25, 83 (1903).

According to Smith and Wallace, and also Smith and Moyer, a separation of these metals may be satisfactorily conducted in a solution containing nitric acid. Since, however, the required conditions of experiment are not given in the respective publications the methods will be here omitted.

Kammerer states that the following conditions are satisfactory for effecting this separation:

Cobalt sulphate in quantity equivalent to 0.15 g cobalt, 0.5 g potassium sulphate and 2 cc sulphuric acid (sp. gr. 1.84) were added to a solution containing 0.15 g of bismuth and 2 cc nitric acid (sp. gr. 1.43). The solution was diluted to 150 cc and electrolysed at a temperature of 45° with a current of $ND_{100} = 0.025$ ampere and a potential-difference of 2 volts. The bismuth was completely deposited in 9 hours, and was free from cobalt. This method serves equally well for the separation of bismuth and nickel.

Cobalt—Lead.

The solution, after the addition of nitric acid, is electrolysed as described under Lead, p. 195.

Cobalt—Silver.

LITERATURE.

Kollock, Journ. Am. Chem. Soc., 21, 911 (1899).

The following experiment is described by Kollock: To a solution containing 0.1 g silver and 0.1 g cadmium, both present as nitrates, 2.75 g of potassium cyanide was added, and the solution was diluted to 125 cc. The electrolysis was carried out with a current of $ND_{100} = 0.02$ ampere and a potential-difference of 2.2 to 2.7 volts. After 5 hours had elapsed the silver was completely precipitated. The temperature of the solution throughout the entire operation was 65°.

Cobalt—Mercury.

LITERATURE:

Kollock, Journ. Am. Chem. Soc., 21, 911 (1899).

Kollock states that the following conditions are suitable for the separation of these elements: The solution contained 0.1216 g of mercury as mercuric chloride and 0.1 g of cobalt as nitrate. To this 2 g potassiun cyanide were added, the total volume was 100 cc, and the electrolysis was conducted at 65° with a current of $ND_{100} = 0.03$ ampere and a potential-difference of 2.9 volts. The mercury was completely precipitated in 5 hours.

NICKEL.

Nickel—Zinc.

LITERATURE:

Vortmann, Monatsch. f. Chemie, 14, 536 (1893).

For the separation of these metals Vortmann suggests a solution containing from 4 to 6 grams of sodium potassium tartrate and an excess of sodium hydroxide. In his experiments about 0.2 g of each metal was present, and the electrolysis was conducted at ordinary temperatures with a current of $ND_{100}=0.3$–0.6 ampere. He states that under these conditions only zinc is precipitated, the nickel remaining in solution.

Nickel—Manganese.

LITERATURE:

Engels, Compt. rend., 15, 5, 20 (1896).

What has been stated (p. 229) with reference to the separation of iron and manganese applies equally to the separation of nickel and manganese.

Nickel—Aluminium.

Similar to the separation of iron from aluminium.

Nickel—Uranium; Nickel—Chromium.

Similar to the corresponding separations from iron.

Nickel—Copper.

LITERATURE:

Classen, Ber. deutsch. chem. Ges., 27, 2000 (1894).
Fernberger and Smith, Jour. Am. Chem. Soc., 21, 1001 (1899).

The separation takes place under the same conditions as the separation of cobalt from copper.

If 1 g each of copper sulphate and nickel sulphate are taken, 6 g ammonium oxalate are required. Larger quantities of metal require correspondingly greater quantities of ammonium oxalate.

EXPERIMENT.

Potential-difference, Volts.	Time, hr. m.	Found		Remarks.
		g Cu.	% Cu.	
1.11–1.3	3 50	0.2552	25.40	Theory 25.33% cu.
1.20–1.3	3 —	0.2559	25.37	Acidified with oxalic acid.
1.20–1.3	3 30	0.2591	25.38	Acidified with tartaric acid.
1.34–1.45	3 50	0.2579	25.45	Acidified with acetic acid. The copper contained nickel.
1.20–1.6	3 50	0.2595	25.33	The copper contained nickel.

The separation of these two metals can be very satisfactorily conducted in a solution containing free nitric acid (see p. 179).

For the separation of nickel and copper in a phosphate solution the following details are given by Fernberger and Smith:

To a solution containing copper sulphate (=0.1239 g Cu) and nickel nitrate (=0.1366 g Ni), 75 cc of a solution of disodium hydrogen phosphate (sp. gr. 1.0358) and 10 cc phosphoric acid (sp. gr. 1.347) were added, and the electrolysis was conducted at 66° with a current of $ND_{100}=0.072$ ampere and a potential-difference of 2.45 volts, the total volume of the solution being 225 cc. The copper was completely precipitated in 6 hours.

Nickel—Lead.

The separation corresponds to the method given under Cobalt.

Nickel—Mercury.

LITERATURE:

Smith, Am. Chem. Journ., 12, 104 (1890).
Rüdorff, Zeit. f. angew. Chem., p. 388 (1894).
Heidenreich, Ber. deutsch. chem. Ges., 28, 1585 (1895).
Kollock, Journ. Am. Chem. Soc., 21, 911 (1899).

The method for the separation of these two metals is similar to that of cobalt from mercury. According to the statements of Smith, the separation may be carried out in a solution of the double cyanides. Heidenreich, who determined in the Aachen laboratory the proper conditions of experiment, found that only the mercury is precipitated when the potential at the electrodes is 1.2–1.6 volts.

EXPERIMENT.

Used about 1 g nickel ammonium sulphate and 3 g potassium cyanide.

Taken g $HgCl_2$.	Current-density, *Amperes.*	Potential-difference, *Volts.*	Time.	Found * *Per Cent Hg.*
0.3687	0.08–0.03	1.2–1.6	5½ hr.	73.65
0.3702	0.05–0.93	1.4–1.5	overnight	73.62
0.3000	0.05–0.03	1.4–1.5	"	73.66

The following conditions are given by Kollock: Two grams of potassium cyanide were added to a solution containing mercuric chloride (=0.1216 g Hg) and nickel nitrate (=0.1 g Ni), the volume of the solution was brought to 125 cc, and the electrolysis was conducted at 65° with a current of $ND_{100}=0.04$ ampere and a potential-difference of 2.2 volts. In four hours the mercury was completely precipitated.

ZINC.

Zinc—Manganese.

LITERATURE:

Riederer, Journ. Am. Chem. Soc., **21**, 789 (1899).
Classen, Ausgewählte Methoden, p. 386 (1902).

The solution of the sulphates, to which 6 grams of ammonium oxalate and free oxalic acid is added, is electrolysed at 50–60° with a potential-difference between the electrodes of 1.1 to 1.3 volts. Under these conditions the manganese

---

* Theory, 73.80% Hg.

remains in solution, the zinc only is deposited. To determine the manganese in the solution, it is precipitated as MnO_2 by adding a few cubic centimeters of hydrogen peroxide solution and a slight excess of ammonia, and the MnO_2 after careful washing is dissolved in a mixture of 25 cc water, 5 cc acetic acid, and 5 cc hydrogen peroxide solution. The excess of hydrogen peroxide is destroyed with CrO_3, and the solution is electrolysed as described on p. 172.

Zinc—Aluminium.

LITERATURE:

Classen, Ber. deutsch. chem. Ges., 14, 2771 (1881).

These elements can be separated by the electrolysis of a solution containing ammonium oxalate and free oxalic acid, under conditions similar to those given for the separation of zinc from manganese.

Zinc—Copper.

LITERATURE:

Rüdorff, Zeit. f. angew. Chem., p. 452 (1893).
Smith and Wallace, Journ. Anal. Chem., 7, 183 (1893).
Heidenreich, Ber. deutsch. chem. Ges., 28, 1585 (1895).
Fernberger and Smith, Journ. Am. Chem. Soc., 21, 1001 (1899).

For this separation Smith and Wallace recommend the precipitation of the copper from a solution containing free nitric acid. Heidenreich, who determined in the Aachen laboratory the proper conditions for analysis, found that if the solution contains about 4 cc free nitric acid (sp. gr. 1.3) to 120 cc of solution, and a potential-difference between the electrodes of 1.4 volt is not exceeded, the copper is precipitated free from zinc. (See p.179.)

EXPERIMENT.

Used copper sulphate (containing 25.29% Cu) to which 0.8 g zinc ammonium sulphate was added.

Taken $CuSO_4.5H_2O$ g.	ND_{100} Ampere.	Potential Difference between Electrodes.	Time.		Found. Cu. %
			hr.	m.	
0.4689	0.2	1.00-1.15 volt	15	30	25.25
0.4728	0.2–0.15	1.0 -1.2 "	15	—	25.25
0.5049	0.15–0.2	1.13 "	18	—	25.31
0.4660	0.5	1.2 "	2	—	25.22

As illustrating the separation of these two elements in a solution containing phosphates and free phosphoric acid, the following experiment is described by Fernberger and Smith:

60 cc of a solution of disodium hydrogen phosphate (sp. gr. 1.0358) and 10 cc phosphoric acid (sp. gr. 1.347) were added to a solution containing 0.1239 g of copper and 0.1 g of zinc as sulphates, the solution was diluted to a total volume of 225 cc, warmed to 60°, and electrolysed with a current of $ND_{100}=0.035$ *ampere and a potential-difference of* 2.5 volts. In 5 hours the copper was completely precipitated.

Zinc—Bismuth.

LITERATURE:

Kammerer, Journ. Am. Chem. Soc., 25, 83 (1903).

The following experiment is described by Kammerer: *To a solution containing 0.15 g bismuth dissolved in* 1 cc nitric acid (sp. gr. 1.42) and 0.15 g zinc as sulphate, 2 cc of sulphuric acid (sp. gr. 1.84) and 0.6 g potassium sulphate were added, the solution was diluted to 150 cc, and electrolysed at a temperature of 50° with a current of $ND_{100}=0.02$ ampere and a potential-difference of 2.0 volts. The bismuth was completely precipitated in 8 hours.

Zinc—Cadmium.

LITERATURE:

Yver, Bull. Soc. Chim., 34, 18 (1880).
Eliasberg, Zeit. f. anal. Chem., 24, 550 (1885).
Smith and Knerr, Am. Chem. Journ., 8, 210 (1886).
Smith, Am. Chem. Journ., 11, 352 (1889).
Waller, Zeit. f. Elektrochem., 4, 241 (1897–98).

A. Yver has recommended the use of a solution of acetates or sulphates treated with an excess of sodium acetate and a few drops of acetic acid; the electrolysis to be conducted with a warm solution, using two Daniell cells.

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 neutralised with sodium hydroxide, 3 g sodium acetate are added, the solution is warmed to about 45°, and electrolysed with a current of $ND_{100} = 0.3$ ampere and a potential-difference of about 2.4 volts.

According to experiments carried out in the author's laboratory by Waller, the separation of these elements can be carried out very satisfactorily under the following conditions: A solution of the chlorides from which the excess of hydrochloric acid has been expelled (containing 0.1 g of each of the metals) is treated with 8 g potassium oxalate and 2 g ammonium oxalate, diluted to 120 cc, and electrolysed at 80–85° with a current of $ND_{100} = 0.02$ ampere. The cadmium *is precipitated. The zinc remaining in the solution* is determined by evaporating this to a suitable volume, and electrolysing at first, for about 5 minutes, with a current of $ND_{100} = 1.0–1.5$ ampere, the temperature of the solution being about 50–60°, and then as described under zinc (p. 165), a tartaric acid solution being dropped slowly into the electrolyte. (Classen, Ausgewählte Methoden, p. 349.)

Zinc—Lead.

This separation can be conducted in a solution containing free nitric acid, the lead being precipitated as peroxide (see Lead, p. 194). To determine the zinc, it is converted into sulphate by evaporation with sulphuric acid, and is precipitated by the method given on page 165.

Zinc—Silver.

LITERATURE:

Smith and Wallace, Journ. Anal. Chem., 6, 87 (1892);
Zeit. f. Elektrochem., 2, 312 (1895–96).
Heidenreich, Ber. deutsch. chem. Ges., 28, 1585 (1895).
Kollock, Journ. Am. Chem. Soc., 21, 911 (1899).

This separation, according to Smith and Wallace, can be conducted from a solution containing potassium cyanide. The experimental conditions ascertained by Heidenreich in the Aachen laboratory were: temperature 60–70°, potential-difference 1.9–2.0 volts, current-density $ND_{100} = 0.02$ to 0.08 ampere. Under these conditions the precipitation of the silver takes place slowly.

The following particulars are given by Kollock: To a solution containing 0.1024 g silver as nitrate and 0.1 g zinc as sulphate, 1 g of potassium cyanide was added and the solution after diluting to 100 cc was electrolysed at 60–70°

with a current of $ND_{100}=0.38$ ampere and a potential-difference of 2.7 volts. The silver was completely precipitated in 3 hours.

Zinc—Mercury.

LITERATURE:

Wallace and Smith, Journ. Am. Chem. Soc., 18, 169 (1896);
Zeit. f. Elektrochem., 2, 312 (1896).
Heidenreich, Ber. deutsch. chem. Ges., 28, 1585 (1895).
Kollock, Journ. Am. Chem. Soc., 21, 911 (1899).
Fernberger and Smith, Journ. Am. Chem. Soc., 21, 1001 (1899).

Smith and Wallace have proposed the separation of these elements in a solution containing potassium cyanide. The following conditions were determined by Heidenreich in the Aachen laboratory: The solution contained about 0.25 g of mercuric chloride and 2–3 g of potassium cyanide, and was electrolysed with a current of $ND_{100}=0.03$ to 0.08 ampere and a potential-difference of 1.65–1.75 volt. The mercury was precipitated free from zinc in 5–14 hours.

According to Kollock the following conditions proved satisfactory: To a solution containing 0.1158 g of mercury as mercuric chloride and 0.1 g zinc as zinc sulphate, 2 g potassium cyanide was added, and the solution having a volume of 125 cc was electrolysed 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.

For the separation of mercury and zinc from a solution containing phosphates and free phosphoric acid, we are indebted to Fernberger and Smith for the following particulars:

60 cc disodium hydrogen phosphate (sp. gr. 1.038) and 10 cc phosphoric acid (sp. gr. 1.347) were added to a solution containing mercuric chloride (=0.1159 g Hg) and zinc sulphate (=0.1010 g zinc). The volume of the final solution was 175 cc, and this solution was electrolysed at 60° with a

current of $ND_{100} = 0.01$ and a potential-difference of 1.5 volt. The mercury was precipitated in 4 to 5 hours.

The separation of these two metals can also be conducted in solutions containing free acid (p. 204).

MANGANESE.

Manganese—Copper.

LITERATURE:

Fernberger and Smith, Journ. Am. Chem. Soc., 21, 1001 (1899).
Classen, Ausgewählte Methoden, p. 386 (1902).

The separation of manganese and copper can be conducted under conditions exactly similar to those given for the separation of manganese and zinc (p. 248).

According to Fernberger and Smith this separation may be conducted in a solution containing phosphates and free phosphoric acid under the following conditions:

To a solution containing about 0.1236 g of each of the metals, 60 cc of a solution of disodium hydrogen phosphate (sp. gr. 1.038) and 10 cc phosphoric acid (sp. gr. 1.347) were added, the solution was diluted to 225 cc, and electrolysed at 56° with a current of $ND_{100} = 0.05$ ampere and a potential-difference of 2.5 volts. The copper was precipitated in about 6 hours.

Manganese—Cadmium.

This separation may be conducted under the same conditions as those given for the separation of manganese and zinc (p. 248).

Manganese—Bismuth.

LITERATURE:

Kammerer, Journ. Am. Chem. Soc., 25, 83 (1903).

This separation, according to Kammerer, can be carried out under the following conditions:

To a solution containing 0.15 g of bismuth dissolved in 1 cc nitric acid (sp. gr. 1.42) and manganous sulphate (=0.15 g Mn), 3 cc sulphuric acid (sp. gr. 1.84) and 0.5 g potassium sulphate were added, the solution was diluted to 150 cc, and was electrolysed at 45° with a current of $ND_{100} = 0.025$ ampere and a potential-difference of 2.0 volts. The bismuth was completely precipitated in 9 hours, and although some manganese dioxide separated at the anode it was not found to contain any bismuth.

Manganese—Lead.

LITERATURE:

Neumann, Chem. Ztg., 20, No. 39 (1896).
Hansen, Chem. Ztg., 25, 393 (1901).
Classen, Ausgewählte Methoden, p. 386 (1902).

The separation depends upon the fact that in a solution containing more than 3 or 4 per cent. of free nitric acid no manganese dioxide is precipitated on electrolysis, while under the same conditions the lead is precipitated as peroxide on the anode. Fairly accurate results can be obtained when the solution does not contain more than 0.03 g Mn in 150 cc, and the electrolysis is conducted at 40–70° with a current of $ND_{100} = 1.5\text{–}2$ amperes and a potential-difference of 2.5 volts. If the solution contains a greater proportion of manganese, or if the electrolysis is continued too long after all the lead peroxide has separated, a flocculent precipitate of MnO_2 will appear in the solution, and the precipitated lead peroxide will contain manganese dioxide (Classen).

