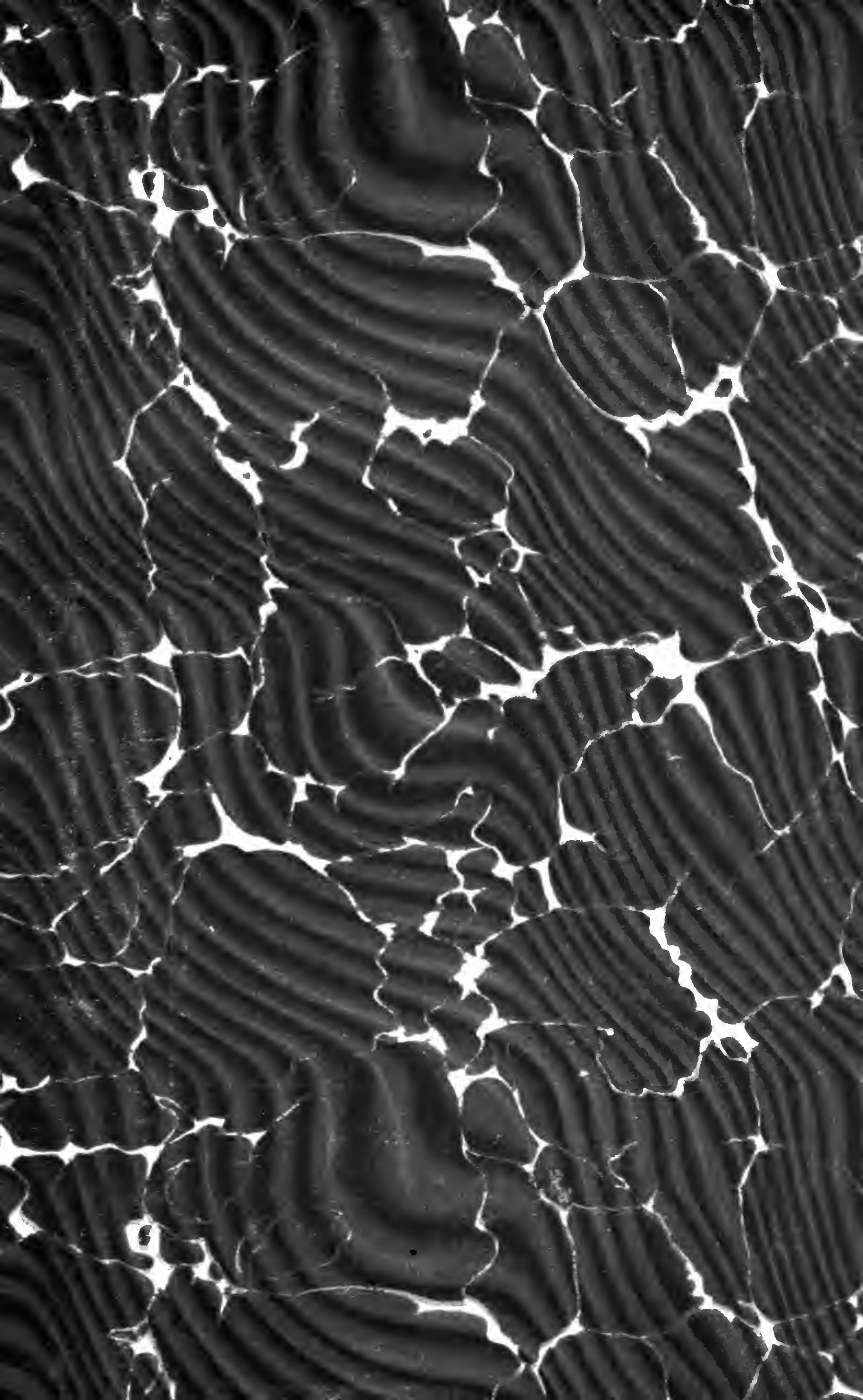

PRACTICAL ELECTRO-CHEMISTRY

Practical Electro-Chemistry

By

BERTRAM BLOUNT

F.I.C., F.C.S., Assoc. Inst. C.E

CONSULTING CHEMIST TO THE CROWN AGENTS FOR THE COLONIES

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Preface

The intention of this book is to give an account of those electro-chemical processes which have been already or are likely to be turned to industrial use. Historical matter has generally been omitted for the sake of conciseness. For the same reason, comparison of electro-chemical processes with chemical or metallurgical methods accomplishing the same results has been confined to the indication of their relative advantages, a knowledge of the older processes being assumed. The relation between the output of a given process and the energy necessary for that output has been dealt with somewhat fully, and in like manner the practical advantages to be gained by the use of electro-chemical methods in certain cases have been indicated. I venture to hope that the book may be found useful by some of those interested in one of the youngest and most promising of modern industries.

B. B.

London, 1900.

Table of Contents

TABLE OF CONTENTS

ERRATUM.

Page 145, line 14, *for* Froman *read* Fromm.

List of Illustrations

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS

SECTION I

Introduction—General Principles

SECTION I. INTRODUCTORY

The Principles of Electro-Chemistry

ALL electro-chemical operations are performed either by the analytical property of electrical energy when passed through an electrolyte or by the heat which is produced when a current of electricity is passed through a conductor which is not an electrolyte. Numerous applications of both have been made, and the principles involved in these applications must be understood before the applications themselves can be considered intelligently.

ELECTROLYSIS

It must be assumed that the reader is familiar with the general principles of chemistry and electricity. This being granted, it is necessary merely to state the meaning of certain special terms in order to make possible the communication of an intelligent idea of the nature of electrolysis.

Electrolysis itself may be defined as the course of chemical changes induced by the passage of a current of electricity through a chemical compound in solution or in the fused state.[1]

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[1] Resolution of a compound by the mere heating effect of the current is not contemplated in this definition.

An *electrolyte* is a compound substance capable of undergoing resolution into its constituent elements or radicles by the passage of a current of electricity.

An *electrode* is a conductor of the metallic class serving to convey a current of electricity into or out of an electrolyte. The electrode by which the current enters the electrolyte is called the *anode*; that by which the current leaves the electrolyte is called the *cathode.*

Those constituent elements or radicles of an electrolyte which are believed to be the material carriers of a current of electricity through an electrolyte are called *ions.*

Ions which appear as such or as their products at the anode are termed *anions*; those appearing at the cathode are called *cations.*

The ions appearing at the anode are negative to those appearing at the cathode; thus, in general, metals or their oxides or hydroxides appear at the cathode, and non-metallic elements or their oxides or hydroxides (bodies of the class of acids) appear at the anode.

It is useful to remember that, just as one generates hydrogen by the action of zinc on a dilute acid, so when a dilute acid is electrolysed hydrogen is evolved at the electrode connected with the zinc plate of the battery. Seeing that hydrogen stands to the other constituents of the acid in the relation of a metal, and is thus the positive element, it is clear that the electrode to which it is attracted must be the negative, *i.e.* the hydrogen or its equivalent metal appears at the *negative* electrode or cathode. Such notions, based on elementary chemical facts, make it easy, when the learner is confronted by two poles labelled + and −, to couple them aright to the apparatus he intends to use. Having thus cleared the ground, we may return to the consideration of the nature of electrolysis.

Many substances, notably metallic salts, when fused or dissolved by a suitable solvent (most commonly water), suffer chemical change when a current of electricity is passed through them. Thus, when zinc chloride is fused, and two platinum plates (electrodes) are immersed therein, one being connected with one pole and one with the other of a sufficiently powerful source of electricity, a current passes through the liquid zinc chloride, and that body is separated into its constituents, zinc appearing at the negative electrode, which is called the cathode, and chlorine at the positive electrode, which is called the anode. Similarly, when zinc chloride is dissolved in water and electrolysed, the same products appear at the same electrodes. In each case the products appear at the surface of the electrodes, and there is no indication of change in the liquid between the two electrodes. But there is reason to believe that many of the molecules of zinc chloride occupying the space between the electrodes undergo change during the passage of the current. It is supposed that each atom of chlorine separated from the zinc chloride at the anode is immediately replaced by another atom from an adjacent molecule of zinc chloride, and that the atom of zinc thus left in its turn requires an atom of chlorine from its neighbour; this process continues until, at the end of a string of molecules, an atom of zinc is left, robbed of its chlorine and without an available neighbour to borrow from. This atom of zinc appears as the free metal at the cathode.

This is a simple case of electrolysis in which the products are the same from the fused salt as from the salt dissolved in water, and where there is little tendency towards the formation of products other than the two primary substances, zinc and chlorine. It must not be supposed that the process of electrolysis is always as simple as this. In many instances the actual products are not those which would be formed by the splitting of the salt into its metallic and non-metallic constituent, but include substances formed by the action of these primary constituents on the solvent. Thus, when sodium chloride is fused and electrolysed, the products are sodium and chlorine. When its aqueous solution is electrolysed, the products are sodium hydroxide, hydrogen, and chlorine. Seeing that free sodium acts violently on water, liberating hydrogen and forming sodium hydroxide (caustic soda), it is convenient to regard the process of electrolysis in this instance as separating sodium from its union with chlorine, and the sodium thus liberated in the midst of an ample supply of water molecules at once reacting with them in precisely the same manner as it does when a piece of the metal is placed in contact with water. But further complexity may arise in this seemingly simple case of the electrolysis of an aqueous solution of sodium chloride. It is true that the products appear at separate electrodes, but as the process of electrolysis goes on the products will encounter each other unless some means of mechanical separation be devised. Considering the products one by one, it is clear that the greater part of the chlorine will escape as gas, but that a small portion will remain in solution. The hydrogen will escape as gas almost entirely; the whole of the caustic soda will remain in the liquid. The portion of the chlorine which is dissolved will eventually encounter the caustic soda and form sodium hypochlorite and sodium chlorate, according to the temperature of the solution; should it chance to meet the hydrogen before the latter escapes from the cathode, hydrochloric acid will be formed. This reacting with the caustic soda will regenerate sodium chloride and water, or encountering sodium hypochlorite will give sodium chloride and chlorine, or meeting sodium chlorate will yield sodium chloride and chloric acid, a body itself always on the verge of splitting up.

All these reactions may be proceeding at once, according to the local conditions of the liquid in contact with the electrodes. Thus a mixture of considerable complexity may result from a resolution which appears simple enough at first sight.

Among all these various possibilities, there is one truth which has the force of a canon. It is that the energy impressed on the solution serving as an electrolyte can have as its outcome only its strict equivalent in the substances which are produced. There may be (and usually is) a waste in transforming the electrical energy of the current used for the decomposition into the chemical energy represented by the products of the decomposition, but there can never be a surplus.

Part of this truth is involved in the hypothesis known as Faraday's law. By a number of well-conceived researches, executed with that skill in experiment which was native in this great chemist and physicist, Faraday established that, for a large number of electrolytes which he examined, the same current produced equivalent quantities of products at the anode and the cathode. Now, as it is known that in a given electrical circuit the current passing between any pair of points is the same as that passing between any other pair of points, it follows that, when any number of electrolytic cells are coupled in series, the products separated at their anodes and cathodes are in all cases equivalent.[1] Thus, a current sent through a cell containing a solution of copper sulphate, and then through one containing fused zinc chloride, will liberate at the cathode of the first 63·5 grammes of Cu for every 65 grammes of Zn liberated at the cathode of the second. Corresponding with each of these quantities there will be produced at the anodes 96 grammes of the hypothetical radicle SO_4 and 71 grammes of chlorine respectively.

The metals copper and zinc, being divalent, are set free atom for atom in their respective electrolytes. The radicle SO_4, being also divalent, is strictly equivalent to one atom of either of the metals. The element chlorine, being monovalent, is set free in quantity equivalent to each of the others, that is, two atoms become free for one atom of zinc or copper. The radicle SO_4 has no objective existence, but what may be termed its natural products appear in strictly equivalent amount, viz., O and SO_3, the latter of course combining with the water of the copper sulphate solution to form H_2SO_4.