The other methods proposed for the separation of these two elements are of questionable accuracy. For further information the original articles should be consulted.

COPPER.

Copper—Cadmium.

LITERATURE:

Smith, Am. Chem. Journ., 12, 329 (1891).
Smith and Moyer, Zeit. f. anorg. Chem., 1, 299 (1892).
Freudenberg, Zeit. f. phys. Chem., 12, 122 (1893).
Smith and Wallace, Journ. Anal. Chem., 7, 253 (1893).
Heidenreich, Ber. deutsch. chem. Ges., 28, 1585 (1895).
Wallace and Smith, Journ. Am. Chem. Soc., 19, 870 (1897).
Rimbach, Zeit. f. anal. Chem., 37, 284 (1898).

According to the statements of Freudenberg, the metals can be separately precipitated from a solution containing 10–20 cc dilute sulphuric acid. When such a solution is electrolysed with a difference of potential between the electrodes of not more than 2 volts only the copper is deposited.

Heidenreich tested this method in the Aachen laboratory and found that the separation is best conducted with a difference of potential not exceeding 1.85 volt.

EXPERIMENT.

The volume of the liquid was 120 cc and it contained 15 cc dilute sulphuric acid (sp. gr. 1.09). The copper sulphate used contained 25.29% Cu.

Taken		Current-density ND_{100}, Amperes.	Potential-difference, Volts.	Time, hrs.	Found Cu, %
$CuSO_4.5H_2O$.	$CdSO_4.8H_2O$.				
0.7078	0.40	0.07–0.05	1.7–1.76	24	25.27

The time required for the precipitation of the copper can be considerably shortened by warming.

Experiments in which it was attempted to replace the sulphuric acid with nitric acid yielded no satisfactory results.

To determine the cadmium remaining in the solution from which the copper has been removed, the solution is neutralised with sodium hydroxide, and the cadmium is precipitated from a solution containing ammonium oxalate or potassium cyanide, as described under Cadmium.

The separation of these two metals can be carried out in a shorter time in a solution containing free nitric acid. The salts are dissolved in water, 5 cc of nitric acid (sp. gr. 1.21) are added, the whole is diluted to 150 cc, and electrolysed at ordinary temperatures with a current of $ND_{100} =$ 1.0 ampere and a potential-difference of 2.8 to 2.9 volts. *The copper is precipitated. To determine the cadmium in* the residual solution this is evaporated with an excess of sulphuric acid, to convert the cadmium into sulphate, and the cadmium is precipitated from a solution containing ammonium oxalate. (Classen, Ausgewählte Methoden, p. 115.)

According to Smith, the separation may also be conducted in a solution containing phosphates and free phosphoric acid. *With this end in view 20 cc disodium hydrogen* phosphate solution (sp. gr. 1.035) and 10 cc phosphoric acid (sp. gr. 1.35) are added to the solution, which is diluted to 125 cc and electrolysed at 60° with a current of $ND_{100} =$ 0.08 ampere and a potential-difference of 2.5 volts. The copper is deposited in about 3 hours.

Copper—Lead.

LITERATURE:

May, Am. Journ. Science, [3] 6, 255 (1873).
Nissenson, Zeit. f. angew. Chem., pp. 452, 646 (1893).
Classen, Ber. deutsch. chem. Ges., 27, 2060 (1894).

To separate copper from lead, 20 cc of nitric acid (sp. gr. 1.35) are added to the solution, which is then diluted to 75 cc, warmed, and electrolysed with a current of $ND_{100} =$ 1.5 to 1.7 ampere, a roughened dish serving as anode. At the end of one hour the greater part (98–99% when not more than 0.5 g is present) of the lead will have separated as peroxide, and the current is then interrupted, no trace of copper having as yet appeared on the cathode. The liquid should then be transferred to a second weighed dish, and the lead peroxide on the first washed with water, dried, and weighed. The washings from the lead peroxide are added to the solution in the second dish, which is treated with ammonia until the well-known deep-blue color appears, and then 5 cc of nitric acid are added. The second platinum dish is connected as cathode, and the perforated platinum dish-electrode described on page 112 is used as anode. The surface of the anode should be roughened, and its weight should be accurately determined before the experiment. The solution is diluted to 120–150 cc, allowed to cool, and electrolysed with a current of $ND_{100} = 1.0–1.2$ ampere. The copper will be precipitated on the cathode and the remainder of the lead as peroxide on the anode. The time required, when 0.25 g of copper is present, is about 4 hours.

This method, which is of great value in technical work is not only rapid (4-5 hours as compared with 14 hours or more), but allows of the complete precipitation of both metals, irrespective of the relative quantities present (see page 292).

Copper—Silver.

LITERATURE:

Luckow, Zeit. f. anal. Chem., 19, 15 (1880).
Smith and Frankel, Am. Chem. Journ., 12, 104 (1891).
Freudenberg, Zeit. f. phys. Chem., 12, 107 (1893).
Smith and Wallace, Zeit. f. Elektrochem., 2, 312 (1895).
Heidenreich, Ber. deutsch. chem. Ges., 28, 1585 (1895).
Küster and Steinwehr, Zeit. f. Elektrochem., 4, 451 (1897–98).
Revay, Zeit. f. Elektrochem., 4, 313 (1897–98).
Kollock, Journ. Am. Chem. Soc., 21, 911 (1899).
Brunck, Ber. deutsch. chem. Ges., 34, 1604 (1901).
Fulweiler and Smith, Journ. Am. Chem. Soc., 23, 582 (1901).

According to Freudenberg, this separation can be carried out in a solution containing 2 to 3 cc nitric acid (sp. gr. 1.2), by conducting the electrolysis with a potential-difference of from 1.3 to 1.4 volt. Under these conditions the silver is precipitated free from copper. The copper remaining in the solution can be afterwards precipitated by increasing the difference of potential to 2 to 3 volts. The time required for the analysis is reduced about one-half by warming the solution.

According to Smith and Frankel, these two metals can be separated in a solution containing the double cyanides with potassium. 4.5 g of potassium cyanide are added to a solution containing about 0.4 g of the metals. The solution is diluted to 120 cc and electrolysed. If the electrolyte *is warmed to 65–75°, the precipitation of the silver is greatly* hastened. M. Heidenreich tested this method in the Aachen laboratory, and determined the following conditions for analysis.

EXPERIMENT.

Used silver nitrate, containing 63.42% silver, and about 0.7 g of copper sulphate in each experiment.

Taken		Current-density, *Amperes.*	Potential-difference, *Volts.*	Time.		Found Ag.
$AgNO_3$. g.	KCN. g.			hr.	m.	%
0.2379	2	0.07–0.03	1.0–1.2	8	—	63.34
0.2303	2	0.04	1.0–1.3	8	—	63.43
0.3099	2	0.03	1.0–1.4	6	30	63.40
0.3327	2	0.09	1.2–1.3	4	(warmed)	63.27
0.6037	6	0.19–0.08	1.2–1.3	6	—	63.33

According to Freudenberg the maximum difference of potential used must not exceed 2.3 volts, or both metals will be precipitated. The copper remaining in the solution after the silver has been removed can be deposited by electrolysing with a higher difference of potential.

Kollock describes the following experiment: Two grams of potassium cyanide were added to a solution containing 0.1024 g silver and 0.098 g copper, both present as nitrate, the solution was diluted to 125 cc, warmed to 65°, and electrolysed with a current of $ND_{100} = 0.03$–0.05 ampere and a potential-difference of 1.1–1.6 volt. The silver was completely precipitated in 3–7 hours.

Fulweiler and Smith recommend that the solution, after the separation of the silver, be diluted to 500 cc and electrolysed with a higher potential-difference to precipitate the copper.

Copper—Mercury.

LITERATURE:

Smith, Journ. Anal. Chem., 3, 254 (1889);
Am. Chem. Journ., 11, 104, 264 (1889);
Journ. Anal. Chem., 5, 489 (1891).
Freudenberg, Zeit. f. phys. Chem., 12, 113 (1893).
Smith, Journ. Am. Chem. Soc., 16, 42 (1894).
Revay, Zeit. f. Elektrochem., 4, 313 (1897–98).
Kollock, Journ. Am. Chem. Soc., 21, 911 (1899).
Spare and Smith, Journ. Am. Chem. Soc., 23, 597 (1901).

According to Edgar F. Smith, the separation can be conducted in a solution containing the double cyanides. The temperature should be about 65°. Under the ordinary conditions of concentration (150 cc) about 2 grams of potassium cyanide are added, and the solution is electrolysed with a current of $ND_{100} = 0.06$–0.08 ampere. The electrolysis requires about 4 hours for every 0.2 g of the metals present. The mercury is deposited, the copper remaining in the solution.

Freudenberg found that in the presence of 2–4 g potassium cyanide when the difference of potential between the electrodes is maintained at 2.5 volts, the mercury separates brilliantly white and entirely free from copper.

The copper remaining in the solution after the mercury has been separated is precipitated by electrolysing the solution warmed to 60° with a potential-difference of 4.2 volts between the electrodes.

The two following experiments are described by Spare and Smith:

1. To a solution containing 0.1211 g of mercury and 0.1520 g of copper, 2.5 g of potassium cyanide were added. The solution after dilution to 125 cc was electrolysed at 63° with a current of $ND_{100}=0.03–0.05$ ampere and a potential-difference of 1.2–1.9 volts. *In from 2½ to 4 hours the mercury was completely precipitated.*

2. To a solution containing 0.0453 g of mercury and 0.5115 g of copper, 5.5–7.5 g of potassium cyanide were added. The solution was diluted to 135 cc, and was electrolysed at 60° with a current of $ND_{100}=0.01–0.03$ ampere and a potential-difference of 1.1–1.5 volts. The mercury was completely precipitated in 2½ to 3½ hours.

Copper—Arsenic; Copper—Antimony.

LITERATURE:

Drossbach, Chem. Zeitung, 16, 819 (1892).
Freudenberg, Zeit. f. phys. Chem., 12, 97 (1893).
Oettel, Chem. Zeitung, 18, 879 (1894).
Schmucker, Zeit. f. anorg. Chem., 5, 199 (1894).
Hollard, Compt. rend., 123, 1063 (1896).
Bead, Berg- u. Hüttenm. Ztg., 57, 139 (1898).
Lucas, Bull. Soc. Chim., 19, 817 (1898).

Freudenberg has shown that the separation of copper and arsenic can be satisfactorily conducted in a solution containing 10–20 cc dilute sulphuric acid if the difference of potential between the electrodes is not allowed to exceed 1.9 volts. It is immaterial whether the arsenic is present as arsenious or arsenic acid. A second method suggested by the same author is the following: Ammonia is added to a solution containing the metals in the form of higher oxides, until there is an excess of about 30 cc of 10% ammonia present. The electrolysis is conducted with a difference of potential between the electrodes of 1.9 volts, and is continued until the solution is completely decolorised, requiring generally 6–8 hours. This method is not suitable for the separation of copper and antimony.

Copper can be separated from arsenic and small quantities of antimony by the electrolysis of a solution containing ammonium nitrate and free ammonia (Rüdorff's method, p. 182) with a current of $ND_{100} = 0.07-0.27$. The proportion of ammonia present must not be too great or too small. If the latter, a brown deposit forms on the anode, which becomes detached and produces black spots on the precipitated copper, causing the weight of this to improperly increase. Large quantities of ammonium nitrate have a beneficial influence. According to Oettel, the concentration of the solution must not exceed 0.8 g of copper in 100 cc (Classen, Ausgewählte Methoden, p. 80).

According to Head, a copper solution containing arsenic and antimony can be freed from the two latter so that on electrolysis only pure copper will be precipitated:

The solution is evaporated to complete dryness and 10 cc of bromine, in which 2 g of sulphur has been dissolved, is added. The mixture is evaporated to a pasty mass, 20 cc of pure bromine is then added, and this mixture is heated until all of the antimony has been driven off as a white vapor and the residue is dry and light gray in color. The dish must be covered as long as there is chance of loss from spattering, and the copper bromide must not be too strongly heated, since in this case loss would occur. The residue contains only traces of antimony, and is suitable for electrolysis after it has been converted into sulphate.

BISMUTH.

Bismuth—Cadmium.

LITERATURE:

Kammerer, Journ. Am. Chem. Soc., 25, 83 (1903).

The following experiment is described by Kammerer: 0.15 g of bismuth was dissolved in 1 cc nitric acid (sp. gr. 1.42) and to this was added 0.15 g of cadmium oxide dissolved in 2 cc of sulphuric acid (sp. gr. 1.84). To the above mixture 1 g of potassium sulphate was added, the solution was diluted to 150 cc, and electrolysed at 50° with a current of $ND_{100}=0.025$ ampere and a potential-difference of 2.0 volts. The cadmium was completely precipitated in 8 hours.

Bismuth—Uranium.

LITERATURE:

Kammerer, Journ. Am. Chem. Soc., 25, 83 (1903).

Kammerer describes this separation as follows: To a solution containing 0.15 g of bismuth dissolved in 1 cc nitric acid (sp. gr. 1.43) and uranium sulphate equivalent to 0.1 g Ur, 1 g of potassium sulphate and 2 cc of sulphuric acid (sp. gr. 1.84) were added, and after diluting to a volume of 150 cc the bismuth was precipitated with a current of $ND_{100}=0.025$ ampere and a potential-difference of 2 volts. The temperature of the solution throughout the operation was 45° and the time required was 8 hours.

CADMIUM.

Cadmium—Lead.

The method is the same as that in the separation of lead from copper, except that the precipitation of the lead is conducted in one operation.

To determine the cadmium in the solution from which the lead has been removed, this is converted into sulphate by evaporation with sulphuric acid, and is precipitated by electrolysis by one of the methods described on page 188.

Cadmium—Silver.

LITERATURE:

Kollock, Journ. Am. Chem. Soc., 21, 911 (1899).

The following experiment is described by Kollock: Two grams of potassium cyanide were added to a solution containing *silver nitrate* ($=0.1024$ *g Ag*) and *cadmium sulphate* ($=0.168$ g Cd), the mixture was diluted to 125 cc, and was electrolysed at 65° with a current of $ND_{100}=0.02$ ampere and a potential-difference of 2.15 volts. At the end of 5 hours the silver was completely precipitated.

Cadmium—Mercury.

LITERATURE:

Freudenberg, *Zeit. f. phys. Chem.*, 12, *97 (1893).*
Smith and Wallace, Journ. Am. Chem. Soc., 17, 612 (1895).
Kollock, Journ. Am. Chem. Soc., 21, 911 (1899).

According to Freudenberg, these metals are best separated *in a solution containing 0.5–1.0 g potassium cyanide.* When the electrolysis is conducted with a potential-difference between the electrodes of from 1.8 to 1.9 volts, only the mercury is precipitated. After the separation of the mercury the cadmium is precipitated from the solution by a current having a higher difference of potential.

Kollock describes an experiment in which 2.5 g of potassium cyanide were added to a solution containing 0.1182 g of mercury as mercuric chloride and 0.2 g of cadmium as sulphate, and the solution having a volume of 125 cc was electrolysed at 65° with a current of $ND_{100} = 0.018$ ampere and a potential-difference of 1.7 volt. The mercury was completely precipitated in 7 hours.

LEAD.

Lead—Silver.

LITERATURE:

Luckow, Zeit. f. angew. Chem., p. 345 (1890).
Smith and Moyer, Zeit. f. anorg. Chem., 4, 267 (1893).

This separation can be carried out like that of lead from copper (see page 257). To determine the silver in the residual solution it is evaporated down to a smaller volume on the water-bath, and the silver is precipitated according to the directions given on page 200.

Lead—Mercury.

LITERATURE:

Smith and Moyer, Zeit. f. anorg. Chem., 4, 267 (1893).
Heidenreich, Ber. deustch. chem. Ges., 28, 1585 (1895).

The method corresponds to that used for the separation of copper and lead. Smith and Moyer have suggested the determination of the lead and mercury at the same time, the lead being precipitated as peroxide on the anode, the mercury as metal on the cathode. The conditions suitable for this separation, according to Heidenreich, are that 20–30 cc nitric acid (sp. gr. 1.3–1.4) must be present in every 120 cc of the solution, which should be electrolysed with a current of $ND_{100}=0.2–0.5$ ampere.

According to Smith (Electro-Chemical Analysis, 1902, p. 152), the solution should have a volume of 175 cc and should contain 20–30 cc of nitric acid (sp. gr. 1.3), and the electrolysis should be conducted at 30° with a current of $ND_{100}=0.13$ to 0.18 ampere and a potential-difference of 2 volts, for 4 hours. A platinum dish should be used as anode.

SILVER.

Silver—Antimony.

LITERATURE:

Freudenberg, Zeit. f. phys. Chem., **12**, 97 (1893).

If the antimony is present as pentoxide, the separation can be carried out in an ammoniacal solution to which several grams of ammonium sulphate have been added. In this case the difference of potential at the electrodes should be so regulated that it is between 1.2–1.3 volts. Since under these conditions the current-density at the cathode is so low that the deposited silver does not adhere firmly to the electrode, it is better to add to the solution 1 g of potassium cyanide for 0.1 g of metal present and conduct the electrolysis with a potential-difference of 2.3–2.4 volts.

Silver—Arsenic.

LITERATURE:

Freudenberg, Zeit. f. phys. Chem., **12**, 97 (1893).

According to Freudenberg, this separation can be carried out in the same manner as the separation of silver from antimony.

MERCURY.

Mercury—Antimony.

LITERATURE:

Freudenberg, Zeit. f. phys. Chem., 21, 97 (1893).

The antimony must be added in the form of a pentavalent salt, since otherwise a reduction of the mercuric salt present will occur. A mixture of the chlorides of the two metals can be brought into solution by the addition of 0.5–1 g of tartaric acid. The solution is diluted with water, neutralised with ammonia, and about 20 cc of a ten-per-cent. solution of ammonia added until the solution is perfectly clear. The electrolysis is conducted with a difference of potential of 1.6 to 1.7 volts. After the mercury has been deposited, the solution is acidified with hydrochloric acid and treated with hydrogen sulphide. The precipitated antimony sulphide can be determined gravimetrically or by electrolysis as described on p. 210.

Mercury—Arsenic.

LITERATURE:

Freudenberg, Zeit. f. phys. Chem., 12, 97 (1893).

According to Freudenberg, this separation can be carried out in a solution containing nitric acid (see page 204) from which the mercury is precipitated by a difference of potential between the electrodes of 1.7–1.8 volts.

ANTIMONY.

Antimony—Tin.

LITERATURE:

Classen, Ber. deutsch. chem. Ges., 17, 2245 (1884);
ibid., 18, 1110 (1885); *ibid.*, 28, 2060 (1895).
Waller, Zeit. f. Elektrochemie, 4, 241 (1897–98).
Ost and Klapproth, Zeit. f. angew. Chem., p. 827 (1900);
Zeit. f. Elektrochem., 7, 376 (1900).

The separation of antimony from tin by the ordinary gravimetric methods, as is well known, is difficult and gives in most cases uncertain results. The electrolytic separation, however, can be conducted with ease and accuracy. Antimony, in the presence of tin, can be completely precipitated from a *concentrated* solution of sodium sulphide to which the proper amount of sodium hydroxide has been added.

The crystallised sodium monosulphide of commerce, aside from the fact that its purity is otherwise uncertain, is not pure monosulphide, but a mixture of several sulphides with varying amounts of sodium hydroxide. This explains the large per cent. of alumina which it often contains. If, therefore, commercial sodium sulphide is used, it must first be dissolved in water, and the solution, with exclusion of air, completely saturated with pure hydrogen sulphide gas. It is then filtered from the precipitated impurities and concentrated by evaporation in a platinum or porcelain dish. The further treatment is given in the chapter on reagents (p. 294). As the purity of the sodium sulphide solution used is of great importance to the success of the process, it is desirable to prepare the solution as directed in the chapter referred to.

The process of separation is as follows: A mixture of the pure sulphides,* or the residue obtained by evaporating a solution of the two metals to dryness, is treated with about 80 cc of a saturated solution of sodium sulphide (saturated at ordinary temperature) and enough *concentrated* solution of *pure* sodium hydroxide to furnish an excess of 1–2 g NaOH. If solution does not take place at once, it is hastened by warming over a low flame. The preparation of this solution is best conducted in the platinum dish in which the electrolysis is to be carried out.

The electrolysis can be conducted at a temperature of 50–60° with a difference of potential between the electrodes of not more than 0.7 volt. Under these conditions the current-density will be about $ND_{100}=0.5$ ampere, and the precipitation of the antimony will be complete in about two hours. The separation can also be conducted in the cold with a current of $ND_{100}=0.2$–0.4 ampere and a potential-difference of 0.5–0.7 volt, in which case the time required will be about fourteen hours. To obtain satisfactory results the inner surface of the platinum dish (cathode) should be roughened.

When the electrolysis begins, the whole inner surface of the dish which is in contact with the solution becomes quickly covered with a dark coating of antimony, which soon takes on a brilliant metallic appearance.

In the earlier part of the process the entire solution appears to be filled with small gas-bubbles, which rise slowly, break at the surface, and project minute portions of the solution against the lower side of the watch-glass covering the liquid. After about two hours the disengagement of

---

* A solution in sodium sulphide of the metal sulphides and sulphur should be treated like a solution of polysulphides (p. 211).

gas ceases and the solution becomes clear. To avoid loss, it is best, at this time, to wash repeatedly the under surface of the cover-glass with a drop of water, which is finally allowed to run down the positive electrode. When the precipitation of the antimony is complete, the deposited metal is washed without interrupting the current, and is then treated according to the directions given on page 211.

Since tin cannot be precipitated by electrolysis from a solution containing sodium sulphide, but can readily be precipitated from one containing ammonium sulphide, the sodium sulphide, after the separation of antimony, must be converted into ammonium sulphide according to the directions given on p. 215.

If tin and antimony are to be determined in a solution containing the yellow polysulphides of the alkalies, the solution must be decolorised with ammoniacal hydrogen peroxide (see Antimony, p. 211), and then evaporated nearly to dryness; about 80 cc of a saturated solution of sodium sulphide and the necessary amount of sodium hydroxide are then added and the process is carried out as described above.

In the following experiments antimony was precipitated from both warm and cold solutions containing tin.

EXPERIMENTS.

Used about 1 g antimony potassium tartrate, an equal weight of ammonium stannic chloride, 80 cc sodium sulphide solution, and about 2 g sodium hydroxide.

Current-density, Amperes.	Potential-difference, Volts.	Temp.	Time, hrs.	Taken Antimony, g.	Found Antimony, g.
1.4–1.5	0.8–0.9	57–67°	2	0.3780	0.3790
1.5–1.6	0.8–0.9	58–60°	2	0.3780	0.3787
0.4–0.2	0.7–0.55	24–30°	15	0.3780	0.3775

The precipitated antimony was gray in color and metallic in appearance, and it contained no tin.

Antimony—Arsenic.

LITERATURE:

Classen and Ludwig, Ber. deutsch. chem. Ges., 19, 323 (1886).
Classen, Zeit. f. Elektrochem., 1, 291 (1894–95).

In an *alkaline* solution arsenious acid is oxidised to arsenic acid by the action of the electric current. If, however, a solution containing both antimony and arsenious acid is electrolysed, 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 a free alkali, the antimony alone is precipitated from a concentrated sodium sulphide solution.

The arsenic if present as arsenious acid must be oxidised to arsenic acid before it can be separated from antimony. Nitric acid or *aqua regia* should be added to the solution, the acid completely expelled by evaporating to dryness on a water-bath, the residue treated with 80 cc of a cold saturated solution of sodium sulphide, a concentrated solution of sodium hydroxide (containing 1–2 g NaOH) added, and this solution electrolysed. The operation is conducted under the same conditions as in the separation of antimony from tin, and the electrolyte can either be warm or at the ordinary temperature.

If the solution containing the arsenic and antimony also contains polysulphides, the latter should be destroyed as described on p. 211.

To determine the arsenic, the antimony-free solution is acidified with dilute sulphuric acid, heated on the water-bath to expel the hydrogen sulphide, 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 weighed filter and weighed, or converted into magnesium pyroarsenate by careful ignition in a porcelain crucible.

EXPERIMENT.

Used about 1 g of antimony potassium tartrate, 1 g sodium arsenate, 80 cc sodium sulphide solution, and 2.5 g sodium hydroxide.

Current-density, Amperes.	Potential-difference, Volts.	Temp.	Time, hrs. m.	Found Sb, g.	Taken Sb, g.
1.55–1.5	1.75–1.1	54–57°	3 30	0.3778	0.3773
1.60–1.5	2.10–1.45	25–38°	6 —	0.3770	0.3773
0.5 –0.4	1.75–0.8	21–24°	overnight	0.3770	0.3770

Antimony—Tin—Arsenic.

LITERATURE:

Classen, Ber. deutsch. chem. Ges., 17. 2245 (1884);
ibid., 18, 1110 (1885); *ibid.*, 28, 2060 (1895).
Classen and Ludwig, *ibid.*, 19, 323 (1886).

If arsenic is present as arsenic acid, antimony alone is precipitated from a concentrated alkaline solution of the three metals in sodium sulphide; tin and arsenic remain in solution. The arsenic is converted into arsenic acid, and the antimony precipitated, exactly as heretofore described.

For the separation of tin from arsenic, the solution poured off from the antimony is treated with dilute sulphuric or hydrochloric acid to decompose the sulpho-salts, the mixture of arsenic sulphide, tin sulphide, and sulphur is filtered off, oxidised with hydrochloric acid and potassium chlorate, and the arsenic separated as described on p. 273. To determine the tin, the solution freed from arsenic is saturated with hydrogen sulphide, filtered, and the tin sulphide dissolved in ammonium sulphide. The tin is determined electrolytically as directed, p. 215.

In the analysis of a substance which contains arsenic, antimony, and tin, the arsenic may also be first eliminated according to the method of E. Fischer-Hufschmidt, simplified by R. Ludwig and the author,* and antimony and tin separated in the arsenic-free solution.

If the sulphides of the metals are to be separated, they are oxidised with concentrated hydrochloric acid and potassium chlorate and the acid evaporated on the water-bath. The residue is washed with fuming hydrochloric acid into a flask of 500–600 cc capacity,† treated with 20–25 cc of a saturated solution of ferrous chloride, or, better, with about 25 g of ammonium ferrous sulphate [$FeSO_4.(NH_4)_2SO_4.6H_2O$], and fuming hydrochloric acid added till the volume is 150 to 200 cc. A strong current of hydrochloric acid gas is now passed into the solution and kept up for at least half an hour after the solution seems fully saturated. Then the solution is reduced to about 50 cc by distilling off the liquid, without a condenser, in a stream of hydrogen chloride gas. A flask of about 1 liter capacity, containing 400–500 cc water, is used as a receiver. If the flask is well cooled during the distillation, not a trace of arsenic passes over into a second receiver, even when as much as 0.5 g, reckoned as As_2O_3, is present.

The arsenic in the distillate may either be saturated with sodium carbonate and titrated with iodine solution or precipitated as As_2S_3 with hydrogen sulphide, and determined

---

* Ber. d. ch. Ges., 18, 1110 (1885).

† A convenient apparatus is illustrated in the author's "Handbuch der Quantitative Analyse," 4th edition, p. 78.

as such on a weighed filter, or the arsenic can be calculated by determining the amount of sulphur in the precipitate. The process in the latter case is as follows: The distillate is mixed with twice its volume of water, air expelled by a strong current of carbon dioxide, and the arsenic precipitated by passing in pure hydrogen sulphide gas. The excess of hydrogen sulphide is removed by passing a strong current of carbon dioxide till lead acetate paper is not colored by the escaping gases. The arsenic sulphide is allowed to subside, and the clear solution siphoned off. The remaining strongly acid solution is saturated with ammonia, which dissolves the arsenic sulphide; the solution is then boiled with an excess of hydrogen peroxide free from sulphuric acid. The solution is acidified with hydrochloric acid, and the sulphuric acid produced by the action of the hydrogen peroxide determined as barium sulphate in the usual way (Classen).

To determine the antimony and tin, the strong acid solution in the flask, which contains the iron, is diluted with three times its volume of water. Antimony and tin are precipitated with hydrogen sulphide. After the precipitate has subsided, the clear solution is poured on a filter, the precipitate washed several times by decantation, and afterwards on the filter, with hot water, till free from hydrochloric acid. Portions of the sulphides often adhere to the walls of the flask in which the precipitation took place. These are washed out with concentrated sodium sulphide solution and the solution is poured on the filter containing the sulphides. The filtrate is collected in a weighed platinum dish. The filter, on which some iron sulphide always remains after the solution of the antimony and tin sulphides, is washed with sodium sulphide solution, the necessary amount of sodium hydroxide is added to the filtrate, and the antimony and tin are separated electrolytically as already directed.

TIN—PHOSPHORIC ACID.

In the determination of metals in the presence of phosphoric acid the latter is often removed as tin phosphate. The phosphoric acid is then usually determined in a separate portion, as its determination in the tin precipitate is too difficult and slow a process. The precipitate of tin oxide and tin phosphate may, however, be dissolved by digesting with ammonium sulphide, the solution diluted, the tin precipitated by electrolysis, and the phosphoric acid determined as usual.

SEPARATION OF GOLD FROM OTHER METALS.

LITERATURE:

Smith and Muhr, Ber. deutsch. chem. Ges., 23, 2175 (1890).
Smith, Am. Chem. Journ., 13, 206 (1892).
Smith and Wallace, Ber. deutsch. chem. Ges., 25, 779 (1892);
Journ. Anal. Chem., 6, 87 (1892).
Smith and Muhr, Am. Chem. Journ., 13, 417 (1892).
Kollock, Journ. Am. Chem. Soc., 21, 911 (1899).

Edgar F. Smith has made an exhaustive study of the action of the electric current on solutions containing the cyanides of the metals, and has applied this method to the separation of gold from palladium, copper, nickel, zinc, and platinum.

Kollock, who carried out a series of experiments in Smith's laboratory, has published the following details for this method:

Gold–Palladium.—2 grams of potassium cyanide were added to a solution containing gold chloride (=0.1256 g Au) and palladium chloride (=0.1 g Pd). The solution was diluted to 125–250 cc, warmed to 65°, and electrolysed with a current of $ND_{100}=0.03$–0.06 ampere and a potential-difference of 2.5 volts. The gold was precipitated free from palladium in 6 hours.

Gold-Copper.—2 grams of potassium cyanide were added to a solution containing gold chloride (=0.1665 g Au) and copper sulphate (=0.1 g Cu). The solution was diluted to 250 cc and electrolysed at 65° with a current of $ND_{100}=0.05$–0.07 ampere and a difference of potential between the electrodes of 1.7–1.9 volts. The gold was completely precipitated in about three hours.

Gold-Nickel.—4 grams of potassium cyanide were added to a solution containing 0.1610 g gold as chloride and nickel nitrate (=0.1 g Ni). The solution was diluted to 125 cc, maintained at a temperature of 65°, and electrolysed with a current of $ND_{100}=0.05$ ampere and a potential-difference of 1.6 volts. After 7 hours the gold was entirely precipitated.

Gold-Cobalt.—The conditions of the experiment were similar to those for the separation of gold and nickel.

Gold-Zinc.—The solution contained 0.1608 g of gold as chloride and zinc sulphate (=0.1 g Zn). To this 4 g potassium cyanide were added, it was diluted to 125–250 cc, and electrolysed at 60° with a current of $ND_{100}=0.06$ ampere and a potential-difference of 2.7 volts. The complete precipitation of the gold required 7 hours.

Gold-Platinum.—The solution contained gold and platinum chlorides (Au=0.1576 g) (Pt=0.1 g). To this solution 1.5 g of potassium cyanide was added, the volume was increased to 250 cc by diluting with water, and the electrolysis was conducted at 70° with a current of $ND_{100}=0.01$ ampere and a potential-difference of 2.7 volts. In three hours the gold was completely precipitated.

PLATINUM—IRIDIUM.

As stated on page 218, platinum can be separated from a hydrochloric acid solution by a current of $ND_{100} = 0.05$ ampere and a potential-difference of 1.2 volts.

This property of platinum may be used for separating it from iridium, which under similar conditions remains in solution.

The platinum is deposited free from iridium (Classen).

POTASSIUM—SODIUM.

The ordinary method of determining potassium and sodium in the same solution is to weigh the mixed chlorides, and the potassium as potassium platinic chloride; the sodium is thus determined by difference. The errors of the work, therefore, all fall on the sodium. The potassium may be determined, as already directed (p. 218), by precipitating as potassium platinic chloride and determining the platinum in the latter by electrolysis. To determine the sodium directly, the filtrate from the potassium platinic chloride is evaporated on the water-bath to remove alcohol, the residue dissolved in water with the addition of a little hydrochloric acid, and the platinum deposited by electrolysis. The sodium chloride in the solution poured off from the platinum is determined by evaporating to dryness and weighing the residue.

SODIUM—AMMONIUM.

The direct determination of both is accomplished as with potassium and sodium; the ammonium is precipitated as ammonium platinic chloride and the process conducted as described above.

SECTION V.

SEPARATION OF THE HALOGENS.

LITERATURE:

Specketer, *Zeit. f. Elektrochem.*, 4, 539 (1898).

The method of separating chlorine, bromine, and iodine suggested by Specketer depends upon the fact that the potential-difference required to effect the separation of iodine, in the form of silver iodide, on a silver anode is lower than that required to separate bromine as silver bromide, which in turn is lower than that required to separate chlorine as silver chloride.

In Specketer's experiments the salts (KI, KBr, KCl) were dissolved in a normal sulphuric acid solution, and this mixture was electrolysed. For the electrolytic cell a narrow cylindrical glass vessel closed with a cork stopper was used. A glass tube dipping into the electrolyte, through which a constant stream of hydrogen was passed during the electrolysis, extended through the stopper to the bottom of the cell. The stopper also carried the cathode, a strip of platinum foil, and the anode, a strip of gauze made from pure silver wire.