But though the quantities of the elements or radicles liberated at the electrodes are all equivalent, yet the energy expended in each cell is not necessarily equal to that expended in any other. The current flowing through each cell is equal, but the fall of voltage from anode to cathode in each cell will vary with the chemical

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[1] For the discussion of matters purely electrical the reader is referred to any good text-book dealing with the branch of physics known as electricity.

energy represented by the union of the anion and cation. It is convenient to measure the energy evolved by the chemical union of two bodies in thermal units. Thus the heat of combination of 23 grammes of sodium and 35·5 grammes of chlorine is 97·69 Cal.[1] To liberate 23 grammes of sodium and 35·5 grammes of chlorine from 58·5 grammes of sodium chloride, 97·69 Cal. or its equivalent in electrical units of energy must be expended. The electrical unit of energy or joule is 0·7375 foot-pound, or 0·00024 Cal. Therefore, for the decomposition of 58·5 grammes of NaCl, assuming no waste to occur, 407,042 joules must be expended. But a joule, being a unit of energy, can be expressed as the product of two values—one of the nature of a quantity, the other of a pressure. Thus 1 joule is the product of 1 coulomb and 1 volt. The coulomb, being the unit of the quantity of electricity, involves in its flow the separation of a definite and equivalent amount of any electrolyte. One coulomb can decompose 0·0006045 gramme of NaCl, and 58·5 grammes of NaCl require 96,540 coulombs for their decomposition. But in order that the passage of 96,540 coulombs should represent the expenditure of 407,042 joules, they must be delivered at a pressure of $\frac{407{,}042}{96{,}540}$ volts, *i.e.* at 4·22 volts.

It will be observed that here no mention is made of time; the work may be done in any time provided the requisite number of coulombs are caused to flow at a pressure not lower than 4·22 volts. For the purpose of

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[1] Throughout this book the unit of heat energy used is the kilogramme-calorie (represented by Cal.) unless a direct statement to the contrary is made. The kilogramme-calorie is the quantity of heat needed to raise 1 kilogramme of water from 15° C. to 16° C.

this argument the figure which is usually accepted for the heat of combination of sodium and chlorine has been taken; seeing, however, that the electrolysis of sodium chloride into its cation sodium and its anion chlorine cannot be effected when the salt is in the solid state (because it is then almost non-conducting), but is carried out with the salt in a state of igneous fusion, a condition which it attains at a moderate red heat, it is certain that this value is too high, for at this working temperature sodium chloride is already approaching its temperature of dissociation, *i.e.* its constituent atoms are less firmly united than they are at the ordinary temperature, and, therefore, the total energy needed to dissever them is smaller than that which would be requisite at the ordinary temperature. In a word, part of the work of disconnecting sodium and chlorine has been performed by the heat needed to fuse sodium chloride, and the electrical energy which has now to be impressed on it is correspondingly smaller in amount. Now, by Faraday's law, each unit of electrical quantity liberates one equivalent of sodium and one of chlorine, and thus the number of coulombs necessary for decomposing 58·5 grammes of sodium chloride at a red heat is the same as that which would be needed at the ordinary temperature; therefore, the factor which suffers change is the electrical pressure or voltage. Thus in this case the minimum voltage necessary to decompose fused sodium chloride at a red heat is smaller than 4·2 volts. Its precise value has not been determined (see p. 20).

In the foregoing argument all consideration of the possibility of a portion of the heat energy impressed on the fused sodium chloride being converted into electrical energy and thereby providing a voltage auxiliary or opposed to the voltage of the external source of electrical energy has been purposely omitted. The one fundamental fact to be thoroughly grasped is that the energy necessary to decompose a given substance at a given temperature is a constant quantity, and that, if Faraday's law be true for that substance, there is a fixed minimum voltage necessary for its decomposition. Any accurately made experiment which tends to show that a given electrolyte can be decomposed by a voltage smaller than that calculated from the heat of formation of the electrolyte at that temperature will invalidate Faraday's law.

There is no need to shrink from such an overthrow, but the experiments needed to accomplish it must be less open to criticism than any which have yet been published.

Perfect understanding of these principles is necessary for intelligent study of any practical process of electrolysis. The efficiency of a process is frequently stated in terms of current alone, *i.e.* the efficiency is stated as the ratio which the weight of product actually obtained bears to the weight of product which should be obtained by the passage of the number of coulombs known to have passed. But this method of statement ignores the equally important factor of voltage, *i.e.* it fails to take into account the pressure at which the coulombs have been delivered. Therefore it is necessary, in addition to giving the current efficiency for a process, to give also the energy efficiency, *i.e.* the ratio of the weight of the product actually obtained to the weight which should be obtained by the theoretically perfect expenditure of the total number of electrical energy units (joules) which have passed through the cell. Thus a solution of sodium chloride may be electrolysed with a voltage of 2·3 volts.

In practice the voltage required is as high as 4 volts; the current efficiency may be 90 per cent., but the energy efficiency under these conditions is only $90 \times \frac{2{\cdot}3}{4} = 51\frac{3}{4}$ per cent.

THE CONSTITUTION OF ELECTROLYTES AND THE MECHANISM OF ELECTROLYSIS

Some aid to clear thought as to the way in which reactions are brought about by electrolysis is afforded by considering the ultimate structure of a typical electrolyte and the molecular mechanism by which electrolysis is effected. A full discussion of this subject is a proper matter for a text-book on chemical physics, but certain of the more important theoretical conceptions and their consequences may be set down here.

NORMAL CONDITION OF A DISSOLVED NON-ELECTROLYTE

This may first be considered as a simpler case, before passing to the discussion of the condition of a dissolved electrolyte. At the present time it is generally held that the molecules of a substance, such as sugar, which is not an electrolyte, are, when dissolved in a solvent capable of no appreciable chemical action on the dissolved substance, in a condition comparable with that of the molecules of a substance existing as a gas. A solution of such a non-electrolyte exercises a pressure proportional to the number of molecules per unit volume occupied, thus behaving precisely in the same manner as a gas.

This pressure, which is termed the osmotic pressure of the dissolved substance, is detected and measured by a device which will be understood from the following concrete case. Suppose the osmotic pressure of a sugar solution is to be determined, a "semi-permeable" membrane is prepared by depositing within the pores of an ordinary porous pot a precipitate of cupric ferrocyanide, a body which is found to allow the diffusion of water but not of sugar. The formation of the semi-permeable membrane is effected by filling the pot with a solution of potassium ferrocyanide and surrounding it by one of copper sulphate. The two liquids, meeting in the interstices of the pot, form there a layer of cupric ferrocyanide which has the property enunciated above.

After removing the pot from the liquids and washing out traces of soluble salts the membrane is ready for use. The pot is filled with sugar solution, the top is closed by a cork carrying a manometer and the pot is then immersed in pure water. On each side of the semi-permeable membrane in the pores of the pot molecules of water are constantly impinging. Those impinging on the inside in contact with the sugar solution are, however, fewer per unit of time than those on the outside in contact with pure water, because a certain part of the volume of the sugar solution is occupied by sugar molecules instead of water molecules. Now those molecules of water from the outside which do not collide with water molecules on the inside pass through the membrane; no corresponding efflux of sugar molecules is possible because the sugar molecules cannot pass through the semi-permeable membrane. The influx of water molecules from the outside goes on until those on the inside are sufficiently crowded together to make the same number of impacts on the inside of the membrane as do those on the outside. That is, the pressure due to water molecules is equal on each side of the membrane. But the pressure of the sugar molecules on the inside is over and above this pressure of the water molecules, and the total pressure of the sugar solution is thereby increased. The amount of the increase is indicated by the manometer. A rough calculation will show the order of magnitude of such osmotic pressures. A porous pot of a capacity of 100 c.c. is filled with sugar solution containing $\frac{1}{10}$ gramme molecule of sugar per litre, *i.e.* 34·2 grammes per litre, or in the 100 c.c. 3·42 grammes of sugar. Now, if it were possible to gasify sugar by heat without decomposition, 342 grammes of sugar-gas would occupy a volume which, corrected to 0° C. and 760 mm. pressure, would equal 2 × 11·2 litres; therefore, 3·42 grammes would occupy ·224 litre, *i.e.* 224 c.c. Regarding the dissolved sugar as being in the same condition as if it were gasified, it is evident that the pressure above that of the atmosphere which the sugar is capable of exerting is $\frac{224}{100} \times 760$ mm. = 1,702 mm. of mercury. Direct experiment in the manner described above gives figures closely corresponding with this. Additional evidence in favour of the belief that a non-electrolyte dissolved in a neutral solvent has its molecules in the same condition as those of a gas is afforded by a variety of other chemico-physical measurements.

Thus, when a solution of sugar in water is frozen, water free from sugar is first separated as ice, and this at a lower temperature than the freezing-point of pure water, viz. 0° C. Now as pure water (in the form of ice) is abstracted from the solution the volume available for the molecules of the dissolved substance is diminished; if the molecules of the dissolved substance be in the same condition as those of a gas, the diminution of the volume which they occupy (pressure being constant) can be effected by the abstraction of a quantity of heat readily calculable. This quantity of heat is found to be measured jointly by the lowering of temperature needed to bring about the diminution of volume and the latent heat of the solvent. The latter being known (*e.g.* 80 Cal. for water), the former can be directly compared with the lowering of temperature experimentally observed. They are found to agree, and it may thus fairly be deduced that the molecules of the dissolved substance are in the same condition as those of a gas. Other means of judging the condition of the molecules of a dissolved non-electrolyte in a neutral solvent, such as the lowering of the vapour pressure of a given solvent by the addition of a soluble substance, lead to the same result. Therefore it may be provisionally accepted as consonant with experiment that the molecules of a non-electrolyte dissolved in a solvent on which it does not act chemically behave in many respects similarly to the molecules of a gas.[1]

CONDITION OF A DISSOLVED ELECTROLYTE

When the methods briefly described above, of examining the condition of a substance which is not an electrolyte dissolved in a solvent on which it does not act chemically, are applied to the examination of solutions of electrolytes, it is found that such solutions give indications of abnormal behaviour. Electrolytes behave in manner similar to that of a compound gas, the molecules of which are dissociated into a larger number of simpler

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[1] When a solution is somewhat strong, the molecules of the dissolved substance do not conform perfectly to gaseous laws. This divergence is comparable with that of gases themselves when highly compressed or near their liquefying point.

units. Thus a dilute solution of NaCl in water behaves as if it contains nearly twice as many ultimate particles as it does molecules. From this it is assumed that most of the molecules NaCl must be split up into their ions Na and Cl.[1] Evidence of complete ionisation is forthcoming only when the solution of sodium chloride is exceedingly dilute, *e.g.* contains $\frac{1}{10000}$ of a gramme molecule per litre, *i.e.* has a strength of 0·000585 per cent. Increasing dilution gives increasing ionisation, and it is assumed that at infinite dilution ionisation would be complete. Solutions of moderate strength, such as those containing 1 gramme equivalent per litre (5·85 per cent. NaCl), behave as if a portion of the molecules were ionised and a portion were present as ordinary molecules.

This ionisation occurs with all electrolytes, and approaches completeness more nearly with substances whose solutions are good conductors than with those which are indifferent conductors. Certain substances give evidence of being split up into more than two ions. Thus the osmotic pressure, depression of freezing-point, etc., of dilute barium chloride solution point to the salt being split up into the three ions Ba, Cl, Cl; similarly, according to its dilution, sulphuric acid may be split up into the two ions H and HSO_4, or into the three ions H, H, and SO_4.

It is evident that if the ions Na and Cl exist free in a solution of NaCl, they must be endowed with properties very different from those of the elements sodium and chlorine in ponderable masses as we know them. Certainly a solution of sodium chloride gives no indication of containing free chlorine, while free metallic sodium could

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[1] An ion is not necessarily an atom; thus the ions of potassium nitrate are K and NO_3.

not exist as such for a moment in the presence of a large quantity of water.