The source of current was a Gülcher thermopile, the current from this being passed through a brass wire. The electrolytic cell was connected in shunt between one terminal of the wire and a sliding contact which could be moved along it (see p. 104). By this arrangement any difference of potential less than 3 volts (that of the thermopile) could be maintained between the electrodes in the electrolytic cell.

For the separation of iodine from bromine and chlorine a potential-difference of 0.13 volts was used. Under these conditions only iodine was deposited (to form AgI). For separating bromine from chlorine the potential-difference used was 0.35 volt, the bromine being deposited under these conditions. Owing to the speed and convenience of the volumetric method, the chlorine in the residual solution was determined by titration according to Volhard's method.

It was found that the purity of the silver used for the anode was very important, and that the presence of even slight traces of copper was detrimental to accurate results, since by the dissolving of copper from the anode the results obtained were too low.

The end of the separation of a given halogen was determined by observing the fall in the current-strength as indicated by a sensitive galvanometer connected in series with the cell. When the separation was complete, practically no current was observed to flow through the electrolytic cell at the given difference of potential.

The mean average of the results obtained in 13 different determinations of iodine was: taken 0.1825 g, found 0.1814 g; of 8 determinations of bromine: taken 0.1936 g, found 0.1926 g.

PART THIRD.

SECTION I.

SOME APPLIED EXAMPLES OF ELECTROCHEMICAL ANALYSIS.*

BRASS.

Alloy of Copper and Zinc (Lead, Tin, Iron).

FOR the complete analysis of this alloy a sample weighing about 0.5 g should be taken. This is dissolved in a small quantity of dilute nitric acid, and the solution evaporated to dryness on the water-bath. The residue is moistened with dilute nitric acid, dissolved in a small quantity of hot water, and any stannic oxide appearing in the solution removed by filtration. The tin can be determined by the ordinary gravimetric method (igniting and weighing the stannic oxide) or by electrolysis according to the method described on p. 213. The filtrate from the oxide of tin is evaporated on the water-bath in the presence of a slight excess of

---

* Most of the applied examples of electrochemical analysis here given appeared in the third German and second English editions of this work, but are not contained in the fourth German edition. Owing to the practical value in these examples the translator has thought it desirable to include them in the present edition, and has, at the same time, made such alterations as the recent advances along the various lines would seem to justify.

sulphuric acid until the odor of nitric acid can no longer be detected. The residue is moistened with a few drops of dilute sulphuric acid, treated with hot water, and any lead sulphate which appears is filtered off and washed with water containing a very small quantity of sulphuric acid.

The quantity of the lead sulphate can be determined by the ordinary gravimetric method, or can be dissolved and the lead determined by electrolysis under the conditions described on p. 196.

About 5 cc of concentrated nitric acid are now added to the filtrate from the lead sulphate, which is diluted to about 150 cc, and the copper is precipitated by the method given on p. 180. When the separation of the copper is complete, the solution containing the zinc is poured off, and is again evaporated on the water-bath to remove nitric acid. The residue is dissolved in a small quantity of water and a slight excess of ammonia added, when any iron present will be precipitated as ferric hydroxide and can be removed by filtration. Ammonium oxalate is now added to the solution containing the zinc, and this element is precipitated as metal by the method described on p. 165. The same electrode upon which the copper has been precipitated can be used for receiving the zinc. By this the necessity of preparing a special copper-plated electrode is avoided.

NICKEL COIN.

Alloy of Copper and Nickel.

About 0.5 g of this alloy is dissolved in dilute nitric acid, 8 cc of dilute sulphuric acid (50%) added, and the solution evaporated on the water-bath until all nitric acid is expelled. The residue is then dissolved by warming with about 100 cc of water—which requires some time since the sulphate of nickel dissolves very slowly—5 cc of dilute nitric acid is added, the liquid is diluted to 150 cc, and electrolysed with a current of $ND_{100} = 0.5$ ampere and a difference of potential of 2.2 volts. By this treatment the copper is completely precipitated in about 6 hours.

After the removal of the copper the solution is evaporated on the water-bath to remove nitric acid, the residue is dissolved by warming with about 80 cc of water, the solution is neutralised with ammonia, and about 40 cc of ammonia (sp. gr. 0.96) are added. After diluting to about 150 cc the nickel in the solution is precipitated by a current of $ND_{100} = 0.5$–1.5 ampere and a potential-difference of 2.8–3.3 volts.

GERMAN SILVER.

Alloy of Copper, Zinc, Nickel (Tin, Lead).

The copper, tin, and lead present in this alloy can be determined by the method given for the determination of these elements in brass (p. 281). About 0.3 g of the alloy should be taken.

For separating the zinc and nickel the method described by Vortmann can be used. For this purpose the solution, after the separation of the copper, is evaporated to remove the nitric acid, and, after dissolving the residue in water, the solution is neutralised with sodium hydroxide. 5 g potassium sodium tartrate is now added to the solution, which is made strongly alkaline with sodium hydroxide, and the zinc is precipitated with a current of $ND_{100} = 0.3$–0.6 ampere and a potential difference of 2 volts. The zinc can be precipitated on the electrode bearing the copper precipitate. In this operation oxide of nickel may separate on the anode, or may appear in the solution in sufficient quantities to slightly discolor the precipitated zinc. This may be prevented by adding a small quantity of potassium iodide to the solution.

According to Neumann * the nickel remaining in the solution after the separation of the zinc, can be determined by slightly acidifying the solution with sulphuric acid, adding the proper excess of ammonia and precipitating the nickel by the method described on page 158.

Since the separation of nickel and zinc by electrolysis is not in all cases entirely satisfactory, it is perhaps better to conduct this separation in a formic-acid solution by treatment with hydrogen sulphide.

This method of separation was first proposed by Hampe,† and the following modification by Prof. H. L. Wells of the Sheffield Scientific School can be especially recommended in the case under consideration.

A sample of the alloy weighing 1 g is taken for the analysis, and after separating the copper as already described, the solution is evaporated to remove nitric acid, and the residue of sulphates is dissolved in water. About 2 or 3 cc of formic acid (sp. gr. 1.12) is now added to the solution, then enough ammonia to change the color to blue, and finally 25 cc of formic acid (sp. gr. 1.12). The solution is now diluted to a volume of 100 cc, heated to boiling, the source of heat removed, and a rather rapid stream of hydrogen sulphide passed into the solution for about 15 minutes.

The precipitated zinc sulphide, which should be pure white, is filtered from the hot solution and washed with hot water. The filtrate is evaporated to dryness, 25 cc each of concentrated hydrochloric and nitric acid added, and heated on the water-bath until effervescence ceases. The solution is then evaporated and heated until all traces of nitric and

---

* Analytischen Elektrolyse. Halle, 1897.

† Zeit. f. anal. Chem., 24, 588 (1885).

hydrochloric acid have been expelled. The residue is dissolved in a small quantity of water, the solution made alkaline with ammonia, and any ferric hydroxide which appears removed by filtration. The ferric hydroxide should be washed, dissolved in a small quantity of warm dilute sulphuric acid, reprecipitated with ammonia, and this filtrate with the washings added to the filtrate from the first precipitation.

For the determination of the nickel, about 40 cc ammonia (sp. gr. 0.96) are added to the solution and the nickel is precipitated under the conditions given on p. 158.

The precipitate of zinc sulphide obtained from the treatment with hydrogen sulphide can be dissolved in a small quantity of sulphuric acid, and the zinc precipitated by electrolysis by one of the methods given under Zinc (p. 163).

COPPER—ALUMINIUM ALLOYS.

For the special determination of copper, in copper-aluminium alloys, Regelsberger * suggests dissolving 3–5 g of the alloy in nitric acid and evaporating the solution down to the consistency of sirup. The sample is diluted, and a measured quantity (corresponding to 0.6–1 g substance) is poured into the electrolytic cell. An excellent precipitate is obtained if the acid solution is neutralised with ammonia and 10 cc of dilute nitric acid (sp. gr. 1.2) are added to 200 cc of the liquid. The clear solution is electrolysed with a current-density of $ND_{100} = 0.4$ amp. When the solution is warmed the separation is completed in about three hours.

---

* Zeit. f. angew. Chem., p. 473 (1891).

BRONZE.

Alloy of Copper and Tin.

The alloy in a finely divided form is treated with *aqua regia*, and the solution is evaporated to dryness. The residue is digested with a concentrated solution of sodium sulphide, which dissolves the tin, and the copper sulphide which remains after filtering is washed thoroughly with sodium sulphide and then with hydrogen sulphide solution, dissolved in the proper quantity of nitric acid, and the copper precipitated under the conditions given under Copper (p. 179).

The solution of tin in sodium sulphide is brought to a volume of about 150 cc, 25–30 g ammonium sulphate is added, and the solution is boiled for about one-half hour to convert the sodium sulphide into ammonium sulphide (see p. 216). The solution thus obtained is treated as described on p. 215.

Accurate results may also be obtained* by treating 0.2–0.4 g of the alloy, best in the form of fine turnings, with 6 cc nitric acid (sp. gr. = 1.5), and adding 3 cc water. When the reaction is over, the solution is heated to boiling, diluted with 15 cc boiling water, and the stannic oxide filtered off. To the solution containing the copper, 5–10 cc of nitric acid is added, and the copper is precipitated as directed on p. 180. The stannic oxide is dissolved in ammonium sulphide and determined electrolytically (p. 215).

PHOSPHOR-BRONZE.

Alloy of Copper, Tin, Zinc, and Phosphorus.

When the alloy is digested with concentrated nitric acid, as stated under Bronze, a precipitate remains, which consists

---

* Neumann, l. c.

of a mixture of tin oxide and tin phosphate, with small quantities of copper oxide. It is filtered off, washed with water containing nitric acid, and heated with a concentrated solution of sodium sulphide. The residue of copper sulphide is dissolved in nitric acid, and added to the principal solution.

The tin is determined by converting the sodium sulphide into ammonium sulphide, and electrolysing as directed, p. 215. The phosphoric acid is determined in the filtrate in the usual manner.

The nitric-acid solution contains the copper and zinc. They are separated according to directions for the analysis of brass (p. 281).

MANGANESE PHOSPHOR-BRONZE.

Alloy of Copper, Tin, Zinc, Manganese, and Phosphorus.

The process is similar to that given for Phosphor-bronze; the manganese remains with the zinc, and is finally separated *as directed p. 248.*

SOLDER.

Alloy of Tin and Lead.

About 0.4 g of the alloy in the form of small pieces is treated with 6 cc nitric acid (sp. gr. = 1.5) and 3 cc water. When the reaction is completed the solution is heated to boiling, and diluted with 15 cc hot water, the precipitate of stannic oxide allowed to settle, filtered off, and washed with water containing a little nitric acid. The stannic oxide may be determined gravimetrically, or may be dissolved in ammonium sulphide and determined by electrolysis according to the directions given on page 215. The lead contained in the filtrate may be determined by the method given on page 195.

WOOD'S METAL.

Alloy of Tin, Lead, Bismuth, and Cadmium.

The alloy is treated similarly to solder, the tin being separated and determined in the same manner. Since it is impossible to separate lead and bismuth by electrolysis, it is necessary to evaporate the solution to a sirup on the water-bath, add water and repeat the operation until the odor of nitric acid can no longer be detected. The solution is then treated with dilute ammonium nitrate solution, and the basic bismuth nitrate is filtered off.* A sufficient excess of nitric acid is added to the filtrate, and the lead is determined by electrolysis. The cadmium is precipitated by one of the methods given under Cadmium (p. 188).

HARD LEAD. TYPE-METAL.

Alloy of Lead and Antimony (Copper).

For the electrolytic determination of the metals Neumann and Nissenson † recommend that 2.5 g of the alloy be dissolved by warming in a mixture of 10 g tartaric acid, 4 cc nitric acid (sp. gr. 1.4) and 15 cc water. 4 cc concentrated sulphuric acid are then added, the solution is diluted somewhat with water, allowed to cool, and further diluted to exactly 250 cc (in a graduated flask). After standing for some time the lead sulphate will be completely precipitated on the bottom of the flask, and the solution will have become quite clear. 50 cc of the clear solution is now removed with a pipette, made strongly alkaline with sodium hydroxide, 50 cc of a saturated solution of sodium sulphide added, the solution heated to boiling and filtered immediately.

---

* Neumann, Analytischen Elektrolyse. Halle, 1897.

† Chem. Ztg., No. 49 (1895).

The precipitate (copper sulphide and traces of lead sulphide) is washed with dilute sodium sulphide solution, and the filtrate electrolysed according to the method given on p. 269. The copper is determined by dissolving the precipitate of copper sulphide in nitric acid, and precipitating the copper by electrolysis (p. 180).

The per cent. of lead present can be determined by difference, but if its direct determination is required 0.5 g of the alloy can be taken and the copper sulphate determined gravimetrically; it is, however, more satisfactory to treat the first solution of the metals directly with sodium hydroxide and sodium sulphide, and to dissolve the precipitate, consisting of the sulphides of lead and copper, in nitric acid. This solution is then treated as described on p. 256.

ANTI-FRICTION METAL.

Alloy of Lead, Antimony, and Tin (Copper).

The analysis of this material is conducted in much the same manner as the analysis of Type-metal. To the solution containing the copper, antimony, and tin, a slight excess of sodium hydroxide and sodium sulphide are added, and copper, if present, is precipitated as sulphide. This precipitate is filtered off and washed first with a saturated solution of sodium sulphide, and finally with water containing hydrogen sulphide. The washings with sodium sulphide are added to the filtrate, which should ultimately contain 80 cc of saturated sodium sulphide solution and an excess of 1–2 g of sodium hydroxide. The antimony and tin in the filtrate are then separated and determined according to the directions on p. 269.

ALLOY OF ANTIMONY AND TIN.

The method of analysis has been already given on p. 268. The alloy is oxidised with nitric acid, and the residue, after evaporation, dissolved in a concentrated solution of sodium sulphide, sodium hydroxide added, and the process followed throughout as given on p. 269.

ALLOY OF ANTIMONY AND ARSENIC.

It has already been stated (p. 271) that the two metals can be separated under conditions similar to those in the *separation of antimony from tin*; the method requires the arsenic to be oxidised to arsenic acid. The alloy is digested with *aqua regia*, the acid removed by evaporation, the residue dissolved in concentrated sodium sulphide, sodium hydroxide added, and the directions given on p. 271 followed throughout.

CINNABAR.

Constituents: Mercury, Manganese, Copper, Alumina, Iron, Calcium, Sulphur.

The mineral is decomposed by heating with *aqua regia*, the solution evaporated on the water-bath, and the metals converted into nitrates by repeated evaporation with nitric acid. Mercury and copper are precipitated from the nitric-acid solution (p. 204), the two metals redissolved in nitric acid, converted into the double cyanides, and determined according to the directions on p. 260. The small amount of manganese present is precipitated, as dioxide, in the electrolytic process, and may be weighed as such.

To determine iron, aluminium, and calcium, the solution decanted from the metals is evaporated to dryness on the water-bath, the nitric acid removed by repeated evaporation with hydrochloric acid, the weak acid solution of the residue treated with ammonium oxalate in great excess, calcium oxalate filtered off, and iron and aluminium determined as directed, p. 232.

For the determination of mercury in this mineral Smith and Wallace [*] treat about 0.2 gram of the finely pulverised sample with 20–25 cc of a solution of sodium sulphide solution (sp. gr. 1.22). The solution obtained is diluted to a volume of 125 cc and electrolysed with a current of $ND_{100} =$ 0.12 ampere at a temperature of 70°. The mercury is completely precipitated (see also p. 204).

MOLYBDENITE.

For the determination of molybdenum and sulphur in this mineral Kollock and Smith have published the following directions: [†]

The pulverised sample is fused with a mixture of alkali carbonate and nitrate, which results in the formation of alkali molybdenate and sulphate. For the determination of molybdenum the fusion is dissolved in water, and the solution is acidified with sulphuric acid so that an excess of about 0.1–0.2 cc (conc.) sulphuric acid is present. The molybdenum is then determined by electrolysis as directed on p. 219.

For the determination of both molybdenum and sulphur the solution obtained by digesting the fusion with water is filtered to remove any insoluble oxides, acidified with acetic acid, boiled to expel carbon dioxide, and electrolysed at 80–85° with a current of $ND_{100} = 0.05–0.07$ ampere and a potential of 2.5–4.4 volts. In from 3 to 8 hours the molybdenum will be completely precipitated as hydrated oxide.

The sulphur, existing as sulphuric acid in the solution poured off from the molybdenum, is determined gravimetrically by precipitation as barium sulphate.

---

[*] Journ. Am. Chem. Soc., 18, 169 (1896).

[†] *Ibid.*, 23, 669 (1901).

DETERMINATION OF COPPER IN SULPHIDE ORES.

According to Heidenreich * 2–5 g of ore are treated with *aqua regia*, and the solution is evaporated to dryness. The residue is taken up with 5 cc dilute hydrochloric acid and 10 cc water, transferred to a flask, diluted to 100 cc, and warmed with an excess of sheet aluminium. When the solution is colorless, showing that all iron is reduced, the residue (Al and Cu) is filtered off and washed until free from chlorides. The filter-paper is incinerated, the copper and aluminium dissolved in nitric acid, and the copper separated by electrolysis (p. 180). The method is stated to be both accurate and rapid.

COPPER AND LEAD IN COPPER MATTE.

H. Nissenson, who employed the method described on p. 258 for determining the copper and lead in copper matte, gives the following directions for carrying out the analysis:

One gram of copper matte is dissolved in 30 cc nitric acid (sp. gr. 1.4) and the resulting solution is diluted to 180 cc. The electrolysis is so conducted that the lead is precipitated as dioxide on the platinum dish, a perforated platinum disk which serves as cathode receiving the copper. The electrolysis is conducted at ordinary room temperature and is started with a current of $ND_{100} = 0.5$ ampere, which at the end of an hour is increased to 1.5–2 amperes. The copper and lead are both completely precipitated in 6–7 hours.

For technical analyses, where the determination is conducted in nitric-acid solutions, the presence of small quantities of silver and bismuth can be neglected. Where the solution contains arsenic, selenium, or manganese, even in very small quantities, the results obtained by the foregoing method are not accurate.

---

* Zeit. f. anal. Chem., 40, 15 (1901).

SECTION II.

REAGENTS.

POTASSIUM OXALATE.

The crystallised potassium oxalate of commerce always contains determinable quantities of iron and lead. To purify it one part of the salt is dissolved in three parts of water in a porcelain dish, and ammonium sulphide is added drop by drop as long as a precipitate forms. The solution is now heated on the water-bath till the precipitate settles, and filtered through a plaited filter. To decompose the slight excess of ammonium sulphide a current of air is conducted through the solution till it is perfectly colorless, and no longer gives a reaction with sodium nitroprusside. The separated sulphur is allowed to settle, and the clear solution siphoned off.

AMMONIUM OXALATE.

The same impurities are present as in potassium oxalate. The salt is purified by precipitating the hot saturated solution with ammonium sulphide. It is heated until the precipitate coheres together, and filtered hot by the use of a water-jacketed funnel. The greater part of the ammonium oxalate crystallises from the filtrate on cooling. The solution is poured off, and the crystals dried by placing them in a funnel stopped with asbestos, and connecting with a filter-pump.

OXALIC ACID.

The impurities are similar to those of the alkali oxalates; it is purified by repeated recrystallisation.

TARTARIC ACID.

This substance often contains considerable quantities of lead and iron salts. It is best purified by dissolving to a concentrated solution in water, treating with hydrogen sulphide, filtering off any precipitate and removing the excess of hydrogen sulphide by blowing air through the filtrate. The tartaric acid can be used in the form of the concentrated solution or can be crystallised out by further concentration.

AMMONIUM SULPHATE.

The method of purifying this salt is similar to that described for the purification of ammonium oxalate.

SODIUM SULPHIDE.

The crystallised sodium sulphide of commerce is not only exceedingly impure, but is frequently a mixture of polysulphides and sodium hydroxide. The presence of the latter explains that of alumina, which is always found in abundance. If commercial sodium sulphide is used, its solution must first be *completely saturated*, without access of air, with hydrogen sulphide gas. It is better, however, to prepare the substance directly, in which case the process is as follows: Sodium hydroxide purified by alcohol is dissolved in water to a solution of sp. gr. 1.35. The solution is divided into two equal parts, and one-half, with exclusion of air, saturated with the purest possible hydrogen sulphide gas till the volume ceases to increase. The hydrogen sulphide is purified by passing it through a wash-bottle of water, and several tubes filled with cotton-wool or wadding. When completely saturated the solution is filtered from the precipitate formed, and mixed with the other half of the sodium hydroxide solution. Hydrogen sulphide is again passed into the mixture, with exclusion of air, and it is filtered again. The nearly colorless filtrate is evaporated in a capacious platinum or porcelain dish, over a *strong* free flame as quickly as possible. It boils without bumping if a platinum spiral is placed in it. As soon as a thin crystalline pellicle forms on the surface the boiling is stopped, and the solution poured while hot into small flasks with well-ground glass stoppers which must be filled full. It is best to completely exclude the air by melted paraffine. For the separation of antimony and tin, the solution should have a sp. gr. of 1.22–1.225.

ALCOHOL.

The alcohol used for washing metals must be free from acid, and, as nearly as possible, absolute. It is left standing in a large flask, for twelve hours, over quicklime, and then distilled off on a water- or steam-bath. The distillate must leave no residue on evaporation.

INDEX OF AUTHORS.

INDEX OF SUBJECTS.

SHORT-TITLE CATALOGUE

OF THE

PUBLICATIONS

OF

JOHN WILEY & SONS,

NEW YORK.

LONDON: CHAPMAN & HALL, LIMITED.

ARRANGED UNDER SUBJECTS.

Descriptive circulars sent on application. Books marked with an asterisk (*) are sold at *net* prices only, a double asterisk (**) books sold under the rules of the American Publishers' Association at *net* prices subject to an extra charge for postage. All books are bound in cloth unless otherwise stated.

AGRICULTURE.

Armsby's Manual of Cattle-feeding	12mo,	$1 75
Principles of Animal Nutrition	8vo,	4 00
Budd and Hansen's American Horticultural Manual:		
Part I. Propagation, Culture, and Improvement	12mo,	1 50
Part II. Systematic Pomology	12mo,	1 50
Downing's Fruits and Fruit-trees of America	8vo,	5 00
Elliott's Engineering for Land Drainage	12mo,	1 50
Practical Farm Drainage	12mo,	1 00
Graves's Forest Mensuration	8vo,	4 00
Green's Principles of American Forestry	12mo,	1 50
Grotenfelt's Principles of Modern Dairy Practice. (Woll.)	12mo,	2 00
Kemp's Landscape Gardening	12mo,	2 50
Maynard's Landscape Gardening as Applied to Home Decoration	12mo,	1 50
* McKay and Larsen's Principles and Practice of Butter-making	8vo,	1 50
Sanderson's Insects Injurious to Staple Crops	12mo,	1 50
Insects Injurious to Garden Crops. (In preparation.)		
Insects Injuring Fruits. (In preparation.)		
Stockbridge's Rocks and Soils	8vo,	2 50
Winton's Microscopy of Vegetable Foods	8vo,	7 50
Woll's Handbook for Farmers and Dairymen	16mo,	1 50

ARCHITECTURE.

Baldwin's Steam Heating for Buildings	12mo,	2 50
Bashore's Sanitation of a Country House	12mo,	1 00
Berg's Buildings and Structures of American Railroads	4to,	5 00
Birkmire's Planning and Construction of American Theatres	8vo,	3 00
Architectural Iron and Steel	8vo,	3 50
Compound Riveted Girders as Applied in Buildings	8vo,	2 00
Planning and Construction of High Office Buildings	8vo,	3 50
Skeleton Construction in Buildings	8vo,	3 00
Brigg's Modern American School Buildings	8vo,	4 00

Carpenter's Heating and Ventilating of Buildings	8vo,	4 00
Freitag's Architectural Engineering	8vo,	3 50
Fireproofing of Steel Buildings	8vo,	2 50
French and Ives's Stereotomy	8vo,	2 50
Gerhard's Guide to Sanitary House-inspection	16mo,	1 00
Theatre Fires and Panics	12mo,	1 50
*Greene's Structural Mechanics	8vo,	2 50
Holly's Carpenters' and Joiners' Handbook	18mo,	75
Johnson's Statics by Algebraic and Graphic Methods	8vo,	2 00
Kidder's Architects' and Builders' Pocket-book. Rewritten Edition.	16mo, mor.,	5 00
Merrill's Stones for Building and Decoration	8vo,	5 00
Non-metallic Minerals: Their Occurrence and Uses	8vo,	4 00
Monckton's Stair-building	4to,	4 00
Patton's Practical Treatise on Foundations	8vo,	5 00
Peabody's Naval Architecture	8vo,	7 50
Rice's Concrete-block Manufacture	8vo,	2 00
Richey's Handbook for Superintendents of Construction	16mo, mor.,	4 00
* Building Mechanics' Ready Reference Book. Carpenters' and Woodworkers' Edition	16mo, morocco,	1 50
Sabin's Industrial and Artistic Technology of Paints and Varnish	8vo,	3 00
Siebert and Biggin's Modern Stone-cutting and Masonry	8vo,	1 50
Snow's Principal Species of Wood	8vo,	3 50
Sondericker's Graphic Statics with Applications to Trusses, Beams, and Arches.	8vo,	2 00
Towne's Locks and Builders' Hardware	18mo, morocco,	3 00
Wait's Engineering and Architectural Jurisprudence	8vo,	6 00
	Sheep,	6 50
Law of Operations Preliminary to Construction in Engineering and Architecture	8vo,	5 00
	Sheep,	5 50
Law of Contracts	8vo,	3 00
Wood's Rustless Coatings: Corrosion and Electrolysis of Iron and Steel	8vo,	4 00
Worcester and Atkinson's Small Hospitals, Establishment and Maintenance, Suggestions for Hospital Architecture, with Plans for a Small Hospital.	12mo,	1 25
The World's Columbian Exposition of 1893	Large 4to,	1 00

ARMY AND NAVY.

Bernadou's Smokeless Powder, Nitro-cellulose, and the Theory of the Cellulose *Molecule*	12mo,	2 50
* Bruff's Text-book Ordnance and Gunnery	8vo,	6 00
Chase's Screw Propellers and Marine Propulsion	8vo,	3 00
Cloke's Gunner's Examiner	8vo,	1 50
Craig's Azimuth	4to,	3 50
Crehore and Squier's Polarizing Photo-chronograph	8vo,	3 00
* Davis's Elements of Law	8vo,	2 50
* Treatise on the Military Law of United States	8vo,	7 00
	Sheep,	7 50
De Brack's Cavalry Outposts Duties. (Carr.)	24mo, morocco,	2 00
Dietz's Soldier's First Aid Handbook	16mo, morocco,	1 25
* Dredge's Modern French Artillery	4to, half morocco,	15 00
Durand's Resistance and Propulsion of Ships	8vo,	5 00
* *Dyer's Handbook of Light Artillery*	12mo,	3 00
Eissler's Modern High Explosives	8vo,	4 00
* Fiebeger's Text-book on Field Fortification	Small 8vo,	2 00
Hamilton's The Gunner's Catechism	18mo,	1 00
* Hoff's Elementary Naval Tactics	8vo,	1 50

Ingalls's Handbook of Problems in Direct Fire	8vo,	4 00
* Ballistic Tables	8vo,	1 50
* Lyons's Treatise on Electromagnetic Phenomena. Vols. I. and II.	8vo, each,	6 00
* Mahan's Permanent Fortifications. (Mercur.)	8vo, half morocco,	7 50
Manual for Courts-martial	16mo, morocco,	1 50
* Mercur's Attack of Fortified Places	12mo,	2 00
* Elements of the Art of War	8vo,	4 00
Metcalf's Cost of Manufactures—And the Administration of Workshops	8vo,	5 00
* Ordnance and Gunnery. 2 vols.	12mo,	5 00
Murray's Infantry Drill Regulations	18mo, paper,	10
Nixon's Adjutants' Manual	24mo,	1 00
Peabody's Naval Architecture	8vo,	7 50
* Phelps's Practical Marine Surveying	8vo,	2 50
Powell's Army Officer's Examiner	12mo,	4 00
Sharpe's Art of Subsisting Armies in War	18mo, morocco,	1 50
* Tupes and Poole's Manual of Bayonet Exercises and Musketry Fencing.	24mo, leather,	50
* Walke's Lectures on Explosives	8vo,	4 00
Weaver's Military Explosives	8vo,	3 00
* Wheeler's Siege Operations and Military Mining	8vo,	2 00
Winthrop's Abridgment of Military Law	12mo,	2 50
Woodhull's Notes on Military Hygiene	16mo,	1 50
Young's Simple Elements of Navigation	16mo, morocco,	2 00

ASSAYING.

Fletcher's Practical Instructions in Quantitative Assaying with the Blowpipe.	12mo, morocco,	1 50
Furman's Manual of Practical Assaying	8vo,	3 00
Lodge's Notes on Assaying and Metallurgical Laboratory Experiments	8vo,	3 00
Low's Technical Methods of Ore Analysis	8vo,	3 00
Miller's Manual of Assaying	12mo,	1 00
Cyanide Process	12mo,	1 00
Minet's Production of Aluminum and its Industrial Use. (Waldo.)	12mo,	2 50
O'Driscoll's Notes on the Treatment of Gold Ores	*8vo,*	*2 00*
Ricketts and Miller's Notes on Assaying	8vo,	3 00
Robine and Lenglen's Cyanide Industry. (Le Clerc.)	8vo,	4 00
Ulke's Modern Electrolytic Copper Refining	8vo,	3 00
Wilson's Cyanide Processes	12mo,	1 50
Chlorination Process	12mo,	1 50

ASTRONOMY.

Comstock's Field Astronomy for Engineers	8vo,	2 50
Craig's Azimuth	4to,	3 50
Doolittle's Treatise on Practical Astronomy	*8vo,*	*4 00*
Gore's Elements of Geodesy	8vo,	2 50
Hayford's Text-book of Geodetic Astronomy	8vo,	3 00
Merriman's Elements of Precise Surveying and Geodesy	8vo,	2 50
* Michie and Harlow's Practical Astronomy	8vo,	3 00
* White's Elements of Theoretical and Descriptive Astronomy	12mo,	2 00

BOTANY.

Davenport's Statistical Methods, with Special Reference to Biological Variation,	16mo, morocco,	1 25
Thomé and Bennett's Structural and Physiological Botany	16mo,	2 25
Westermaier's Compendium of General Botany. (Schneider.)	8vo,	2 00

CHEMISTRY.

Adriance's Laboratory Calculations and Specific Gravity Tables	12mo,	1 25
Alexeyeff's General Principles of Organic Synthesis. (Matthews.)	8vo,	3 00
Allen's Tables for Iron Analysis	8vo,	3 00
Arnold's Compendium of Chemistry. (Mandel.)	Small 8vo.	3 50
Austen's *Notes for Chemical Students*	12mo,	1 50
Bernadou's Smokeless Powder.—Nitro-cellulose, and Theory of the Cellulose Molecule	12mo,	2 50
* Browning's Introduction to the Rarer Elements	8vo,	1 50
Brush and Penfield's Manual of Determinative Mineralogy	8vo,	4 00
Classen's Beet-sugar Manufacture. (Hall and Rolfe.)	8vo,	3 00
Classen's Quantitative Chemical Analysis by Electrolysis. (Boltwood.)	8vo,	3 00
Cohn's *Indicators and Test-papers*	12mo,	2 00
Tests and Reagents	8vo,	3 00
Crafts's Short Course in Qualitative Chemical Analysis. (Schaeffer.)	12mo,	1 50
Dolezalek's Theory of the Lead Accumulator (Storage Battery). (Von Ende,)	12mo,	2 50
Drechsel's Chemical Reactions. (Merrill.)	12mo,	1 25
Duhem's Thermodynamics and Chemistry. (Burgess.)	8vo,	4 00
Eissler's *Modern High Explosives*	8vo,	4 00
Effront's Enzymes and their Applications. (Prescott.)	8vo,	3 00
Erdmann's Introduction to Chemical Preparations. (Dunlap.)	12mo,	1 25
Fletcher's Practical Instructions in Quantitative Assaying with the Blowpipe.	12mo, morocco,	1 50
Fowler's Sewage Works Analyses	12mo,	2 00
Fresenius's Manual of Qualitative Chemical Analysis. (Wells.)	8vo,	5 00
Manual of Qualitative Chemical Analysis. Part I. Descriptive. (Wells.)	8vo,	3 00
System of Instruction in Quantitative Chemical Analysis. (Cohn.) 2 vols.	8vo,	12 50
Fuertes's Water and Public Health	12mo,	1 50
Furman's Manual of Practical Assaying	8vo,	3 00
* Getman's *Exercises in Physical Chemistry*	12mo,	2 00
Gill's Gas and Fuel Analysis for Engineers	12mo,	1 25
Grotenfelt's Principles of Modern Dairy Practice. (Woll.)	12mo,	2 00
Groth's Introduction to Chemical Crystallography (Marshall)	12mo,	1 25
Hammarsten's Text-book of Physiological Chemistry. (Mandel.)	8vo,	4 00
Helm's Principles of Mathematical Chemistry. (Morgan.)	12mo,	1 50
Hering's Ready Reference Tables (Conversion Factors)	16mo, morocco,	2 50
Hind's *Inorganic Chemistry*	8vo,	3 00
* Laboratory Manual for Students	12mo,	1 00
Holleman's Text-book of Inorganic Chemistry. (Cooper.)	8vo,	2 50
Text-book of Organic Chemistry. (Walker and Mott.)	8vo,	2 50
* Laboratory Manual of Organic Chemistry. (Walker.)	12mo,	1 00
Hopkins's Oil-chemists' Handbook	8vo,	3 00
Jackson's Directions for Laboratory Work in Physiological Chemistry	8vo,	1 25
Keep's *Cast Iron*	8vo,	2 50
Ladd's Manual of Quantitative Chemical Analysis	12mo,	1 00
Landauer's Spectrum Analysis. (Tingle.)	8vo,	3 00
* Langworthy and Austen. The Occurrence of Aluminium in Vegetable Products, Animal Products, and Natural Waters	8vo,	2 00
Lassar-Cohn's Practical Urinary Analysis. (Lorenz.)	12mo,	1 00
Application of Some General Reactions to Investigations in Organic *Chemistry.* (Tingle.)	12mo,	1 00
Leach's The Inspection and Analysis of Food with Special Reference to State Control	8vo,	7 50
Löb's Electrochemistry of Organic Compounds. (Lorenz.)	8vo,	3 00
Lodge's Notes on Assaying and Metallurgical Laboratory Experiments	8vo,	3 00
Low's Technical Method of Ore Analysis	8vo,	3 00
Lunge's Techno-chemical Analysis. (Cohn.)	12mo	1 00