Still more conclusive is the consideration that the severing of NaCl into Na and Cl needs the expenditure of 97·69 Cal. per gramme molecule, and no such energy is impressed on it by the mere act of dissolving the salt in water. Therefore it is clearly impossible to regard the ions Na and Cl as free sodium and chlorine in the ordinary sense. To meet these objections to the belief in the existence of free ions, it is assumed that each ion carries a charge of electricity, the cations a charge of positive electricity and the anions one of negative electricity, and that their properties are profoundly modified by the possession of these charges, the total number and amount of which are equal and opposite and counterbalance each other, so that the solution as a whole gives no indication of possessing any charge at all.

This conception is a mode of thought and not an objective reality, and may eventually be replaced by a hypothesis involving fewer and less sweeping assumptions.

Further, it is believed that these ions in solutions of moderate concentration are at times free, and at times united to form an ordinary molecule, and that they move through the solution forming and breaking unions with ions of the opposite kind. It is also considered that each kind of ion moves at its own pace, and that an ion may remain free in its solution for an appreciable time.

The mechanism of electrolysis, according to this theory, is as follows:—On a current being passed through an electrolyte, such as the aqueous solution of a metallic salt between two unattackable electrodes, the cations carrying positive charges flow to the cathode and there give up their charges, becoming *ipso facto* ordinary molecules and appearing at the surface of the cathode as metal, or as the products of the action of this metal on water, viz. hydrogen and a metallic hydroxide. Similarly, the anions carrying negative charges flow to the anode and there give up their charges, appearing as ordinary molecules of the same composition as the ions themselves, or as the products of their action on water. The function of the current is to neutralise the charges thus given up at each electrode, and to allow the ions to assume the ordinary molecular condition. The conception of the existence of an ion as carrying a charge of electricity, and of the transference of electricity through an electrolyte being dependent on the flow of charged ions, has been extended to form a theory of the primary cell. Thus, in a Daniell cell, consisting of zinc in zinc sulphate and copper in copper sulphate, it is considered that the zinc possesses a "dissolution pressure" whereby its molecules tend to become ions in the solution of zinc sulphate with which it is in contact. In order to attain this ionised state an equal number of ions already existing in the solution must be changed from the ionised to the molecular state. Such a transformation happens to the copper ions in the other compartment of the cell, because the dissolution pressure of the zinc is greater than that of the copper. The zinc ions require to be positively charged, and equally the copper ions in the act of becoming ordinary molecules give up their positive charges, which are transmitted through the exterior circuit to the zinc plate. The difference between the dissolution pressures of copper and zinc is a measure of the voltage of the cell.

In the foregoing sketch I have endeavoured to state fairly and clearly the chief ideas embodied in the ionic theory of electrolysis. The theory at present serves to correlate facts rather than to explain the real mechanism of electrolysis. As now expounded it is not completely convincing, involving as it does a good many assumptions not very probable nor even wholly consonant with experiment. Fortunately all practical applications of electrolysis can be satisfactorily considered without having recourse to this hypothesis, and the practician who is equipped with a sound knowledge of the principles of chemistry and electricity can grapple successfully with any problem in electrolysis which is likely to present itself, irrespective of the precise explanation which may be at the moment most agreeable with the teachings of the ionic hypothesis.

METHOD OF CALCULATING OUTPUT IN ELECTROLYTIC PROCESSES

In the foregoing sections sufficient has been said to give some idea of the nature of electrolytic changes, the mechanism by which they are possibly brought about, and the quantitative relations of the electrical energy used and the products obtained. This last-named subject has only been touched on lightly and incidentally, merely as far as was necessary to illustrate the other two, and seeing that it is all-important in practical work, a special section may conveniently be devoted to its consideration, even though it involve occasional repetition of what has already been said.

The best way to understand the quantitative relations 24 of any process of electrolysis is to consider the process on the basis of the amount of energy which it requires. To bring about a given chemical change which is endothermic the expenditure of a definite quantity of energy is requisite, and the electrical energy supplied to cause this change by electrolysis must be equal to or greater than this quantity. It matters not what cunning arrangement for conducting the electrolysis may be devised, this fundamental law cannot be circumvented.

Thus, if a process be schemed for the electrolytic decomposition of sodium chloride into sodium and chlorine, the amount of electrical energy which will be needed for the decomposition of 1 gramme molecule (58·5 grammes) is not smaller than that equivalent to 97·69 Cal., assuming this to be the heat of combination of sodium and chlorine. The fact that all electrolytic processes for the direct decomposition of sodium chloride require the salt to be fused, and are therefore carried out at a red heat, in no way invalidates the general truth of this statement. At a red heat the heat of combination of sodium and chlorine is not 97·69 Cal., but a smaller value, *e.g.* 88·21 Cal.[1] Accepting this value, it is certain that a quantity of electrical energy not smaller than 88·21 Cal., when translated from electrical into heat units, must be impressed on the salt kept just at its fusing-point by extraneous heat. The quantity needed may be larger than this for a number of reasons, which will become evident when this particular electrolytic process

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[1] This figure may be approximately arrived at by deducting from the heat of combination the quantity of heat needed to raise 58·5 grammes of salt from 15° C. to its melting-point, 772° C., taking the specific heat of salt as 0·214, and neglecting its latent heat of fusion, which is probably small.

and others cognate with it are discussed in their proper place, but it will certainly not be smaller unless the sensible heat supplied from without is capable of conversion in the decomposing cell into electrical energy, and of this we have no evidence. Now the unit of electrical energy is the joule, and is equal to 0·00024 Cal., *i.e.* 0·00024 kilo of water raised from 15° C. to 16° C.[1] Therefore the decomposition of 58·5 grammes of sodium chloride at its fusing-point into sodium and chlorine requires 88·21 Cal. = 367,542 joules. But according to Faraday's law (see p. 7) the isolation by electrolysis of a chemical equivalent of any substance requires the passage of the same number of units of current. For 1 gramme equivalent of any substance this number of units of current is 96,540 coulombs. Now 1 unit of electrical energy may be expressed as the product of 1 unit of electrical quantity × by 1 unit of electrical pressure, *i.e.* 1 joule = 1 coulomb × 1 volt.

In order to represent 367,542 joules, 96,540 coulombs must be delivered at a certain electrical pressure,

$$\begin{aligned} \textit{i.e.}\ 367{,}542 &= 96{,}540 \times x \text{ volts.} \\ \therefore\quad x &= 3{\cdot}807 \text{ volts.} \end{aligned}$$

This means that, accepting the heat of formation of sodium chloride at its fusing-point as 88·21 Cal. and assuming the truth of Faraday's law, the minimum

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[1] Formerly the calorie was taken to be the quantity of heat needed to raise the temperature of 1 kilo of water from 0° C. to 1° C., but of late years it has been found convenient to choose a somewhat higher temperature, because the specific heat of water exhibits certain irregularities near its point of maximum density (4° C.) and its freezing-point (0° C.), and first becomes approximately constant for a considerable range of temperature at 15° C. The unit, like most others, is essentially arbitrary, and the precise value chosen is merely a matter of convenience and convention.

voltage necessary to effect the electrolytic decomposition of fused sodium chloride into sodium and chlorine is 3·807 volts. It means neither more nor less than this. It does not mean that sodium chloride at any temperature requires this voltage, and it does mean that no smaller voltage will decompose sodium chloride under the conditions given. Such steadfast data are continually available in electrolytic work, and in those cases where they appear not available it is our knowledge either of the precise heat of combination of the constituents of the electrolyte at the temperature chosen or of the precise products obtained by electrolysis which is at fault, and not the truth of the doctrine of the conservation of energy or of Faraday's law.

Thus in practice he who is firmly grounded in these primary principles can deal with each particular case as it arises, not experimenting blindly, but with certain definite and exact generalisations to guide him.

It is evident from this that the output of any given substance for a given current can be calculated from the single datum, *One chemical equivalent of any electrolyte expressed in grammes requires the passage of* 96,540 *coulombs for its liberation or decomposition*, and that the critical pressure for the decomposition of any given electrolyte can be calculated from the single datum, *The energy of combination expressed in joules of* 1 *gramme equivalent of any electrolyte, divided by* 96,540 *coulombs, equals the minimum pressure in volts necessary to bring about the electrolysis.*

It is unnecessary to give an elaborate table of the chemical equivalents of a long list of substances, together with their calculated output per coulomb or per ampere second (the same thing as a coulomb) or their ampere hour (a convenient commercial unit). It will suffice to set down a few both to give some idea of the order of magnitude of the quantities obtained and for convenience of reference to those numbers which are constantly occurring in electro-chemical work.

Element.	Atomic weight.	Valency.	Equivalent weight.	Output per coulomb, *i.e.* per *ampere second.* Milli-grammes.	Output per 3,600 coulombs, *i.e.* per *ampere hour.* Grammes.
Aluminium (Al) .	27	3	9	0·093	0·3356
Chlorine (Cl) . .	35·5	1	35·5	0·368	1·3237
Copper (Cu) (Cupric) .	63·5	2	31·75	0·329	1·1837
„ „ (Cuprous)	63·5	1	63·5	0·658	2·3674
Hydrogen (H) . .	1	1	1	0·0103584	0·03729
Iron (Fe) (Ferrous) .	56	2	28	0·290	1·0441
Lead (Pb) (as cation) .	207	2	103·5	1·072	3·8595
„ „ (as anion) .	207	4	51·75	0·536	1·9297
Nickel (Ni) . . .	58·5	2	29·25	0·303	1·0907
Oxygen (O) . . .	16	2	8	0·083	0·2983
Silver (Ag) . . .	108	1	108	1·119	4·0273
Sodium (Na) . .	23	1	23	0·238	0·8577
Zinc (Zn) . . .	65	2	32·5	0·337	1·2119

THE CONVERSION OF ELECTRICAL ENERGY INTO HEAT FOR ELECTRO-CHEMICAL PROCESSES

Up to this point the electro-chemical principles which have been discussed are those which relate to electrolysis. There is another method of applying electrical energy to chemical and metallurgical processes, and that is by direct conversion into heat. In an electrolytic operation every unit of heat appearing means waste, for in one working ideally all energy impressed on the electrolyte should appear in the form of chemical energy of the products of electrolysis. Where heating alone is to be accomplished any electrolytic decomposition means waste; a complete conversion of electrical energy into heat in the vessel in which the process is to be carried out should be achieved. There are, however, certain electro-chemical processes in which electrical energy is used both for heating and for effecting electrolytic resolution; the most noteworthy instance is in the manufacture of aluminium (*q.v.*) by the electrolysis of alumina dissolved in a double fluoride of aluminium and sodium. The bath is not only decomposed electrolytically, but is also kept fused by heat obtained at the expense of electrical energy passing between the electrodes. The principles which have been laid down for electrolysis without heating and those about to be enunciated for heating without electrolysis may be applied to these mixed cases; any special considerations for particular instances will be discussed under the individual heads of processes of this type.

The principles of electrical heating as far as they concern the electro-chemist may be very briefly dealt with.

The passage of a current of electricity through a conductor of the metallic class is always attended by the production of heat. When the conductor is of large section and of a material which conducts well, the quantity of heat produced is small compared with the total quantity of energy transmitted; when the conductor is of small section and conducts badly, the quantity of heat produced is relatively great. These qualitative statements are made quantitative by saying that the heat produced by the passage of electrical energy through a metallic conductor is measured by the drop of voltage from one end of the conductor to the other, multiplied by the total current passing. Thus if a current of 1,000 amperes be passed through a conductor, and there is a drop of voltage from one end of the conductor to the other of 50 volts, energy is being expended at the rate of 50,000 watts, *i.e.* 50,000 joules, per second. Therefore in one second the number of units of heat generated in that conductor will be $50{,}000 \times \cdot 00024$ Cal. $=12$ Cal.

If the conductor be of small mass, and if the specific heat of the conductor be also small, the temperature of the conductor will be greatly raised. Further, if the conductor be enveloped in a sheath which will not conduct heat, every unit of heat generated is retained, and the temperature of the conductor is a direct measure of the energy expended. Under theoretical conditions, therefore, any conductor contained in a sheath perfectly non-conducting for heat and conveying any current however small, will ultimately attain an infinite temperature. In practice this goal is approached by encasing the conductor in a mass of material as nearly non-conducting for heat, as possible, and passing through it so large a current as to generate heat more rapidly than the heat can be conveyed away until the temperature (heat potential) becomes extremely high.

These requirements are fulfilled by the apparatus known as the electric furnace. Two forms are commonly used. In one an arc is produced in the midst of the mass to be heated, and in the other a current is passed through a continuous core of refractory material (usually a thin rod of carbon) which has a small section, a small heat capacity, and a high electrical resistance. When a large current is passed through such a core, its temperature rises until it becomes so high that losses by radiation and conduction balance the energy impressed upon it. But besides this limiting condition there may be in electric furnace operations a direct demand on the electrical energy supplied in the shape of energy needed to effect some chemical change in the mass to be heated. Thus if a mixture of lime and coke is to be converted into calcium carbide (*q.v.*), energy is required to bring about the formation of calcium carbide irrespective of that necessary to heat the charge. Therefore it is clear that every electro-chemical furnace process must be considered individually, and that no general principles can be usefully laid down other than that already enunciated, viz. that the total heating effect of a current passing through a given conductor is measured by the current and the drop of voltage between the ends of the conductor.

RELATIVE VALUE OF ELECTRO-CHEMICAL PROCESSES AND PURELY CHEMICAL PROCESSES

From the point of view of the practical worker, choice between an electro-chemical process and one which does not depend on the application of electrical energy from without depends solely on the relative monetary advantages of the two methods.

In almost all cases a given product which can be obtained by electrolytic means can be prepared equally well by purely chemical methods.

For example, pure copper can be prepared by precipitation of cuprous oxide with glucose in alkaline solution and reduction of the cuprous oxide in hydrogen, as well as by the electrolysis of copper sulphate. Pure zinc can be prepared by fractional distillation of the commercial metal *in vacuo* at least as well as it can be obtained by any electrolytic process.

Chlorine and caustic soda have been made for nearly a century successfully, on a large scale and of excellent quality, without having recourse to electrical processes. Sodium, although originally prepared by the electrolysis of caustic soda, has been manufactured for more than fifty years by reduction of sodium carbonate with carbon; quite recently the electrolytic method has again been used, and is now the only remunerative process. On the other hand, there are certain products which have only come into existence (actual or industrial) since electrical methods have been developed. The most noteworthy instance of such a product is silicon carbide (carborundum) (*q.v.*). This body, as far as we know, does not exist naturally in the earth's crust, and has certainly not been prepared by ordinary chemical methods. It has been created by the electric furnace, and there is no question as to what process must be used in preparing it. Calcium carbide (*q.v.*) stands on a similar, but not identical, footing. It can be prepared by chemical methods, but they are commercially impracticable, whereas it is already made on a large scale at a low cost by an electrical process. In like manner persulphates, which find a somewhat limited use as oxidising agents, can, as far as we know, be prepared only by electrolytic means.

In all such cases there is no difficulty in choosing a process; the selection is made on the principle of Hobson's choice. But in many other instances several possible processes are available; adoption of one rather than another depends on many considerations which must be taken into account in each individual case. Here it will suffice to indicate the chief conditions which make an electrical process preferable to a chemical process having the same product, or *vice versâ*.

When these are thoroughly understood, it is possible to decide what method should be adopted under any given local circumstances. The following generalisations may be found of utility.

When an operation requires a large quantity of heat at a temperature not exceeding 2,000° C. = 3,632° F., there is strong *primâ facie* ground for choosing a chemical rather than an electrical method. This is because heat obtained from electrical energy is greatly more costly unit for unit than heat obtained directly by combustion. Electrical energy, if obtained from the heat energy of coal through the agency of the intermediaries —boiler, engine and dynamo—does not represent more than one-tenth of the energy given out by the original combustion of the fuel under the boiler. Its costliness in money as distinct from energy is higher still, because an expensive plant, representing heavy interest and upkeep charges, is required for the conversion of heat energy into electrical energy. Where water power is available, these charges still make electrical energy much dearer than heat energy directly obtained by the combustion of fuel. Thus, the energy from a water power represented by 1 H.P. acting for a year of 365 days, each of 24 hours, costs in interest and maintenance not less than £2 under the most favourable condition. One H.P. year = 5,646·2 Cal. = 705·8 kilos of coal of calorific value 8,000, which, at 10*s*. per ton, costs 7*s*. Competition is therefore out of the question if the object to be obtained is merely heating.

But when the heating has to be conducted by transmission through a refractory envelope, as in the reduction and distillation of zinc, the aspect of affairs is altogether changed. Much loss of heat takes place in such transmission, and the cost of renewal of the envelope, *e.g.* a fireclay retort, is extremely heavy. Heat can be generated electrically in the interior of a refractory vessel, and loss of heat and cost of renewal of the receptacle can be reduced to a small value. Thus the more costly form of heat (electrical energy) may enter into successful competition with the intrinsically cheaper method of direct heating by the combustion of fuel.

Again, when the temperature necessary for a given operation exceeds 2,000° C. = 3,632° F., the electrical method stands unrivalled, because no other means exists of obtaining so high a temperature. Into a box made of refractory and non-conducting material electrical energy can be poured, so that the attainable temperature is limited only by the stability of the materials composing the hearth and the conductors. All known substances can be fused, and in most cases volatilised, under these conditions, and operations needing a temperature ranging between 2,000° C. = 3,632° F. and 3,500° C. = 6,332° F. can be performed thus and only thus. The ultimate reason for the impossibility of attaining these high temperatures by chemical means is that all reactions which generate heat are annulled at these temperatures, only those reactions which absorb heat occurring. Hydrogen and oxygen co-exist at 2,000° C. without uniting, and carbides, *e.g.* those of the type of acetylene, which, it is reasonable to suppose, are endothermic compounds, are freely produced. In fact, at such temperatures certain borides, carbides and silicides are almost the only substances which are stable. Thus, all ordinary fuel ceases to act as such, and the electric furnace is the only effective apparatus.

When an operation requires the application of energy in the form of heat, and the product is liable to deterioration by contact with fuel and the substances generated by its combustion, electrical methods of heating possess an advantage over chemical methods which may more than compensate for their greater cost per unit of heat.

For example, the fusion of steel of the highest grade in an ordinary furnace is attended by some risk of change by oxidation or by absorption of sulphur from the fuel; fusion by the direct application of electrical energy could evidently be effected without incurring such risks.

Regarding processes which can be carried out almost as well chemically or metallurgically as electrolytically, such as the refining of copper, the precipitation of gold from cyanide solutions, the parting of gold and silver alloys, no better or more informative generalisation can be made than that given at the head of this section, viz. that the whole matter is one of cost. For a product of equal quality, electrolytic copper is cheaper than copper refined by the ordinary methods of metallurgy; therefore the greater part of the industry is already electrolytic. But lead of surpassing purity can be prepared quite as easily by metallurgical as by electrolytic methods; therefore no displacement of existing processes is probable. Silver and gold can be separated effectively by parting with nitric acid or sulphuric acid, but electrolytic "parting" is believed to be somewhat cheaper, and is accordingly making headway. Where fuel is dear, water power abundant, raw materials weighty but close at hand, and the finished material relatively small in weight and of relatively high price, it may be feasible to carry out an electrolytic or electrometallurgical operation rather than attempt one requiring either fuel brought to the distant seat of the works or raw materials conveyed to a remote centre where fuel is cheap.

To sum up, there is no magic in electrical or electrolytic methods. With a few exceptions they are simply alternative processes, and choice between them and chemical or metallurgical operations capable of arriving at the same goal can be made only when all the circumstances proper to each case are competently considered and their influence computed.

SECTION II

Winning and Refining of Metals by Electrolytic Means in Aqueous Solution

COPPER

THE ELECTROLYTIC REFINING OF COPPER

THIS is the largest of all electrolytic industries. It is practised in this country and on the Continent, but the place of its greatest development is the United States; the output there is said to be at least ten times that of all European factories put together. The electrolytic winning of copper, as distinct from its refining, is even now scarcely beyond the experimental stage; an account of the most hopeful processes will be found in a separate section.

PRINCIPLES OF THE ELECTROLYTIC REFINING OF COPPER

The copper to be refined is already as metal, although the metal is crude, containing not more than 98 per cent. of Cu, and sometimes a smaller percentage. The rationale of electrolytic refining is to transfer this copper, by the selective action of the current, from the anode to the cathode and to leave the impurities behind as a sludge or dissolved in the electrolyte—preferably in the sludge. On first principles it is evident that this mere transference of copper should require no expenditure of energy, because metallic copper is both the raw material and the product; the energy needed to precipitate it from its solution is precisely balanced by the energy set free by its dissolution. This theoretical deduction is entirely consonant with experiment, but there are limitations—commercial and industrial rather than technical—which prevent the full advantage of this economy of energy being reaped in practice. They will be discussed in the ensuing section.

The only other principles needing mention are that the electrolyte should be maintained sufficiently rich in copper to ensure the presence of an ample supply of copper ions at the cathode, so that the electrical energy passing may not be expended on any work but that of depositing the copper, that the copper should be deposited in a coherent and manageable form, and that the conditions of electrolysis should be so adjusted that copper and copper only is the product at the cathode.

THE PRACTICE OF ELECTROLYTIC COPPER REFINING

Various methods of carrying out the process of electrolytic copper refining are in use. In the most usual arrangement the anodes are plates of crude copper, the cathodes are thin sheets of pure electrolytic copper, and the electrolyte is a solution of copper sulphate acidulated with sulphuric acid.

The details of the process, such as the composition of the crude copper, the strength and acidity of the electrolyte and the arrangement of the electrodes, will differ in different works according to local conditions, but a general statement may usefully be made before proceeding to the description of any particular works.

In this typical works the anodes are of crude copper similar in grade to the commercial product known as Chili bars, and having a composition such as that given below:—

	Per cent.
Cu	98·60
As	0·80
Sb	0·10
Pb	0·10
Bi	0·05
Fe	0·10
Ni	0·10
S	0·10
Ag	0·05
	100·00

This metal is cast into plates about 3 feet long, 18 inches wide, and $\frac{3}{4}$ inch thick. The cathodes are of similar length and width, but about $\frac{1}{20}$ inch in thickness. The anodes and cathodes are suspended opposite to each other at a distance of 2 inches and connected in the manner shown diagrammatically in the accompanying sketches.

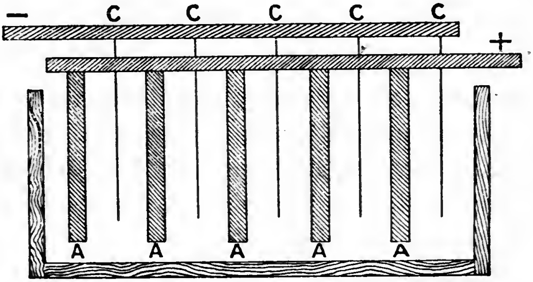

Fig. 1.

Fig. 1 shows the length of the vat (which is of wood, lined with lead), and Fig. 2 shows the top of the vat in plan. The anodes, marked A, are suspended from the positive lead, and the cathodes, C, from the negative. The vats are arranged in series, as is shown in Fig. 3, and for convenience the leads are coupled so that the same lead serves for the anodes of one vat and for the cathodes of the next; by this arrangement no crossing of connections from side to side of the row of vats is necessary.

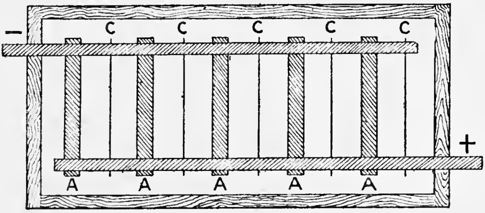

Fig. 2.