* McKay and Larsen's Principles and Practice of Butter-making	8vo	1 50
Mandel's Handbook for Bio-chemical Laboratory	12mo,	1 50
* Martin's Laboratory Guide to Qualitative Analysis with the Blowpipe	12mo,	60
Mason's Water-supply. (Considered Principally from a Sanitary Standpoint.) 3d Edition, Rewritten.	8vo,	4 00
Examination of Water. (Chemical and Bacteriological.)	12mo,	1 25
Matthew's The Textile Fibres.	8vo,	3 50
Meyer's Determination of Radicles in Carbon Compounds. (Tingle.).	12mo,	1 00
Miller's Manual of Assaying.	12mo,	1 00
Cyanide Process	12mo,	1 00
Minet's Production of Aluminum and its Industrial Use. (Waldo.)	12mo,	2 50
Mixter's Elementary Text-book of Chemistry.	12mo,	1 50
Morgan's An Outline of the Theory of Solutions and its Results	12mo,	1 00
Elements of Physical Chemistry.	12mo,	3 00
* Physical Chemistry for Electrical Engineers	12mo,	1 50
Morse's Calculations used in Cane-sugar Factories.	16mo, morocco,	1 50
Mulliken's General Method for the Identification of Pure Organic Compounds. Vol. I.	Large 8vo,	5 00
O'Brine's Laboratory Guide in Chemical Analysis.	8vo,	2 00
O'Driscoll's Notes on the Treatment of Gold Ores.	8vo,	2 00
Ostwald's *Conversations on Chemistry. Part One. (Ramsey.).*	*12mo,*	1 50
" " " " Part Two. (Turnbull.)	12mo,	2 00
* Penfield's Notes on Determinative Mineralogy and Record of Mineral Tests.	8vo, paper,	50
Pictet's *The* Alkaloids and their Chemical Constitution. (Biddle.)	8vo,	5 00
Pinner's Introduction to Organic Chemistry. (Austen.).	12mo	1 50
Poole's Calorific Power of Fuels.	8vo,	3 00
Prescott and Winslow's Elements of Water Bacteriology, with Special Reference to Sanitary Water Analysis.	12mo,	1 25
* Reisig's Guide to Piece-dyeing.	8vo,	25 00
Richards and Woodman's Air, Water, and Food from a Sanitary Standpoint.	8vo,	2 00
Ricketts and Russell's Skeleton Notes upon Inorganic Chemistry. (Part I. Non-metallic Elements.)	8vo, morocco,	75
Ricketts and Miller's Notes on Assaying.	8vo,	3 00
Rideal's Sewage and the Bacterial Purification of Sewage.	8vo,	3 50
Disinfection and the Preservation of Food.	8vo,	4 00
Riggs's Elementary Manual for the Chemical Laboratory	8vo,	1 25
Robine and Lenglen's Cyanide Industry. (Le Clerc.).	8vo,	4 00
Rostoski's Serum Diagnosis. (Bolduan.).	12mo,	1 00
Ruddiman's Incompatibilities in Prescriptions.	8vo,	2 00
* Whys in Pharmacy	12mo,	1 00
Sabin's Industrial and Artistic Technology of Paints and Varnish.	8vo,	3 00
Salkowski's Physiological and Pathological Chemistry. (Orndorff.)	8vo,	2 50
Schimpf's Text-book of Volumetric Analysis.	12mo,	2 50
Essentials of Volumetric Analysis.	12mo,	1 25
* Qualitative Chemical Analysis.	8vo,	1 25
Smith's Lecture Notes on Chemistry for Dental Students.	8vo,	2 50
Spencer's Handbook for Chemists of Beet-sugar Houses.	16mo, morocco,	3 00
Handbook for Cane Sugar Manufacturers.	16mo, morocco,	3 00
Stockbridge's Rocks and Soils.	8vo,	2 50
* Tillman's Elementary Lessons in Heat	8vo,	1 50
* Descriptive General Chemistry.	8vo,	3 00
Treadwell's Qualitative Analysis. (Hall.).	8vo,	3 00
Quantitative Analysis. (Hall.).	8vo,	4 00
Turneaure and Russell's Public Water-supplies	8vo,	5 00
Van Deventer's Physical Chemistry for Beginners. (Boltwood.)	12mo,	1 50
* Walke's Lectures on Explosives.	8vo,	4 00
Ware's Beet-sugar Manufacture and Refining	*Small 8vo, cloth,*	4 00
Washington's Manual of the Chemical Analysis of Rocks.	8vo,	2 00

Wassermann's Immune Sera: Hæmolysins, Cytotoxins, and Precipitins. (Bolduan.)	12mo,	1 00
Weaver's Military Explosives	8vo,	3 00
Wehrenfennig's Analysis and Softening of Boiler Feed-Water	8vo,	4 00
Wells's Laboratory Guide in Qualitative Chemical Analysis	8vo,	1 50
Short Course in Inorganic Qualitative Chemical Analysis for Engineering Students	12mo,	1 50
Text-book of Chemical Arithmetic	12mo,	1 25
Whipple's Microscopy of Drinking-water	8vo,	3 50
Wilson's Cyanide Processes	12mo,	1 50
Chlorination Process	12mo,	1 50
Winton's Microscopy of Vegetable Foods	8vo,	7 50
Wulling's Elementary Course in Inorganic, Pharmaceutical, and Medical Chemistry	12mo,	2 00

CIVIL ENGINEERING.

BRIDGES AND ROOFS. HYDRAULICS. MATERIALS OF ENGINEERING. RAILWAY ENGINEERING.

Baker's Engineers' Surveying Instruments	12mo,	3 00
Bixby's Graphical Computing Table	Paper 19½ × 24¼ inches.	25
** Burr's Ancient and Modern Engineering and the Isthmian Canal. (Postage, 27 cents additional.)	8vo,	3 50
Comstock's Field Astronomy for Engineers	8vo,	2 50
Davis's Elevation and Stadia Tables	8vo,	1 00
Elliott's Engineering for Land Drainage	12mo,	1 50
Practical Farm Drainage	12mo,	1 00
*Fiebeger's Treatise on Civil Engineering	8vo,	5 00
Flemer's Phototopographic Methods and Instruments	8vo,	5 00
Folwell's Sewerage. (Designing and Maintenance.)	8vo,	3 00
Freitag's Architectural Engineering. 2d Edition, Rewritten	8vo,	3 50
French and Ives's Stereotomy	8vo,	2 50
Goodhue's Municipal Improvements	12mo,	1 75
Goodrich's Economic Disposal of Towns' Refuse	8vo,	3 50
Gore's Elements of Geodesy	8vo,	2 50
Hayford's Text-book of Geodetic Astronomy	8vo,	3 00
Hering's Ready Reference Tables (Conversion Factors)	16mo, morocco,	2 50
Howe's Retaining Walls for Earth	12mo,	1 25
* Ives's Adjustments of the Engineer's Transit and Level	16mo, Bds.	25
Ives and Hilts's Problems in Surveying	16mo, morocco,	1 50
Johnson's (J. B.) Theory and Practice of Surveying	Small 8vo,	4 00
Johnson's (L. J.) Statics by Algebraic and Graphic Methods	8vo,	2 00
Laplace's Philosophical Essay on Probabilities. (Truscott and Emory.)	12mo,	2 00
Mahan's Treatise on Civil Engineering. (1873.) (Wood.)	8vo,	5 00
* Descriptive Geometry	8vo,	1 50
Merriman's Elements of Precise Surveying and Geodesy	8vo,	2 50
Merriman and Brooks's Handbook for Surveyors	16mo, morocco,	2 00
Nugent's Plane Surveying	8vo,	3 50
Ogden's Sewer Design	12mo,	2 00
Parsons's Disposal of Municipal Refuse	8vo,	2 00
Patton's Treatise on Civil Engineering	8vo half leather,	7 50
Reed's Topographical Drawing and Sketching	4to,	5 00
Rideal's Sewage and the Bacterial Purification of Sewage	8vo,	3 50
Siebert and Biggin's Modern Stone-cutting and Masonry	8vo,	1 50
Smith's Manual of Topographical Drawing. (McMillan.)	8vo,	2 50
Sondericker's Graphic Statics, with Applications to Trusses, Beams, and Arches.	8vo,	2 00

Taylor and Thompson's Treatise on Concrete, Plain and Reinforced	8vo,	5 00
* Trautwine's Civil Engineer's Pocket-book	16mo, morocco,	5 00
Venable's Garbage Crematories in America	8vo,	2 00
Wait's Engineering and Architectural Jurisprudence	8vo,	6 00
	Sheep,	6 50
Law of Operations Preliminary to Construction in Engineering and Architecture	8vo,	5 00
	Sheep,	5 50
Law of Contracts	8vo,	3 00
Warren's Stereotomy—Problems in Stone-cutting	8vo,	2 50
Webb's Problems in the Use and Adjustment of Engineering Instruments.	16mo, morocco,	1 25
Wilson's Topographic Surveying	8vo,	3 50

BRIDGES AND ROOFS.

Boller's Practical Treatise on the Construction of Iron Highway Bridges	8vo,	2 00
* Thames River Bridge	4to, paper,	5 00
Burr's Course on the Stresses in Bridges and Roof Trusses, Arched Ribs, and Suspension Bridges	8vo,	3 50
Burr and Falk's Influence Lines for Bridge and Roof Computations	8vo,	3 00
Design and Construction of Metallic Bridges	8vo,	5 00
Du Bois's Mechanics of Engineering. Vol. II	Small 4to,	10 00
Foster's Treatise on Wooden Trestle Bridges	4to,	5 00
Fowler's Ordinary Foundations	8vo,	3 50
Greene's Roof Trusses	8vo,	1 25
Bridge Trusses	8vo,	2 50
Arches in Wood, Iron, and Stone	8vo,	2 50
Howe's Treatise on Arches	8vo,	4 00
Design of Simple Roof-trusses in Wood and Steel	8vo,	2 00
Symmetrical Masonry Arches	8vo,	2 50
Johnson, Bryan, and Turneaure's Theory and Practice in the Designing of Modern Framed Structures	Small 4to,	10 00
Merriman and Jacoby's Text-book on Roofs and Bridges:		
Part I. Stresses in Simple Trusses	8vo,	2 50
Part II. Graphic Statics	8vo,	2 50
Part III. Bridge Design	8vo,	2 50
Part IV. Higher Structures	8vo,	2 50
Morison's Memphis Bridge	4to,	10 00
Waddell's De Pontibus, a Pocket-book for Bridge Engineers	16mo, morocco,	2 00
* Specifications for Steel Bridges	12mo,	50
Wright's Designing of Draw-spans. Two parts in one volume	8vo,	3 50

HYDRAULICS.

Barnes's Ice Formation	8vo,	3 00
Bazin's Experiments upon the Contraction of the Liquid Vein Issuing from an Orifice. (Trautwine.)	8vo,	2 00
Bovey's Treatise on Hydraulics	8vo,	5 00
Church's Mechanics of Engineering	8vo,	6 00
Diagrams of Mean Velocity of Water in Open Channels	paper,	1 50
Hydraulic Motors	8vo,	2 00
Coffin's Graphical Solution of Hydraulic Problems	16mo, morocco,	2 50
Flather's Dynamometers, and the Measurement of Power	12mo,	3 00
Folwell's Water-supply Engineering	8vo,	4 00
Frizell's Water-power	8vo,	5 00

Fuertes's Water and Public Health	12mo,	1 50
Water-filtration Works	12mo,	2 50
Ganguillet and Kutter's General *Formula for the Uniform Flow of Water in* Rivers and Other Channels. (Hering and Trautwine.)	8vo,	4 00
Hazen's *Filtration of Public Water-supply*	8vo,	3 00
Hazlehurst's Towers and Tanks for Water-works	8vo,	2 50
Herschel's 115 Experiments on the Carrying Capacity of Large, Riveted, Metal Conduits	8vo,	2 00
Mason's Water-supply. (Considered Principally from a Sanitary Standpoint.)	8vo,	4 00
Merriman's Treatise on Hydraulics	8vo,	5 00
* Michie's Elements of Analytical Mechanics	8vo,	4 00
Schuyler's Reservoirs for Irrigation, Water-power, and Domestic Water-supply	Large 8vo,	5 00
** *Thomas and Watt's Improvement of Rivers* (Post., 44c. additional.)	4to,	6 00
Turneaure and Russell's Public Water-supplies	8vo,	5 00
Wegmann's Design and Construction of Dams	4to,	5 00
Water-supply of the City of New York from 1658 to 1895	4to,	10 00
Williams and Hazen's Hydraulic Tables	8vo,	1 50
Wilson's Irrigation Engineering	Small 8vo,	4 00
Wolff's Windmill as a Prime Mover	8vo,	3 00
Wood's Turbines	8vo,	2 50
Elements of Analytical Mechanics	8vo,	3 00

MATERIALS OF ENGINEERING.

Baker's Treatise on Masonry Construction	8vo,	5 00
Roads and Pavements	8vo,	5 00
Black's United States Public Works	Oblong 4to,	5 00
* Bovey's Strength of Materials and Theory of Structures	8vo,	7 50
Burr's Elasticity and Resistance of the Materials of Engineering	8vo,	7 50
Byrne's Highway Construction	8vo,	5 00
Inspection of the Materials and Workmanship Employed in Construction.	16mo,	3 00
Church's Mechanics of Engineering	8vo,	6 00
Du Bois's Mechanics of Engineering. Vol. I	Small 4to,	7 50
*Eckel's Cements, Limes, and Plasters	8vo,	6 00
Johnson's Materials of Construction	Large 8vo,	6 00
Fowler's Ordinary Foundations	8vo,	3 50
Graves's Forest Mensuration	8vo,	4 00
* Greene's Structural Mechanics	8vo,	2 50
Keep's Cast Iron	8vo,	2 50
Lanza's Applied Mechanics	8vo,	7 50
Marten's Handbook on Testing Materials. (Henning.) *2 vols.*	8vo,	7 50
Maurer's Technical Mechanics	8vo,	4 00
Merrill's Stones for Building and Decoration	8vo,	5 00
Merriman's Mechanics of Materials	8vo,	5 00
Strength of Materials	12mo,	1 00
Metcalf's Steel. *A Manual for Steel-users*	12mo,	2 00
Patton's Practical Treatise on Foundations	8vo,	5 00
Richardson's Modern Asphalt Pavements	8vo,	3 00
Richey's Handbook for Superintendents of Construction	16mo, mor.,	4 00
* Ries's Clays: Their Occurrence, Properties, and Uses	8vo,	5 00
Rockwell's Roads and Pavements in France	12mo,	1 25
Sabin's Industrial and Artistic Technology of Paints and Varnish	8vo,	3 00
Smith's Materials of Machines	12mo,	1 00
Snow's Principal Species of Wood	8vo,	3 50

Spalding's Hydraulic Cement	12mo,	2 00
Text-book on Roads and Pavements	12mo,	2 00
Taylor and Thompson's Treatise on Concrete, Plain and Reinforced.	8vo,	5 00
Thurston's Materials of Engineering. 3 Parts.	8vo,	8 00
Part I. Non-metallic Materials of Engineering and Metallurgy	8vo,	2 00
Part II Iron and Steel	8vo,	3 50
Part III. A Treatise on Brasses, Bronzes, and Other Alloys and their Constituents	8vo,	2 50
Thurston's Text-book of the Materials of Construction	8vo,	5 00
Tillson's Street Pavements and Paving Materials	8vo,	4 00
Waddell's De Pontibus (A Pocket-book for Bridge Engineers.)	16mo, mor.,	2 00
Specifications for Steel Bridges	12mo,	1 25
Wood's (De V.) Treatise on the Resistance of Materials, and an Appendix on the Preservation of Timber	8vo,	2 00
Wood's (De V.) Elements of Analytical Mechanics	8vo,	3 00
Wood's (M. P.) Rustless Coatings: Corrosion and Electrolysis of Iron and Steel	8vo,	4 00

RAILWAY ENGINEERING.