The drop of pressure in each vat is about 0·2 volt, and the current passing is such as to be equivalent to about 10 amperes per square foot. The farther side of the end anode is not faced by a cathode, and so its surface is not fully effective. Assuming that it has about half the efficiency of a surface directly opposed to a cathode, and that the full surface of the remaining four anodes in each vat is utilised, the total available anode surface will be 4 (3 × 1·5) 2 + 3 × 1·5 square feet = 40·5 square feet (neglecting the area of the edges of the anodes). Each vat will therefore require 405 amperes, and, assuming

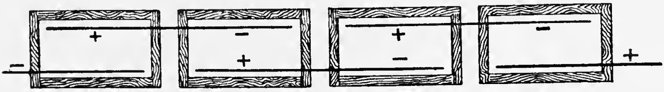

Fig. 3.

theoretical current efficiency and that 1·1827 grammes of copper is deposited by one ampere in one hour, will deposit 479 grammes of copper per hour, or in the 24 hours very approximately 25¼ pounds. This simple calculation shows how small is the yield of electrolytic copper per unit of plant, and makes clear that in a works of any magnitude the vats must be very numerous. Great increase of the size of the vats or of the number of plates which they contain is not feasible for practical reasons, such as the difficulty of maintaining a uniform current density over very large surfaces and the difficulty of ensuring a rapid and thorough circulation of the electrolyte throughout a large vat. It is also obvious that if a larger current density can be employed, a proportionally larger output per unit of area of the electrodes will be obtained. In practice 10 amperes per square foot is not usually exceeded (though it is said that a current density of nearly 20 amperes per square foot has been successfully used in the United States), as it is found that with a high current density the copper tends to be deposited in warty and cauliflower-like masses, to be of inferior purity, of feeble coherence and to tend to grow across to the anode and form a short circuit.

As regards the consumption of energy for the deposition of this copper, it is evidently directly proportional to the voltage necessary for each bath. In theory with an infinite electrode surface and an infinitely small internal resistance this is *nil*. In practice this cannot be approached because the current density would thereby be so far reduced that the output of copper per unit of plant would be unduly small. The interest on the capital represented by a huge plant would be too heavy a charge, and yet more the interest on the capital represented by the value of the copper temporarily locked up as anodes would be prohibitorily great. Moreover, seeing that the price of copper fluctuates considerably, every electrolytic copper refiner would be in the position of an enforced large holder of a gambling stock which he could handle more slowly and with more restrictions than those affecting other holders; thus he would always be financially at the mercy of a less burdened operator.

Therefore a very appreciable voltage must be used to get a reasonable output on a given stock of copper, *i.e.* to obtain a fairly rapid turnover. 0·2 volt is not a high estimate of what the voltage would be in our typical works. Accepting this, the watts necessary for each vat are $405 \times 0{\cdot}2 = 81$ watts, *i.e.* $\frac{81}{746} = 0{\cdot}109$ H.P. Each horse power hour in a set of vats identical with that which has been described would deposit 4,394 grammes of copper, *i.e.* a horse power acting for 24 hours would deposit 232 pounds of copper. A plant of 1,000 H.P. would deposit 232,000 pounds of copper per 24 hours, or 37,803 tons per year of 365 days of 24 hours each. With a drop of voltage for each vat of 0·5 volt, which approximates more closely to what would be expended in practice, all the above figures representing output must be multiplied by $\frac{2}{5}$, *i.e.* the output per horse power for 24 hours would be 93 pounds, and for 1,000 H.P. for a year of 365 days 15,121 tons.

Even this reduced amount corresponds with a turnover of £750,000 worth of copper per year; at a moderate estimate the weight of copper permanently present in each vat will be one-twelfth of the output per year of that vat, so that the cost of the stock of copper alone which is necessary for carrying on the business is £62,500, representing an interest charge of £3,125. It is clear from this that any saving in the stock of copper relative to the output will be worth achieving, even if the cost of the energy expended be somewhat increased. In other words, in order to get the maximum output per vat it will pay to drive each vat at a sufficiently high voltage to obtain the maximum current density which will still permit of the deposition of coherent copper of good quality. Where power is cheap a considerable waste of energy can be permitted with pecuniary profit in order to make the turnover large compared with the stock of copper permanently in the vats.

In our typical works the electrolyte will be circulated throughout the vats so as to replace that part of the solution which has passed over the surface of the cathodes and has been thereby impoverished in copper, with liquor which has passed over the surface of the anodes and has been enriched in copper. Any stagnation would result in lack of copper at the cathodes and separation of hydrogen and possibly of metallic impurities together with the copper, and would also cause a superfluity of copper sulphate at the anodes, upon which the salt would crystallise, hindering their dissolution.

At intervals the electrolyte will become inconveniently impure, and will have to be purified or replaced by fresh sulphate of copper. Save for this the work will proceed continuously, crude copper being used up and pure copper obtained in a merchantable form.

The black mud which comes from the anodes, and represents the insoluble impurities of the crude copper, contains gold and silver, and is worked up for the recovery of these metals.

Such being a general outline of the essential parts of an electrolytic copper refinery and of the process of refining, the various portions of the plant may be considered in detail.

SOURCE OF POWER

Water or steam power is used according to the situation of the works. The former is less advantageous than would appear at first sight, because its cost per unit of energy is by no means negligible, being represented by the interest on the plant and the upkeep of the plant; the former is a heavy item. In general, water power is utilised by choosing a river (which may have to be impounded so as to equalize its flow) at a point where its bed makes a considerable fall, and conveying the water through an artificial channel to turbines which are coupled direct to dynamos. The construction of a reservoir, channel, turbine pit, and tail race involves a large expenditure of money, and the turbines and dynamos are costly machines. The precise capital sum expended per horse power will differ in each case, and its consideration is a purely engineering matter. It is sufficient to say here that the capital is so large that the lowest probable estimate which has been arrived at for the cost of the power obtained is £2 10*s.* per horse power year of 365 days of 24 hours each, *i.e.* 0·0685*d.* per horse power hour. Under less favourable conditions the cost would probably be double this, *i.e.* £5 per horse power year or 0·137*d.* per horse power hour. The lowest probable cost of steam power is 0·25*d.* per horse power hour, or £9 16*s.* per horse power year with fuel at 8*s.* per ton, and under less favourable conditions it may reach £15 per horse power year or 0·411*d.* per horse power hour. In each case it is assumed that the horse power used is large, 1,000 I.H.P. or more. The difference in favour of water power is considerable, but its monetary advantage is smaller than would be supposed, because the cost of the energy required in copper refining is not the chief item of expenditure, as is evident from the appended table:—

COST OF ENERGY IN COPPER REFINING

	Cost per horse power hour.	Cost per horse power year.	Cost per ton of copper refined.
Water power	0·0685*d.* 0·137*d.*	£2 10*s.* £5 0*s.*	3*s.* 4*d.* 6*s.* 8*d.*
Steam power	0·25*d.* 0·411*d.*	£9 16*s.* £15 0*s.*	12*s.* 0*d.* 20*s.* 0*d.*

Even the highest of these sums is not much more than 1% on the selling price of the pure metal.

It is in processes such as the manufacture of calcium carbide (*q.v.*), in which the quantity of energy expended is extremely large, that its cost becomes great relatively to the total cost of working, and the economy effected by the use of water power becomes sensible.

The power, however obtained, is used to drive dynamos which in modern installations are generally coupled direct to the turbines or steam engines. For practical reasons it would be inconvenient to work with a single large engine and dynamo, because a breakdown would necessitate the stoppage of the whole works. Therefore a unit of 200–300 H.P. is chosen, and each dynamo coupled direct will yield 130–200 kilo watts. These may be delivered at any convenient pressure, say 100 volts; the current will therefore be 1,300–2,000 amperes. The voltage for which the dynamos are wound of course depends on the number of vats it is proposed to run in series and the voltage necessary for each. These will vary with each installation, and it can only be said that a fairly high voltage is desirable as diminishing the requisite cross-section, and therefore cost of the leads, while any very high voltage should be avoided as likely to cause loss by leakage from bare conductors constantly liable to be accidentally wetted from the baths.

RAW MATERIAL

In all cases the raw material is crude copper containing about 98 per cent. of Cu. It will vary in composition according to the character of the ore and the method of dry refining adopted. The following figures will indicate the nature and extent of these variations :—

	I.	II.	III.	IV.	V.	VI.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Cu . . .	96·35	97·19	98·32	98·53	94·06	98·24
As . . .	0·08	2·68	0·19	0·62	4·36	0·94
Sb . . .	0·10	0·01	0·06	—	0·57	0·40
Sn . . .	0·22	—	Trace	—	—	—
Pb . . .	1·19	—	0·16	—	0·13	0·02
Bi . . .	0·05	0·08	0·07	0·06	0·02	0·04
Fe . . .	0·61	0·02	0·01	0·01	0·02	Trace
Ni . . .	—	0·02	0·25	0·14	0·37	0·28
S . . .	0·69	—	0·68	0·01	0·37	0·03
O and loss	0·71	—	0·26	0·63	0·10	0·05
	100·00	100·00	100·00	100·00	100·00	100·00

Besides these, the crude copper will contain a little silver and a much smaller quantity of gold, *e.g.* 30 ounces of silver and $\frac{1}{10}$ ounce of gold per ton. The value of these at 2*s.* and £3 15*s.* per ounce respectively is £3 7*s.* 6*d.*

Before electrolytic refining had become as well established an industry as it is to-day, copper containing these small proportions of precious metals was sold simply as crude copper. Nowadays the natural effect of competition among refineries has caused sellers to exact a fair price for the gold and silver found by analysis to be present in the crude copper. It is thus particularly advantageous for a copper-smelting works to have its own electrolytic refinery.

It may be stated that in general it is not remunerative to refine very crude metal. It is better to bring it to a content of about 98 per cent. of Cu, because a cruder copper speedily causes the electrolyte to contain such large quantities of soluble impurities that the deposition of pure copper is hindered, and the electrolyte has to be renewed. The behaviour during refining of the various impurities commonly present in crude copper may be summarised thus:—

Using a copper anode in a solution of copper sulphate acid with sulphuric acid, silver and gold remain undissolved in the anode sludge as metals. Lead also remains as sulphate. Antimony, tin and bismuth dissolve partly to form unstable sulphates, from which oxides or basic sulphates are deposited on standing; the larger part, however, of each remains with the anode sludge. Arsenic, iron and nickel dissolve and are not redeposited; thus they contaminate the electrolyte, but do not contaminate the purified copper under ordinary working conditions. Cuprous oxide remains partly in the sludge and partly dissolves according to the acidity of the electrolyte. Its only evil effect is to neutralise a portion of the free sulphuric acid which is essential to clean working. Copper sulphide distributes itself similarly. Tellurium and selenium are sometimes found in the anode sludge, but their quantity is naturally small. It might be supposed from this that it would be possible to purify very crude copper by electrolysis, and, indeed, numerous attempts in this direction have been made. They have all failed, not because it is impossible to separate the bulk of the impurities and obtain a pure copper at a single operation, but because anodes of even a moderate crudeness are dissolved unevenly and wastefully, the electrolyte penetrating into the interior of the plate, causing local corrosion and eventually detaching portions of the anode, still rich in copper, bodily. Besides this, the electrolyte has to be purified or renewed more often than when working with a fairly pure raw material.

The composition of the anode sludge will evidently vary with the composition of the crude copper. Thus the various elaborate analyses which have been published from time to time are of purely local interest. It may be taken that an ordinary sample rich in silver will contain about 30 per cent. of copper (partly as oxide, antimoniate, sulphide, etc.), 30 per cent. of silver, and 30 per cent. of lead sulphate, oxides of antimony and tin, and the various small impurities, such as bismuth, sulphur, selenium, tellurium, and gold. The working up of the anode sludge will be dealt with elsewhere. The composition will vary enormously according to the richness of the alloy in silver (and gold), but in general it may be said that copper, silver, and lead are the three chief metals commonly present.

COMPOSITION OF THE ELECTROLYTE

In all cases the electrolyte consists of copper sulphate acid with sulphuric acid; a usual strength is 1½ pounds of crystallised copper sulphate and a ½ pound of sulphuric acid per gallon. Much mystery is sometimes made about the precise composition of the electrolyte, but the only principles to be observed are: (1) That there should be plenty of copper, short of saturating the solution and causing risk of crystallisation; (2) That there should be sufficient sulphuric acid to prevent the separation at the cathode of hydrated cupric oxide; (3) That the quantity of sulphuric acid should not be so great as to cause hydrogen instead of copper to be separated at the cathode.

These conditions are fulfilled within a fairly large range of composition, and thus secret recipes are of small importance. The electrolyte may be kept warm, *e.g.* at a temperature of 35° C. = 95° F., whereby circulation is aided and the use of a high current density with the production of sound coherent copper is facilitated.

ARRANGEMENT OF VATS

The vats themselves are of wood, strong, well-jointed and lined with pitch or sheet lead autogenously soldered. Like all tanks for chemical purposes, they should be arranged with a clear space round each, so that any leak may be at once detected and remedied. The vats are sometimes placed in steps in order that the electrolyte may flow from one to the other throughout the whole series, and be finally collected at the end of the series and returned to the beginning by the aid of a pump. The appended figure (Fig. 4) illustrates this method. The overflow from the vat A passes through the pipe E to the bottom of the vat B; in like manner the overflow from B passes through the pipe F to the bottom of the vat C.

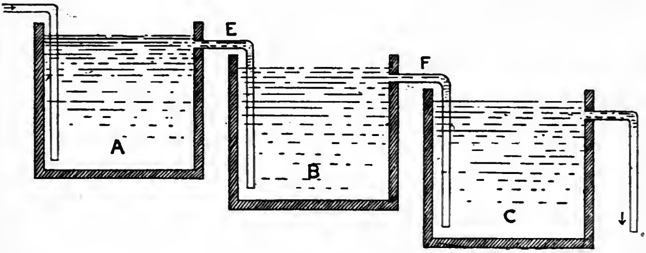

Fig. 4.

From the last vat of a series such as this the liquor flows into a collecting tank, whence it is pumped to an overhead distributing tank at the upper end of the series. When the tanks are not arranged terrace-wise, circulation is effected as it were in parallel instead of in series; Fig. 5 illustrates the method, A, B, and C being the tanks, D the supply pipe, and E the exit pipe; both are connected by branches to each vat.

It is evident that in strictness the circulation of the electrolyte should be so arranged that the liquor never passes from one vat to another when the two are coupled in series, but only when the two vats are in parallel. Otherwise a leakage of current along the stream of liquid flowing from vat to vat will occur. That it is possible to fulfil this condition is clear from the appended diagram (Fig. 6). In the figure only two plates (one anode and one cathode) are shown in each tank, for the sake of simplicity, but the same scheme holds good whatever the number of plates in each vat. In the group of vats shown there are sixteen individual vats arranged in groups of four coupled in parallel and four in series. The members of the group A, A, A, A, are in parallel; similarly the members of the group B, B, B, B, are in parallel; the same is true of C, C, C, C, and D, D, D, D. But the whole of the group A is in series with the remaining groups B, C, and D. Therefore, the electrolyte is

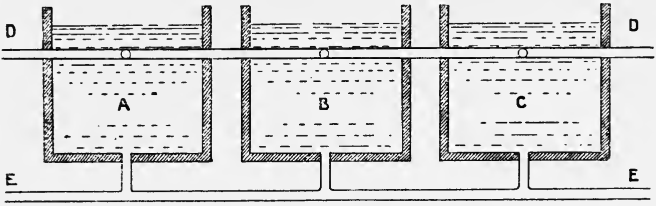

FIG. 5.

circulated through the group A by the connecting pipes *p*, *p*, *p*, *p*, and similarly through each of the three remaining groups. It does not, however, pass from group A to group B. A circuitous connection through the tank whence all the distributing pipes start may exist, but the resistance of each long narrow column of electrolyte would be so large that no appreciable leakage of current could occur. Though this is the best method of circulation, it does nct follow, however, that one in which the circulating pipe connects the tanks which are in series would necessarily fail.

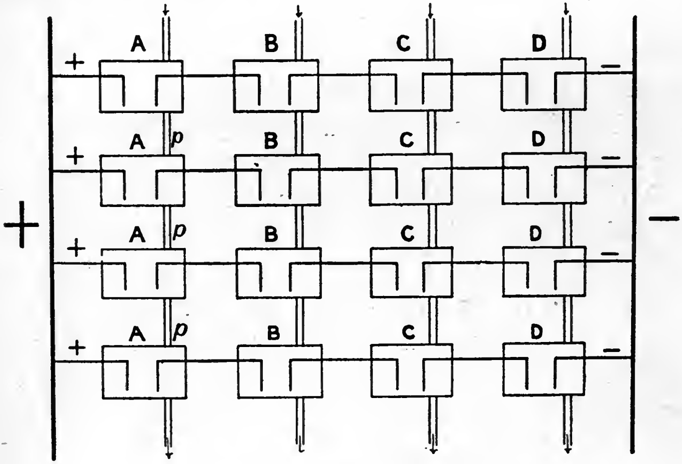

Fig. 6.

Leakage of current, though inevitable with such an arrangement as is shown in Fig. 7, would be small. Thus in the vat A the anode E has not only its legitimate cathode F opposed to it, but also the plate G of the vat B, because the connecting pipe between the vats makes A and B electrically one cell. This current passing from A to B through the connecting pipe will tend to make G a cathode and to deposit copper on it. But G is the anode of the vat B, and therefore loses copper instead of receiving it. This does not necessarily involve a loss of energy, save that fraction spent by the current traversing the connecting pipe of small sectional area and high resistance, but it does involve a smaller output of refined copper per unit of plant, and is to that extent objectionable.

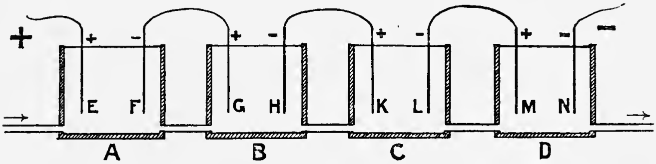

Fig. 7.

Devices for regulating the flow of the electrolyte, such as cocks on the pipes or screw clamps on rubber distributing tubes, are necessary, to ensure that every vat may receive its quota of liquid and that there shall be no risk of overflow. In like manner the exit tubes may take the form of syphons of sufficient bore to take the maximum quantity of liquid which is likely to flow into the vats, and at the same time to avoid any chance of the outflow being so free as to empty the vats. The principle of such arrangements may be gathered from Fig. 8,

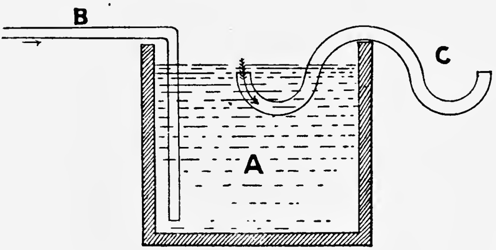

Fig. 8.

which illustrates a common laboratory apparatus for maintaining a constant circulation and a constant level of any liquid. The tank A is kept filled to the level shown by a constant or approximately constant small flow through the delivery tube B, any surplus beyond that level being carried off by the intermittent syphon C. This syphon has equal limbs, and the flow through it is therefore determined by the height of the liquid in the tank above the level of the end of the limb in the tank. Both its limbs being upturned, and its head *per se* being *nil*, the syphon is incapable of emptying itself, and remains full under all conditions, ready to come into action immediately the level in the tank rises. Nothing but a supply so inordinate as to be beyond the capacity of the syphon to carry off can derange the working of this device. An equivalent design is shown in Fig. 9. Here the syphon is dispensed with and an exit tube is provided, passing through the bottom of the tank, and of such width that with a very small head above its upper end it can discharge the whole of the liquid supplied

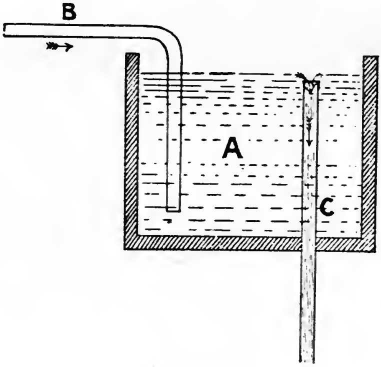

Fig. 9.

through the pipe B. It is obvious that many such contrivances can be adopted for or adapted to the circulation of an electrolyte; their use is not peculiar to the electrolytic refining of copper, but is a matter of ordinary engineering.

A method of circulating the electrolyte in copper refining has been worked out by Messrs. K. and H. Borchers, of Goslar, and may be briefly described. The circulation of liquid from vat to vat is abolished, and, as a substitute for this, the liquid in each vat is caused to circulate in such a way as not to stir up the sludge from the anodes and make the liquid muddy. The accompanying figure (Fig. 10) shows the chief features of the method.

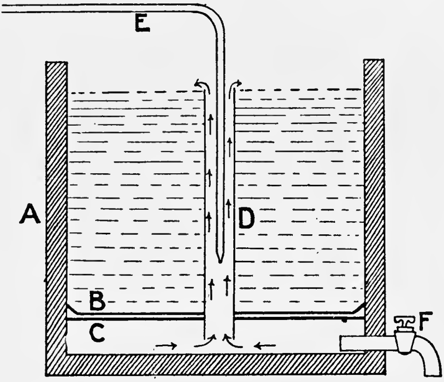

FIG. 10.

The vat A has a leaden pipe D passing down through the false bottom C, carrying the leaden tray B (which is ordinarily used in electrolytic refining vats for the collection of the anode sludge). Inside the pipe D is a narrow glass tube E, drawn out to a point at the lower end. Through this, air is blown and is distributed in fine bubbles, which, by giving an upward motion to the liquid in the leaden pipe, cause the liquid in the pipe to flow over at the upper end and to be replaced by fresh liquid from without at the lower end, thereby securing a gentle and continuous circulation of the liquid in the vat. The contents of the vat may be drawn off when the proportion of impurities becomes excessive, by the cock F, but during the whole time that the electrolyte remains usable the same liquid remains in any given tank, and there is no need to provide the ordinary system of circulation from tank to tank, which is comparatively complicated. It is claimed as a collateral advantage that the air blown in primarily to cause circulation acts in addition as an oxidising agent, and purifies the electrolyte to a great extent by precipitating iron and arsenic jointly as ferric arseniate. The correctness of this claim has been contested, and having regard to the fact that the electrolyte is kept fairly strongly acid, it is intrinsically improbable. The merit of the invention consists rather in the employment of air, which is a convenient agent for agitating the liquid in such a way as to induce circulation of the electrolyte without stirring up the anode sludge.

ARRANGEMENT OF THE ELECTRODES

Usually all the electrodes in a single vat are connected in parallel. There may be many electrodes in each vat, but electrically all the anodes constitute a single electrode, and all the cathodes another. This is the most sensible and effective method, but other systems have been put forward, concerning which a few words must be said. In these the object has been to do away with all connections except two for each vat. This can be easily arranged by relying on the moderately regular drop of voltage that occurs from one electrode to its fellow at the other end of a long vat. Plates placed between the anode and cathode in an electrolyte, and unconnected with either, will act as intermediate electrodes, the side of each facing the anode functioning as a cathode, and that facing the cathode as an anode. The simplest and at first glance the most plausible of these arrangements is shown in Fig. 11; it is due to Hayden, and is said to have been largely used in America and to be even now in use by the Baltimore Electrical Refining Company. The anode A is a plate of crude cast copper; the cathode B is a thin sheet of pure copper; the intermediate electrodes C, D, E, F, G are of crude cast copper.