Andrew's Handbook for Street Railway Engineers	3×5 inches, morocco,	1 25
Berg's Buildings and Structures of American Railroads	4to,	5 00
Brook's Handbook of Street Railroad Location	16mo, morocco,	1 50
Butt's Civil Engineer's Field-book	16mo, morocco,	2 50
Crandall's Transition Curve	16mo, morocco,	1 50
Railway and Other Earthwork Tables	8vo,	1 50
Dawson's "Engineering" and Electric Traction Pocket-book	16mo, morocco,	5 00
Dredge's History of the Pennsylvania Railroad: (1879)	Paper,	5 00
* Drinker's Tunnelling, Explosive Compounds, and Rock Drills	4to, half mor.,	25 00
Fisher's Table of Cubic Yards	Cardboard,	25
Godwin's Railroad Engineers' Field-book and Explorers' Guide	16mo, mor.,	2 50
Howard's Transition Curve Field-book	16mo, morocco,	1 50
Hudson's Tables for Calculating the Cubic Contents of Excavations and Embankments	8vo,	1 00
Molitor and Beard's Manual for Resident Engineers	16mo,	1 00
Nagle's Field Manual for Railroad Engineers	16mo, morocco,	3 00
Philbrick's Field Manual for Engineers	16mo, morocco,	3 00
Searles's Field Engineering	16mo, morocco,	3 00
Railroad Spiral	16mo, morocco,	1 50
Taylor's Prismoidal Formulæ and Earthwork	8vo,	1 50
* Trautwine's Method of Calculating the Cube Contents of Excavations and Embankments by the Aid of Diagrams	8vo,	2 00
The Field Practice of Laying Out Circular Curves for Railroads.	12mo, morocco,	2 50
Cross-section Sheet	Paper,	25
Webb's Railroad Construction	16mo, morocco,	5 00
Economics of Railroad Construction	Large 12mo,	2 50
Wellington's Economic Theory of the Location of Railways	Small 8vo.	5 00

DRAWING.

Barr's Kinematics of Machinery	8vo	2 50
* Bartlett's Mechanical Drawing	8vo,	3 00
* " " " Abridged Ed.	8vo,	1 50
Coolidge's Manual of Drawing	8vo, paper,	1 00

Coolidge and Freeman's Elements of General Drafting for Mechanical Engineers	Oblong 4to,	2 50
Durley's Kinematics of Machines	8vo,	4 00
Emch's Introduction to Projective Geometry and its Applications	8vo,	2 50
Hill's Text-book on Shades and Shadows, and Perspective	8vo,	2 00
Jamison's Elements of Mechanical Drawing	8vo,	2 50
Advanced Mechanical Drawing	8vo,	2 00
Jones's Machine Design:		
Part I. Kinematics of Machinery	8vo,	1 50
Part II. Form, Strength, and Proportions of Parts	8vo,	3 00
MacCord's Elements of Descriptive Geometry	8vo,	3 00
Kinematics; or, Practical Mechanism	8vo,	5 00
Mechanical Drawing	4to,	4 00
Velocity Diagrams	8vo,	1 50
MacLeod's Descriptive Geometry	Small 8vo,	1 50
* Mahan's Descriptive Geometry and Stone-cutting	8vo,	1 50
Industrial Drawing. (Thompson.)	8vo,	3 50
Moyer's Descriptive Geometry	8vo,	2 00
Reed's Topographical Drawing and Sketching	4to,	5 00
Reid's Course in Mechanical Drawing	8vo,	2 00
Text-book of Mechanical Drawing and Elementary Machine Design	8vo,	3 00
Robinson's Principles of Mechanism	8vo,	3 00
Schwamb and Merrill's Elements of Mechanism	8vo,	3 00
Smith's (R. S.) Manual of Topographical Drawing. (McMillan.)	8vo,	2 50
Smith (A. W.) and Marx's Machine Design	8vo,	3 00
* Titsworth's Elements of Mechanical Drawing	Oblong 8vo,	1 25
Warren's Elements of Plane and Solid Free-hand Geometrical Drawing	12mo,	1 00
Drafting Instruments and Operations	12mo,	1 25
Manual of Elementary Projection Drawing	12mo,	1 50
Manual of Elementary Problems in the Linear Perspective of Form and Shadow	12mo,	1 00
Plane Problems in Elementary Geometry	12mo,	1 25
Primary Geometry	12mo,	75
Elements of Descriptive Geometry, Shadows, and Perspective	8vo,	3 50
General Problems of Shades and Shadows	8vo,	3 00
Elements of Machine Construction and Drawing	8vo,	7 50
Problems, Theorems, and Examples in Descriptive Geometry	8vo,	2 50
Weisbach's Kinematics and Power of Transmission. (Hermann and Klein.)	8vo,	5 00
Whelpley's Practical Instruction in the Art of Letter Engraving	12mo,	2 00
Wilson's (H. M.) Topographic Surveying	8vo,	3 50
Wilson's (V. T.) Free-hand Perspective	8vo,	2 50
Wilson's (V. T.) Free-hand Lettering	8vo,	1 00
Woolf's Elementary Course in Descriptive Geometry	Large 8vo,	3 00

ELECTRICITY AND PHYSICS.

Anthony and Brackett's Text-book of Physics. (Magie.)	Small 8vo,	3 00
Anthony's Lecture-notes on the Theory of Electrical Measurements	12mo,	1 00
Benjamin's History of Electricity	8vo,	3 00
Voltaic Cell	8vo,	3 00
Classen's Quantitative Chemical Analysis by Electrolysis. (Boltwood.)	8vo,	3 00
* Collins's Manual of Wireless Telegraphy	12mo,	1 50
	Morocco,	2 00
Crehore and Squier's Polarizing Photo-chronograph	8vo,	3 00
Dawson's "Engineering" and Electric Traction Pocket-book	16mo, morocco,	5 00

Dolezalek's Theory of the Lead Accumulator (Storage Battery). (Von Ende.)	12mo,	2 50
Duhem's Thermodynamics and Chemistry. (Burgess.)	8vo,	4 00
Flather's Dynamometers, and the Measurement of Power	12mo,	3 00
Gilbert's De Magnete. (Mottelay.)	8vo,	2 50
Hanchett's Alternating Currents Explained	12mo,	1 00
Hering's Ready Reference Tables (Conversion Factors)	16mo, morocco,	2 50
Holman's Precision of Measurements	8vo,	2 00
Telescopic Mirror-scale Method, Adjustments, and Tests	Large 8vo,	75
Kinzbrunner's Testing of Continuous-current Machines	8vo,	2 00
Landauer's Spectrum Analysis. (Tingle.)	8vo,	3 00
Le Chatelier's High-temperature Measurements. (Boudouard—Burgess.)	12mo,	3 00
Löb's Electrochemistry of Organic Compounds. (Lorenz.)	8vo,	3 00
* Lyons's Treatise on Electromagnetic Phenomena. Vols. I. and II.	8vo, each,	6 00
* Michie's Elements of Wave Motion Relating to Sound and Light	8vo,	4 00
Niaudet's Elementary Treatise on Electric Batteries. (Fishback.)	12mo,	2 50
* Parshall and Hobart's Electric Machine Design	4to, half morocco,	12 50
* Rosenberg's Electrical Engineering. (Haldane Gee—Kinzbrunner.)	8vo,	1 50
Ryan, Norris, and Hoxie's Electrical Machinery. Vol. I.	*8vo,*	2 50
Thurston's Stationary Steam-engines	8vo,	2 50
* Tillman's Elementary Lessons in Heat	8vo,	1 50
Tory and Pitcher's Manual of Laboratory Physics	Small 8vo,	2 00
Ulke's Modern Electrolytic Copper Refining	8vo,	3 00

LAW.

* Davis's Elements of Law	8vo,	2 50
* Treatise on the Military Law of United States	8vo,	7 00
*	Sheep,	7 50
Manual for Courts-martial	16mo, morocco,	1 50
Wait's Engineering and Architectural Jurisprudence	8vo,	6 00
	Sheep,	6 50
Law of Operations Preliminary to Construction in Engineering and Architecture	8vo,	5 00
	Sheep,	5 50
Law of Contracts	8vo,	3 00
Winthrop's Abridgment of Military Law	12mo,	2 50

MANUFACTURES.

Bernadou's Smokeless Powder—Nitro-cellulose and Theory of the Cellulose Molecule	12mo,	2 50
Bolland's Iron Founder	12mo,	2 50
"The Iron Founder," Supplement	12mo,	2 50
Encyclopedia of Founding and Dictionary of Foundry Terms Used in the Practice of Moulding	12mo,	3 00
Claassen's Beet-sugar Manufacture. (Hall and Rolfe.)	8vo,	3 00
* Eckel's Cements, Limes, and Plasters	8vo,	6 00
Eissler's Modern High Explosives	8vo,	4 00
Effront's Enzymes and their Applications. (Prescott.)	8vo,	3 00
Fitzgerald's Boston Machinist	12mo,	1 00
Ford's Boiler Making for Boiler Makers	18mo,	1 00
Hopkin's Oil-chemists' Handbook	8vo,	3 00
Keep's Cast Iron	8vo,	2 50

Leach's The Inspection and Analysis of Food with Special Reference to State Control	Large 8vo,	7 50
* McKay and Larsen's Principles and Practice of Butter-making	8vo,	1 50
Matthews's The Textile Fibres	8vo,	3 50
Metcalf's Steel. A Manual for Steel-users	12mo,	2 00
Metcalfe's Cost of Manufactures—And the Administration of Workshops	8vo,	5 00
Meyer's Modern Locomotive Construction	4to,	10 00
Morse's Calculations used in Cane-sugar Factories	16mo, morocco,	1 50
* Reisig's Guide to Piece-dyeing	8vo,	25 00
Rice's Concrete-block Manufacture	8vo,	2 00
Sabin's Industrial and Artistic Technology of Paints and Varnish	8vo,	3 00
Smith's Press-working of Metals	8vo,	3 00
Spalding's Hydraulic Cement	12mo,	2 00
Spencer's Handbook for Chemists of Beet-sugar Houses	16mo, morocco,	3 00
Handbook for Cane Sugar Manufacturers	16mo, morocco,	3 00
Taylor and Thompson's Treatise on Concrete, Plain and Reinforced	8vo,	5 00
Thurston's Manual of Steam-boilers, their Designs, Construction and Operation	8vo,	5 00
* Walke's Lectures on Explosives	8vo,	4 00
Ware's Beet-sugar Manufacture and Refining	Small 8vo,	4 00
Weaver's Military Explosives	8vo,	3 00
West's American Foundry Practice	12mo,	2 50
Moulder's Text-book	12mo,	2 50
Wolff's Windmill as a Prime Mover	8vo,	3 00
Wood's Rustless Coatings: Corrosion and Electrolysis of Iron and Steel	8vo,	4 00

MATHEMATICS.

Baker's Elliptic Functions	8vo,	1 50
* Bass's Elements of Differential Calculus	12mo,	4 00
Briggs's Elements of Plane Analytic Geometry	12mo,	1 00
Compton's Manual of Logarithmic Computations	12mo,	1 50
Davis's Introduction to the *Logic of Algebra*	8vo,	1 50
* Dickson's College Algebra	Large 12mo,	1 50
* Introduction to the Theory of Algebraic Equations	Large 12mo,	1 25
Emch's Introduction to Projective Geometry and its Applications	8vo,	2 50
Halsted's Elements of Geometry	8vo,	1 75
Elementary Synthetic Geometry	8vo,	1 50
Rational Geometry	12mo,	1 75
* *Johnson's (J. B.) Three-place Logarithmic Tables: Vest-pocket size* paper,		15
	100 copies for	5 00
* Mounted on heavy cardboard, 8 × 10 inches,		25
	10 copies for	2 00
Johnson's (W. W.) Elementary Treatise on Differential Calculus	Small 8vo,	3 00
Elementary Treatise on the Integral Calculus	Small 8vo,	1 50
Johnson's (W. W.) Curve Tracing in Cartesian Co-ordinates	12mo,	1 00
Johnson's (W. W.) Treatise on Ordinary and Partial Differential Equations.	Small 8vo,	3 50
Johnson's (W. W.) Theory of Errors and the Method of Least Squares	12mo,	1 50
* Johnson's (W. W.) Theoretical Mechanics	12mo,	3 00
Laplace's Philosophical Essay on Probabilities. (Truscott and Emory.)	12mo,	2 00
* Ludlow and Bass. Elements of Trigonometry and Logarithmic and Other Tables	8vo,	3 00
Trigonometry and Tables published separately	Each,	2 00
* Ludlow's Logarithmic and Trigonometric Tables	8vo,	1 00
Manning's Irrational Numbers and their Representation by Sequences and Series	12mo	1 25

Mathematical Monographs. Edited by Mansfield Merriman and Robert S. Woodward.	Octavo, each	1 00
No. 1. History of Modern Mathematics, by David Eugene Smith. No. 2. *Synthetic Projective Geometry, by George Bruce Halsted.* No. 3. Determinants, by Laenas Gifford Weld. No. 4. Hyperbolic Functions, by James McMahon. No. 5. Harmonic Functions, by William E. Byerly. No. 6. Grassmann's Space Analysis, by Edward W. Hyde. No. 7. Probability and Theory of Errors, by Robert S. Woodward. No. 8. Vector Analysis and Quaternions, by Alexander Macfarlane. No. 9. Differential Equations, by William Woolsey Johnson. No. 10. The Solution of Equations, by Mansfield Merriman. No. 11. Functions of a Complex Variable, by Thomas S. Fiske.		
Maurer's Technical Mechanics.	8vo,	4 00
Merriman's Method of Least Squares.	8vo,	2 00
Rice and Johnson's Elementary Treatise on the Differential Calculus.	Sm. 8vo,	3 00
Differential and Integral Calculus. 2 vols. in one.	*Small 8vo,*	*2 50*
Wood's Elements of Co-ordinate Geometry.	8vo,	2 00
Trigonometry: Analytical, Plane, and Spherical	12mo,	1 00

MECHANICAL ENGINEERING.

MATERIALS OF ENGINEERING, STEAM-ENGINES AND BOILERS.

Bacon's Forge Practice.	12mo,	1 50
Baldwin's Steam Heating for Buildings.	12mo,	2 50
Barr's Kinematics of Machinery.	8vo,	2 50
* Bartlett's Mechanical Drawing.	8vo,	3 00
* " " " Abridged Ed.	8vo,	1 50
Benjamin's Wrinkles and Recipes.	12mo,	2 00
Carpenter's Experimental Engineering.	8vo,	6 00
Heating and Ventilating Buildings.	8vo,	4 00
Cary's Smoke Suppression in Plants using Bituminous Coal. (In Preparation.)		
Clerk's Gas and Oil Engine.	Small 8vo,	4 00
Coolidge's Manual of Drawing.	8vo, paper,	1 00
Coolidge and Freeman's Elements of General Drafting for Mechanical Engineers.	Oblong 4to,	2 50
Cromwell's Treatise on Toothed Gearing.	12mo,	1 50
Treatise on Belts and Pulleys.	12mo,	1 50
Durley's Kinematics of Machines.	8vo,	4 00
Flather's Dynamometers and the Measurement of Power.	12mo,	3 00
Rope Driving.	12mo,	2 00
Gill's Gas and Fuel Analysis for Engineers.	12mo,	1 25
Hall's Car Lubrication.	12mo,	1 00
Hering's Ready Reference Tables (Conversion Factors).	16mo, morocco,	2 50
Hutton's The Gas Engine.	8vo,	5 00
Jamison's Mechanical Drawing.	8vo,	2 50
Jones's Machine Design:		
Part I. *Kinematics of Machinery.*	*8vo,*	*1 50*
Part II. Form, Strength, and Proportions of Parts.	8vo,	3 00
Kent's Mechanical Engineers' Pocket-book.	16mo, morocco,	5 00
Kerr's Power and Power Transmission.	8vo,	2 00
Leonard's Machine Shop, Tools, and Methods.	8vo,	4 00
* Lorenz's Modern Refrigerating Machinery. (Pope, Haven, and Dean.)	8vo,	4 00
MacCord's Kinematics; or Practical Mechanism.	8vo,	5 00
Mechanical Drawing.	4to,	4 00
Velocity Diagrams.	8vo,	1 50

MacFarland's Standard Reduction Factors for Gases	8vo,	1 50
Mahan's Industrial Drawing. (Thompson.)	8vo,	3 50
Poole's Calorific Power of Fuels	8vo,	3 00
Reid's Course in Mechanical Drawing	8vo,	2 00
Text-book of Mechanical Drawing and Elementary Machine Design	8vo,	3 00
Richard's Compressed Air	12mo,	1 50
Robinson's Principles of Mechanism	8vo,	3 00
Schwamb and Merrill's Elements of Mechanism	8vo,	3 00
Smith's (O.) Press-working of Metals	8vo,	3 00
Smith (A. W.) and Marx's Machine Design	8vo,	3 00
Thurston's Treatise on Friction and Lost Work in Machinery and Mill Work	8vo,	3 00
Animal as a Machine and Prime Motor, and the Laws of Energetics	12mo,	1 00
Warren's Elements of Machine Construction and Drawing	8vo,	7 50
Weisbach's Kinematics and the Power of Transmission. (Herrmann—Klein.)	8vo,	5 00
Machinery of Transmission and Governors. (Herrmann—Klein.)	8vo,	5 00
Wolff's Windmill as a Prime Mover	8vo,	3 00
Wood's Turbines	8vo,	2 50

MATERIALS OF ENGINEERING.