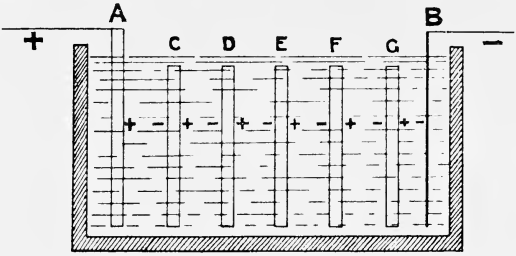

Fig. 11.

During the passage of a current from A to B, copper is dissolved from A and precipitated on the side of C facing A. At the same time, the other side of C (remote from A) acts as an anode, and copper is dissolved therefrom and deposited on the side of D facing C, which acts as a cathode. This proceeds throughout the series of immersed intermediate electrodes until B is reached; this receives copper from G and acts purely as a cathode. It will be seen that a continuation of this process will gradually convert these intermediate electrodes into plates of pure copper, and, supposing the change to have proceeded with perfect regularity, each intermediate plate will have become shifted towards the anode A by a distance equal to the thickness of an intermediate plate. Nothing could well be neater than this arrangement, provided everything would go smoothly. Many connections are abolished, the whole of the intermediate plates may be immersed so that there should be no waste anode ends to melt down and re-cast, and the need for separate cathodes of pure copper sheet is done away with. In practice, however, the disadvantages are numerous and serious. The dissolution of the intermediate electrodes does not proceed regularly. Cavities appear on the anode side and continue to form until they reach the pure copper already deposited on the cathode side, which is corroded in its turn. Complete clearance of the half of the plate acting as an anode does not always occur, and the resulting plate is still partly composed of crude copper, and has to be scrapped and melted down again for anode making.

There are several other systems using intermediate electrodes, differing chiefly in the arrangement of the plates, whether vertical or horizontal, with the cathode faces looking up or down, with a single plate for each intermediate electrode, or a composite plate made by attaching electrically a thin plate of some conducting material, *e.g.* pure copper, to one side of a thick plate of crude copper. They are all of doubtful utility. Their genesis is probably to be traced to the inherent belief in many minds that in some way the law of the conservation of energy may be evaded. Inventors proceeding on this principle are ignorant of the fact (stated above) that the mere transference of copper from anode to cathode requires no expenditure of energy; that the need for a considerable expenditure of energy in practice arises from the necessity of keeping the size of the plant and the stock of copper for a given output within reasonable limits. Such inventors have therefore striven to force an open door, and have gone the wrong way to work to do so. Assuming smooth-working conditions, the total energy necessary to refine a given weight of copper is the same whether the electrodes are arranged in the ordinary manner or are of the intermediate class. Choice between the two methods is to be arrived at purely from considerations of convenience, and experience has shown that the so-called "series" system, *i.e.* the method of using intermediate electrodes unconnected directly with the terminals of the dynamo, is not the most convenient.

MODE OF WORKING THE PROCESS

With an installation arranged on the lines given above, the running becomes a matter of simple routine. A switch-board in the works manager's office should enable him to read the current and voltage for each vat at pleasure. In large works an automatic recorder put into action periodically by a commutator driven by clock-work allows a regular record of the conditions obtaining in each vat throughout the twenty-four hours to be secured. The anodes and cathodes are hoisted into and out of the vats by overhead travelling cranes or some equivalent device. In short, the methods of handling the raw material and finished product are precisely those which would be adopted by any competent engineer to whom the matter was submitted. It is not proposed to give detailed descriptions of devices which are well known and in constant use in many industries; the whole plant is of a perfectly simple character, its only peculiarities arising from the large number of identical units necessary for an installation of any considerable size.

The circulation of the electrolyte may be effected by compressed air in an "acid egg," such as is used in vitriol making. This apparatus, which is designed to save moving parts in contact with corrosive liquids, consists essentially of a closed chamber with an exit pipe from its lowest part for the liquid to be conveyed, and another pipe in its upper part for the entrance of compressed air. The whole arrangement is represented diagrammatically in the annexed figure (Fig. 12), where A is the pressure vessel, B the inlet for compressed air, and C the exit for the liquid to be conveyed and distributed. The distribution may be most conveniently effected by gravitational flow from an overhead tank, and the acid egg or its equivalent used to return the electrolyte to this tank after its passage through the vats.

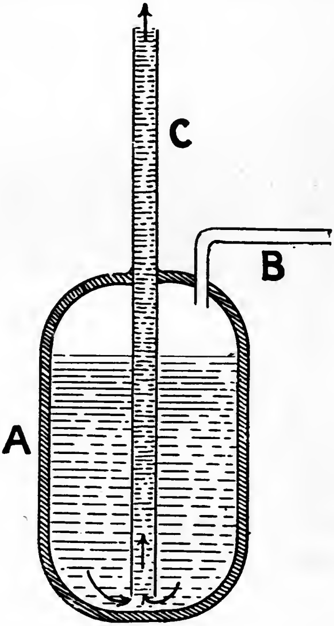

Fig. 12.

QUALITY OF THE PRODUCT

In all well-conducted electrolytic refineries the copper is very approximately chemically pure. The following analyses, by the author, of copper deposited by the Elmore process (see below) indicate the very small quantity of foreign matter present:—

	I.	II.
	Per cent.	Per cent.
Copper	99·961	99·938
Arsenic	*Nil*	*Nil*
Antimony	0·002	0·002
Tin	*Nil*	*Nil*
Lead	*Nil*	*Nil*
Bismuth	*Nil*	*Nil*
Iron	0·005	0·004
Nickel	*Nil*	*Nil*
Sulphur	Trace	Trace
Oxygen and loss . . .	0·032	0·056
	100·000	100·000

In this case the copper was deposited in the form in which it was to be used, viz. in that of a tube, and had not been subjected to any operation after it had left the depositing vat. Ordinary electrolytic copper, however, which is deposited in the form of plates, has to be fused and cast into ingots before it can be worked in any way, *e.g.* be drawn into wire for electrical purposes. In this fusion there is a risk of the metal absorbing oxygen (cuprous oxide being soluble in metallic copper), to its detriment in conductivity, and probably in tensile strength. This can be guarded against by conducting the fusion in a neutral or reducing atmosphere, and in practice some such precaution seems to be adopted, inasmuch as wire made of electrolytic copper is usually of excellent quality, having a conductivity nearly or quite as high as that of the best metal that can be prepared in the laboratory.

WORKING UP THE ANODE SLUDGE

A typical anode sludge contains (as stated above) copper and insoluble compounds thereof,[1] silver, and sulphate of lead as its principal ingredients, as well as small quantities of numerous impurities varying with the nature of the crude copper used as a raw material.

The chief valuable constituents are silver, together with a little gold. Their recovery may be effected, if they are present in sufficient quantity, by cupellation with lead, the silver and gold being left and parted by boiling with sulphuric acid or by electrolysis (see the section on the electrolytic refining of silver) in the ordinary way. Direct treatment of the sludge with boiling sulphuric acid is also practicable, the silver being converted into silver sulphate and dissolved by diluting the acid liquid with hot water, running off the silver sulphate solution from the lead sulphate, and precipitating the silver with copper. The gold and lead sulphate can be reduced by fusion with charcoal to an ingot of auriferous lead, which can then be cupelled, leaving the gold fairly pure. There is little else worth recovering, except perhaps selenium and tellurium, the trade in which is very small. Special wet methods, involving the reduction of these elements with sulphur dioxide,

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[1] It has lately been observed by F. Foerster and O. Liedel that the quantity of copper in anode sludge is smaller when working at a fairly high current density, *e.g.*, 10 amperes per sq. ft., than when using a current density of about 3 amperes per sq. ft. This condition is observed in modern refineries.

are necessary for their recovery, and the working up of the silver and gold would then be carried out on the lines given above. The processes of working up the anode sludge must obviously vary with the composition of the sludge, in its turn ultimately dependent on the character of the crude copper. A suitable method for any given case can be devised and worked out by any competent chemist. The question, though of great importance, presents no special electrolytic interest, and cannot be dealt with here.

The vast growth of the process of electrolytically refining copper in the United States may be understood from a very clear historical statement given in *The Mineral Industry* for 1896. The first plant of any considerable size was worked successfully in 1890 by the Baltimore Copper Company; a Hayden plant (*v.s.*) was then put up in 1891 by the Baltimore Electric Refining Company. The next year the capacity of this plant was doubled, and thus the great Baltimore Copper Works was developed, which now refines two-thirds of the Anaconda output, viz. about 100 tons daily. The world's production of electrolytic copper in 1892 was 32,000 tons, produced in 30 refineries.

In 1893 the production in the States alone was 37,500 tons, *i.e.* a quarter of the whole output in the States; in 1894 it was 57,500 tons, or one-third; in 1895, 87,000, or a half; in 1896, 124,000, or three-fifths; this amounts to one-third of the whole world's production. This very large quantity is turned out by eleven refineries, which jointly yield 14,000,000 ounces of silver and 68,000 ounces of gold per year.

The cost of refining has been considerably reduced of late years. It was 20 dollars (say £4) per ton in 1892, and about 8 dollars (£1 12*s.*) per ton in 1896. This sum is the manufacturing as distinct from the commercial cost, and does not include the expense of management. Comparing these figures with those given above for the cost of power, it will be seen that the latter, although a large item, is by no means the largest; interest on plant and that on copper locked up in the process are heavy charges. The cost in Europe is put down at 13–18 dollars per ton (£2 12*s.*–£3 12*s.*). The reason for this difference is that many of the European plants are antique and almost obsolete, and that many refiners in Europe buy copper ore or crude copper instead of themselves owning and working mines, and thus are charged with the miner's and smelter's profit. The largest works in Europe is that of Bolton & Sons, at Widnes, which turns out about 7,000 tons of copper per year. Elliott's Metal Company's works at Pembry, South Wales, is credited with 3,120 tons.

SPECIAL METHODS OF DEPOSITING REFINED COPPER

Owing to the fact that electrolytic copper is usually deposited in rough plates, and has to be fused before it can be formed into ingots suitable for rolling into rods (for drawing into wire) or plates, or for drawing into tubes, there is an extra cost incurred in thus bringing it into a workable form, and there is also a risk of contaminating it, especially with oxygen, during the process. Thus it comes about that any process capable of depositing the metal in the form in which it is to be used presents obvious advantages. It would seem at first sight simple to deposit copper in the most complicated shapes, and the fact that electrotyping (see below) was successfully practised long before copper refining became an industry lends colour to the view. But it is quite impracticable in the ordinary vat to cause the deposition of the metal to take place regularly enough to give a uniform thick coating on a mould even of a simple shape. Moreover, the metal as usually deposited is not particularly homogeneous, and the strength of a plate is by no means great. Special means must therefore be adopted to deposit the copper in a coherent form.

One of these methods is that devised by Elmore. Crude copper of the grade of Chili bars is granulated and placed on trays at the bottom of a vat, where it serves as an anode. The electrolyte is a solution of copper sulphate acidulated with sulphuric acid. The cathode is a roller of metal, or wood coated with plumbago so as to be conductive; this roller must not, however, be so perfectly conductive as to allow the copper deposited on it to adhere, as the copper must afterwards be stripped from it. This roller revolves in trunnions, which also serve to convey current to it. On a carriage like that of a screw-cutting lathe is mounted a rod tipped with agate, which is pressed against the surface of the roller and traverses its length, being automatically reversed when it comes to the end of the roller and sent back again. By this means the copper, as it is deposited, is subjected to a continuous burnishing action, and small rugosities are planished down. If once a visible excrescence forms, it is almost impossible to prevent its growing, because *ipso facto* it increases the current density at that point; the burnisher suffices to keep down microscopic eminences and to maintain a smooth surface under ordinary working conditions. Tubes of great regularity of shape and closeness of structure may be thus prepared. The metal is, of course, almost perfectly pure,[1] and may have a tensile strength as high as 20 tons per square inch, ordinary "tough pitch" copper made by dry processes having a tensile strength of about 14 tons per square inch. The tubes, being seamless and very strong, are well adapted for use as steam pipes; it is, however, not easy to make bends by the Elmore process.