* Bovey's *Strength of Materials and Theory of Structures*	8vo,	7 50
Burr's Elasticity and Resistance of the Materials of Engineering. 6th Edition. Reset	8vo,	7 50
Church's Mechanics of Engineering	8vo,	6 00
* Greene's Structural Mechanics	8vo,	2 50
Johnson's Materials of Construction	8vo,	6 00
Keep's Cast Iron	8vo,	2 50
Lanza's Applied Mechanics	8vo,	7 50
Martens's Handbook on Testing Materials. (Henning.)	8vo,	7 50
Maurer's Technical Mechanics	8vo,	4 00
Merriman's Mechanics of Materials	8vo,	5 00
Strength of Materials	12mo,	1 00
Metcalf's Steel. A manual for Steel-users	12mo,	2 00
Sabin's Industrial and Artistic Technology of Paints and Varnish	8vo,	3 00
Smith's Materials of Machines	12mo,	1 00
Thurston's Materials of Engineering	3 vols., 8vo,	8 00
Part II. Iron and Steel	8vo,	3 50
Part III. A Treatise on Brasses, Bronzes, and Other Alloys and their Constituents	8vo,	2 50
Text-book of the Materials of Construction	8vo,	5 00
Wood's (De V.) Treatise on the Resistance of Materials and an Appendix on the Preservation of Timber	8vo,	2 00
Elements of Analytical Mechanics	8vo,	3 00
Wood's (M. P.) Rustless Coatings: Corrosion and Electrolysis of Iron and Steel	8vo,	4 00

STEAM-ENGINES AND BOILERS.

Berry's Temperature-entropy Diagram	12mo,	1 25
Carnot's Reflections on the Motive Power of Heat. (Thurston.)	12mo,	1 50
Dawson's "Engineering" and Electric Traction Pocket-book	16mo, mor.,	5 00
Ford's Boiler Making for Boiler Makers	18mo,	1 00
Goss's Locomotive Sparks	8vo,	2 00
Hemenway's Indicator Practice and Steam-engine Economy	12mo,	2 00

Hutton's Mechanical Engineering of Power Plants	8vo,	5 00
Heat and Heat-engines	8vo.	5 00
Kent's Steam boiler Economy	8vo,	4 00
Kneass's Practice and Theory of the Injector	8vo,	1 50
MacCord's Slide-valves	8vo,	2 00
Meyer's Modern Locomotive Construction	4to,	10 00
Peabody's Manual of the Steam-engine Indicator	12mo,	1 50
Tables of the Properties of Saturated Steam and Other Vapors	8vo,	1 00
Thermodynamics of the Steam-engine and Other Heat-engines	8vo,	5 00
Valve-gears for Steam-engines	8vo,	2 50
Peabody and Miller's Steam-boilers	8vo,	4 00
Pray's Twenty Years with the Indicator	Large 8vo,	2 50
Pupin's Thermodynamics of Reversible Cycles in Gases and Saturated Vapors. (Osterberg.)	12mo,	1 25
Reagan's Locomotives: Simple Compound, and Electric	12mo,	2 50
Rontgen's Principles of Thermodynamics. (Du Bois.)	8vo,	5 00
Sinclair's Locomotive Engine Running and Management	12mo,	2 00
Smart's Handbook of Engineering Laboratory Practice	12mo,	2 50
Snow's Steam-boiler Practice	8vo,	3 00
Spangler's Valve-gears	8vo,	2 50
Notes on Thermodynamics	12mo,	1 00
Spangler, Greene, and Marshall's Elements of Steam-engineering	8vo,	3 00
Thomas's Steam-turbines	8vo,	3 50
Thurston's Handy Tables	8vo,	1 50
Manual of the Steam-engine	2 vols., 8vo,	10 00
Part I. History, Structure, and Theory	8vo,	6 00
Part II. Design, Construction, and Operation	8vo,	6 00
Handbook of Engine and Boiler Trials, and the Use of the Indicator and the Prony Brake	8vo,	5 00
Stationary Steam-engines	8vo,	2 50
Steam-boiler Explosions in Theory and in Practice	12mo,	1 50
Manual of Steam-boilers, their Designs, Construction, and Operation	8vo,	5 00
Wehrenfenning's Analysis and Softening of Boiler Feed-water (Patterson)	8vo,	4 00
Weisbach's Heat, Steam, and Steam-engines. (Du Bois.)	8vo,	5 00
Whitham's Steam-engine Design	8vo,	5 00
Wood's Thermodynamics, Heat Motors, and Refrigerating Machines	8vo,	4 00

MECHANICS AND MACHINERY.

Barr's Kinematics of Machinery	8vo,	2 50
* Bovey's Strength of Materials and Theory of Structures	8vo,	7 50
Chase's The Art of Pattern-making	12mo,	2 50
Church's Mechanics of Engineering	8vo,	6 00
Notes and Examples in Mechanics	8vo,	2 00
Compton's First Lessons in Metal-working	12mo,	1 50
Compton and De Groodt's The Speed Lathe	12mo,	1 50
Cromwell's Treatise on Toothed Gearing	12mo,	1 50
Treatise on Belts and Pulleys	12mo,	1 50
Dana's Text-book of Elementary Mechanics for Colleges and Schools	12mo,	1 50
Dingey's Machinery Pattern Making	12mo,	2 00
Dredge's Record of the Transportation Exhibits Building of the World's Columbian Exposition of 1893	4to half morocco,	5 00
u Bois's Elementary Principles of Mechanics:		
Vol. I. Kinematics	8vo,	3 50
Vol. II. Statics	8vo,	4 00
Mechanics of Engineering. Vol. I.	Small 4to,	7 50
Vol. II.	Small 4to,	10 00
Durley's Kinematics of Machines	8vo,	4 00

Fitzgerald's Boston Machinist.	16mo,	1 00
Flather's Dynamometers, and the Measurement of Power.	12mo,	3 00
Rope Driving.	12mo,	2 00
Goss's Locomotive Sparks.	8vo,	2 00
* Greene's Structural Mechanics.	8vo,	2 50
Hall's Car Lubrication.	12mo,	1 00
Holly's Art of Saw Filing.	18mo,	75
James's *Kinematics of a Point and the Rational Mechanics of a Particle.*	Small 8vo,	2 00
* Johnson's (W. W.) Theoretical Mechanics.	12mo,	3 00
Johnson's (L. J.) Statics by Graphic and Algebraic Methods.	8vo,	2 00
Jones's Machine Design:		
Part I. Kinematics of Machinery.	8vo,	1 50
Part II. Form, Strength, and Proportions of Parts.	8vo,	3 00
Kerr's Power and Power Transmission.	8vo,	2 00
Lanza's Applied Mechanics.	8vo,	7 50
Leonard's Machine Shop, Tools, and Methods.	8vo,	4 00
* Lorenz's Modern Refrigerating Machinery. (Pope, Haven, and Dean.)	8vo,	4 00
MacCord's Kinematics; or, Practical Mechanism.	8vo,	5 00
Velocity Diagrams.	8vo,	1 50
* *Martin's Text Book on Mechanics, Vol. I, Statics.*	12mo,	1 25
Maurer's Technical Mechanics.	8vo,	4 00
Merriman's Mechanics of Materials.	8vo,	5 00
* Elements of Mechanics.	12mo,	1 00
* Michie's Elements of Analytical Mechanics.	8vo,	4 00
* Parshall and Hobart's Electric Machine Design.	4to, *half morocco,*	12 50
Reagan's Locomotives: Simple, Compound, and Electric.	12mo,	2 50
Reid's Course in Mechanical Drawing.	8vo,	2 00
Text-book of Mechanical Drawing and Elementary Machine Design.	8vo,	3 00
Richards's Compressed Air.	12mo,	1 50
Robinson's Principles of Mechanism.	8vo,	3 00
Ryan, Norris, and Hoxie's Electrical Machinery. Vol. I.	8vo,	2 50
Sanborn's Mechanics: Problems.	Large 12mo,	1 50
Schwamb and Merrill's Elements of Mechanism.	8vo,	3 00
Sinclair's *Locomotive-engine Running and Management.*	12mo,	2 00
Smith's (O.) Press-working of Metals.	8vo,	3 00
Smith's (A. W.) Materials of Machines.	12mo,	1 00
Smith (A. W.) and Marx's Machine Design.	8vo,	3 00
Spangler, Greene, and Marshall's Elements of Steam-engineering.	8vo,	3 00
Thurston's Treatise on Friction and Lost Work in Machinery and Mill Work.	8vo,	3 00
Animal as a Machine and Prime Motor, and the Laws of Energetics.	12mo,	1 00
Warren's Elements of Machine Construction and Drawing.	8vo,	7 50
Weisbach's Kinematics and Power of Transmission. (Herrmann—Klein.)	8vo,	5 00
Machinery of Transmission and Governors. (Herrmann—Klein.)	8vo,	5 00
Wood's Elements of Analytical Mechanics.	8vo,	3 00
Principles of Elementary Mechanics.	12mo,	1 25
Turbines.	8vo,	2 50
The World's Columbian Exposition of 1893	4to,	1 00

METALLURGY.

Egleston's Metallurgy of Silver, Gold, and Mercury:		
Vol. I. Silver.	8vo,	7 50
Vol. II. Gold and Mercury.	8vo,	7 50
Goesel's Minerals and Metals: a Reference Book.	16mo, mor.	3 00
** Iles's Lead-smelting. (Postage 9 cents additional.)	12mo,	2 50
Keep's Cast Iron.	8vo,	2 50

Kunhardt's Practice of Ore Dressing in Europe	8vo,	1 50
Le Chatelier's High-temperature Measurements. (Boudouard—Burgess.)	12mo,	3 00
Metcalf's Steel. A Manual for Steel-users	12mo,	2 00
Miller's Cyanide Process	12mo,	1 00
Minet's Production of Aluminum and its Industrial Use. (Waldo.)	12mo,	2 50
Robine and Lenglen's Cyanide Industry. (Le Clerc.)	8vo,	4 00
Smith's Materials of Machines	12mo,	1 00
Thurston's Materials of Engineering. In Three Parts	8vo,	8 00
Part II. Iron and Steel	8vo,	3 50
Part III. A Treatise on Brasses, Bronzes, and Other Alloys and their Constituents	8vo,	2 50
Ulke's Modern Electrolytic Copper Refining	8vo,	3 00

MINERALOGY.

Barringer's Description of Minerals of Commercial Value.	Oblong, morocco,	2 50
Boyd's Resources of Southwest Virginia	8vo,	3 00
Map of Southwest Virignia	Pocket-book form.	2 00
Brush's Manual of Determinative Mineralogy. (Penfield.)	8vo,	4 00
Chester's Catalogue of Minerals	8vo, paper,	1 00
	Cloth,	1 25
Dictionary of the Names of Minerals	8vo	3 50
Dana's System of Mineralogy	Large 8vo, half leather	12 50
First Appendix to Dana's New "System of Mineralogy."	Large 8vo,	1 00
Text-book of Mineralogy	8vo,	4 00
Minerals and How to Study Them	12mo.	1 50
Catalogue of American Localities of Minerals	Large 8vo,	1 00
Manual of Mineralogy and Petrography	12mo.	2 00
Douglas's Untechnical Addresses on Technical Subjects	12mo,	1 00
Eakle's Mineral Tables	8vo,	1 25
Egleston's Catalogue of Minerals and Synonyms	8vo,	2 50
Goesel's Minerals and Metals: A Reference Book	16mo, mor.	3 00
Groth's Introduction to Chemical Crystallography (Marshall)	12mo,	1 25
Hussak's The Determination of Rock-forming Minerals. (Smith.)	Small 8vo,	2 00
Merrill's Non-metallic Minerals: Their Occurrence and Uses	8vo,	4 00
* Penfield's Notes on Determinative Mineralogy and Record of Mineral Tests.	8vo, paper,	50
Rosenbusch's Microscopical Physiography of the Rock-making Minerals. (Iddings.)	8vo,	5 00
* Tillman's Text-book of Important Minerals and Rocks	8vo,	2 00

MINING.

Beard's Ventilation of Mines	12mo,	2 50
Boyd's Resources of Southwest Virginia	8vo,	3 00
Map of Southwest Virginia	Pocket-book form.	2 00
Douglas's Untechnical Addresses on Technical Subjects	12mo,	1 00
* Drinker's Tunneling, Explosive Compounds, and Rock Drills	4to, hf. mor.,	25 00
Eissler's Modern High Explosives	8vo,	4 00
Goesel's Minerals and Metals: A Reference Book	16mo, mor.	3 00
Goodyear's Coal-mines of the Western Coast of the United States	12mo,	2 50
Ihlseng's Manual of Mining	8vo,	5 00
** *Iles's Lead-smelting. (Postage 9c. additional.)*	*12mo,*	*2 50*
Kunhardt's Practice of Ore Dressing in Europe	8vo,	1 50
Miller's Cyanide Process	12mo,	1 00

O'Driscoll's *Notes on the Treatment of Gold Ores.*	8vo,	2 00
Robine and Lenglen's Cyanide Industry. (Le Clerc.)	8vo,	4 00
* Walke's Lectures on Explosives.	8vo,	4 00
Weaver's Military Explosives.	8vo,	3 00
Wilson's Cyanide Processes.	12mo,	1 50
Chlorination Process.	12mo,	1 50
Hydraulic and Placer Mining.	12mo,	2 00
Treatise on Practical and Theoretical Mine Ventilation.	12mo,	1 25

SANITARY SCIENCE.

Bashore's *Sanitation of a Country House*	12mo,	1 00
* Outlines of Practical Sanitation.	12mo,	1 25
Folwell's Sewerage. (Designing, Construction, and Maintenance.)	8vo,	3 00
Water-supply Engineering.	8vo,	4 00
Fowler's Sewage Works Analyses.	12mo,	2 00
Fuertes's Water and Public Health.	12mo,	1 50
Water-filtration Works.	12mo,	2 50
Gerhard's Guide to Sanitary House-inspection	16mo,	1 00
Goodrich's Economic Disposal of Town's Refuse.	Demy 8vo,	3 50
Hazen's Filtration of Public Water-supplies.	8vo,	3 00
Leach's The Inspection and Analysis of Food with Special Reference to State Control.	8vo,	7 50
Mason's Water-supply. (Considered principally from a Sanitary Standpoint)	8vo,	4 00
Examination of Water. (Chemical and Bacteriological.)	12mo,	1 25
Ogden's Sewer Design.	*12mo,*	2 00
Prescott and Winslow's Elements of Water Bacteriology, with Special Reference to Sanitary Water Analysis.	12mo,	1 25
* Price's Handbook on Sanitation.	12mo,	1 50
Richards's Cost of Food. A Study in Dietaries.	*12mo,*	1 00
Cost of Living as Modified by Sanitary Science.	12mo,	1 00
Cost of Shelter	12mo,	1 00
Richards and Woodman's Air, Water, and Food from a Sanitary Standpoint.	8vo,	2 00
* *Richards and Williams's The Dietary Computer.*	8vo,	1 50
Rideal's Sewage and Bacterial Purification of Sewage.	8vo,	3 50
Turneaure and Russell's Public Water-supplies.	8vo,	5 00
Von Behring's Suppression of Tuberculosis. (Bolduan.)	12mo,	1 00
Whipple's Microscopy of *Drinking-water.*	8vo,	3 50
Winton's Microscopy of Vegetable Foods.	8vo,	7 50
Woodhull's Notes on Military Hygiene.	16mo,	1 50
* Personal Hygiene.	12mo,	1 00

MISCELLANEOUS.

De Fursac's *Manual of Psychiatry.* (Rosanoff and Collins.)	Large 12mo,	2 50
Ehrlich's Collected Studies on Immunity (Bolduan)	8vo,	6 00
Emmons's Geological Guide-book of the Rocky Mountain Excursion of the International Congress of Geologists.	Large 8vo,	1 50
Ferrel's Popular Treatise on the Winds.	8vo.	4 00
Haines's American Railway *Management.*	12mo,	2 50
Mott's Fallacy of the Present Theory of Sound	16mo,	1 00
Ricketts's History of Rensselaer Polytechnic Institute, 1824–1894.	Small 8vo,	3 00
Rostoski's Serum Diagnosis. (Bolduan.)	12mo,	1 00
Rotherham's Emphasized New Testament.	Large 8vo,	2 00

Steel's Treatise on the *Diseases of the Dog*	8vo,	3 50
The World's Columbian Exposition of 1893	4to,	1 00
Von Behring's Suppression of Tuberculosis. (Bolduan.)	12mo,	1 00
Winslow's Elements of Applied Microscopy	12mo,	1 50
Worcester and Atkinson. Small Hospitals, Establishment and Maintenance; Suggestions for Hospital Architecture: Plans for Small Hospital	12mo,	1 25

HEBREW AND CHALDEE TEXT-BOOKS.

Green's Elementary Hebrew Grammar	12mo,	1 25
Hebrew Chrestomathy.	8vo,	2 00
Gesenius's Hebrew and Chaldee Lexicon to the Old Testament Scriptures. (*Tregelles.*)	*Small 4to, half morocco,*	5 00
Letteris's Hebrew Bible	8vo,	2 25