Another application of the method is the manufacture of wire. For this purpose the metal is deposited in the form of a tube, which is then cut spirally from end to end into a strip of square section capable of being drawn down into wire in the usual way. Technically, the Elmore process is a success; commercially, it has been in most cases a failure owing to reckless financing.

A modification of the Elmore process consists in the use of a small hammer continuously tapping the metal as it is deposited, and consolidating it much as does the agate burnisher.

A different method is that of Thofern, who causes the electrolyte to play on the surface of the cathode in jets. By this means it is said that a current density of 50–100 amperes per square foot can be used in place of 10–20, common in ordinary copper refining; also it is stated that the copper is consolidated, and is deposited in felted microscopic filaments.

Details of a similar process are given in a patent by Graham (Eng. Pat. 986 of 1896). In this specification it is proposed to deliver the electrolyte under a head of 1—2 feet in jets $\frac{3}{8}$ inch in diameter, at a distance of $1\frac{1}{2}$ inches from the surface of the cathode. It is alleged that a current density of 300 amperes per square foot may be used within the area influenced by each jet,

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[1] For analysis of Elmore copper by the author see p. 58.

which is found to have an effective radius of about 5 inches.

It must be noted that no authentic information is forthcoming as to whether these plans have actually been worked successfully on a manufacturing scale, but they merit attention because a rush of liquid directed against the surface on which the metal is being deposited is more likely to prevent local impoverishment of the electrolyte in copper than is any ordinary method of circulation; similarly, a slight but constant pressure and attrition may tend to keep the metal smooth; a relatively small pressure is certainly effective in the Elmore process, and it would be rash to deny that a similar result may be attained by the use of a jet of liquid. Thus there is a *primâ facie* case for methods of this kind which warrants further experiment. Quite apart from the consolidation of the copper, any device which allows a high current density to be used is worthy consideration, because the output of copper for a given stock carried and for a given number of cells is proportionately increased, and the money advantage thus secured (cf. p. 39) is evident enough.[1]

THE ELECTROLYTIC WINNING OF COPPER

The electrolytic winning of copper stands on a very different footing from its electrolytic refining. Some fifteen years ago the great success which even then could be seen to be attainable in the refining of copper by electrolytic means led to efforts being made to use a

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[1] In Cowper Coles's process, the use of a high current density is made feasible by rapid rotation of the cathode. The copper deposited is smooth and coherent.

product much cruder than ordinary crude copper as a raw material. In the usual process of copper smelting the metal is separated from the gangue accompanying its ores by taking advantage of the ease with which copper sulphide is formed, and of the comparative stability of that sulphide and of its insolubility in a siliceous slag. These properties are utilised by smelting ores containing copper in such a manner as to form a matte containing approximately equal parts by weight of copper, iron, and sulphur, corresponding nearly in composition with pure copper pyrites ($Cu_2SFe_2S_3$). This matte, called "coarse metal," is sufficiently coherent and conductive to permit it to be cast into plates and used as the anode of an electrolytic cell. The quantity of impurities (iron and sulphur) is, however, so great that the uniform dissolution of the anode soon ceases, its surface becomes protected by a coating of sulphur, and the electrolyte is rapidly contaminated with iron. Coarse metal being unsuitable, a more advanced product of the dry smelting of copper was tried, viz. white metal, which is essentially cuprous sulphide (Cu_2S). This has also been found wanting, the attack being irregular and the quantity of separated sulphur excessive. Ultimately, after the expenditure of much time and money, all these attempts have been abandoned, and I do not propose to occupy space with their description and discussion.[1]

More recent and more nearly successful methods have been devised on different lines. Instead of smelting

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[1] The Marchese process, using anodes of copper matte, was tried on a considerable scale, and with much expenditure of ingenuity and money. At Casarza it failed utterly, but is said to be used in a modified form by Nicolajew at Nishni-Novgorod. If this be true, the modifications must be radical, because the original process was faulty in principle.

copper ore to a matte and using this as an anode, the ore itself is extracted by a suitable solvent and the solution containing copper is electrolysed with an insoluble anode. It must be observed that in this case the electrical energy is not used merely to transfer metallic copper already existing at the anode to the cathode, and there deposit it precisely in the same condition (save for the absence of impurities) as that in which it was at the anode. This operation, as has been already shown (p. 39), requires an indefinitely small amount of energy. The reduction of copper from its salts, however, needs a very appreciable quantity of energy, which must be furnished by the current. Thus the ultimate products of a solution of copper sulphate, electrolysed with insoluble anodes, are copper, oxygen and dilute sulphuric acid; the requisite energy is therefore that represented by the heat of combination of Cu and O to form CuO, and of CuO and H_2SO_4Aq to form $CuSO_4$ Aq. That is 63·5 grammes of copper uniting with 16 grammes of oxygen liberate 37·16 Cal., and the resulting CuO dissolved in dilute sulphuric acid liberate 18·80 Cal. To perform the decomposition into Cu, O and dilute H_2SO_4, $37{\cdot}16 + 18{\cdot}80 = 55{\cdot}96$ Cal. are needed.

Now assuming that the decomposition of copper sulphate takes place (as it does) in accordance with Faraday's law, each gramme equivalent of copper, *i.e.* $\frac{63{\cdot}5}{2}$[1]

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[1] Confusion constantly arises from the fact that the number of units of electrical quantity (coulombs) needed for the liberation of an element is always reckoned on the gramme *equivalent* of that element, whereas the heat of combination of that element is reckoned on its gramme atom. For a monovalent element these are identical, but for a divalent element, such as copper in the cupric state, the gramme atom represents two gramme equivalents of the metal.

grammes, needs 96,540 coulombs for its liberation, *i.e.* 63·5 grammes of copper require 2 × 96,540 (= 193,080) coulombs. But the heat representing the energy necessary to liberate by electrolysis 63·5 grammes of copper from an aqueous solution of its sulphate is 55·96 Cal.; this is equivalent to 233,167 joules; therefore, in order to yield this amount of electrical energy, 193,080 coulombs must be delivered at a pressure of 1·2 volts. The maximum possible output of copper per horse power hour is therefore 735 grammes. This is equivalent to 38·9 pounds per horse power per 24 hours. Thus the process differs radically from copper refining, in which, as has been shown on p. 39, any desired output can theoretically be obtained with an indefinitely small expenditure of energy, and in which as much as 93 pounds per horse power per twenty-four hours may be obtained in practice. To this calculated minimum expenditure of energy for reducing the copper there must be added certain extra quantities common to all electrolytic processes, which are needed for overcoming the resistance of the leads and that of the electrolyte (as distinct from that corresponding with the heat of combination of the substances separated). Thus the minimum working voltage of a copper-reducing plant will be about 1·5 volts, and the output per horse power hour 585·9 grammes of copper, *i.e.* 30·9 pounds per horse power acting for twenty-four hours. Thus a plant of 1,000 H.P. would deposit 5,040 tons of copper per year if run day and night for 365 days. Given water power at a cost of £2 10*s.* per horse power year, the cost for power alone for winning one ton of copper is 9*s.* 11*d.*; and if steam power be used at £9 16*s.* per horse power year, each ton of copper will cost £1 19*s.* 10*d.* to win. (These figures may be compared with those for the refining of copper given on p. 43.) This very moderate expense warrants the idea that an electrolytic process for winning copper from its ores should be exceedingly remunerative.

But the cost of the power required is not the largest part of the expense. The roasting of an ore containing the copper as pyrites is necessary in most processes, and in all the need for leaching out the ore occurs. The solvent usually becomes charged with matter other than copper extracted in the leaching process, and has to be purified or renewed at fairly frequent intervals. The upkeep of the depositing vats, electrodes and diaphragms is a heavy item, and finally the risk of obtaining impure copper or bad and non-coherent deposits, is considerable. Thus the cost of the energy required, though important, is not of such extreme moment as to give a water-power plant an overwhelming advantage over one using coal.

The processes giving greatest promise of commercial success in the electrolytic winning of copper from its ores are as follows:—

THE SIEMENS-HALSKE PROCESS

This process depends on the extraction of copper from its ore by a solution of ferric sulphate, which is thereby reduced to ferrous sulphate, the deposition of the copper thus dissolved by passage of the liquor through the cathode compartment of an electrolytic cell, and the oxidation of the ferrous sulphate by subsequent passage of the liquor through the anode compartment. The liquor thus regenerated is sent back to extract a further quantity of copper from a fresh portion of ore.

The details of the scheme of working first proposed may be stated thus. An ore containing copper as pyrites is roasted at a low temperature so as to oxidise the sulphide of iron which it contains to ferric oxide, and to free the cuprous sulphide originally forming a constituent of copper pyrites ($Cu_2SFe_2S_3$) in the ore. In the course of this roasting, part of the cuprous sulphide is oxidised to cupric sulphate ($CuSO_4$); this is no disadvantage, as that part of the copper is at once rendered soluble in water, irrespective of the solvent action of the ferric sulphate subsequently used for leaching. The sulphur dioxide (SO_2) given off in roasting may be used for making vitriol, which is needed for acidulating the leaching liquor. In this case the roasting is effected in Gerstenhofer kilns, which are narrow vertical structures down which the ore passes, meeting a limited supply of air on its way, and thus generating gases sufficiently rich in SO_2 to be practically available for vitriol making. The roasted ore is placed in leaching tanks and extracted systematically; by this is meant that fresh liquor always comes in contact with nearly exhausted ore, and nearly saturated liquor with fresh ore containing its full percentage of copper. The copper already existing in the roasted ore as sulphate dissolves as such; copper existing as cuprous sulphide is also dissolved by the action of the ferric sulphate, which may be represented thus

$$\underset{\substack{\text{Cuprous}\\\text{sulphide}}}{Cu_2S} + \underset{\substack{\text{Ferric}\\\text{sulphate}}}{2\,Fe_2(SO_4)_3} = \underset{\substack{\text{Cupric}\\\text{sulphate}}}{2\,CuSO_4} + \underset{\substack{\text{Ferrous}\\\text{sulphate}}}{4\,FeSO_4} + \underset{\text{Sulphur}}{S}$$

When a solution containing cupric sulphate and ferrous sulphate and acid with sulphuric acid is electrolysed, copper is deposited to the exclusion of iron. If this electrolysis be performed in a cell without a porous diaphragm, the ferrous sulphate is oxidised at the anode to ferric sulphate, and reduced again at the cathode to ferrous sulphate. The energy represented by these changes is provided by the current, and appears as heat, which is lost. Thus it is desirable to keep the liquor at the anode separate from that at the cathode, and it is also necessary on account of the fact that the liquor to be returned to the leaching vats must contain its iron as ferric sulphate.

The process as thus described seems satisfactory enough, but in working serious difficulties are encountered. Selective roasting of the ore is not an easy matter; it must be done slowly, at a low temperature, and with constant stirring; these are somewhat expensive conditions of working. The leaching needs much attention, and the leached liquors may be muddy with basic iron salts and require filtration; an ordinary iron filter press is not adapted for liquors containing copper and iron salts, as the frames and plates are attacked; wooden presses are needed, and these wear rapidly. The anodes must be insoluble and withstand the disintegrating action of the current. This point is of great importance in many electrolytic operations and it cannot be said that complete success has yet been attained in devising a permanent anode. Platinum is too costly for any ordinary process. All other commercial metals are attacked. Ferro-silicon, which is a difficultly attackable substance, has been suggested, but does not appear to have proved successful in practice. In almost all cases carbon is the only substance which can be employed with fair results. The quality of carbons prepared for electrical and electrolytical purposes varies considerably, but even the best are eventually destroyed. The choice of a diaphragm is even more difficult than that of an anode.

In the original arrangement a porous cell or membrane was employed, the disposition of the various parts being such as is shown diagrammatically in the appended figure (Fig. 13). C, C, C are the cathode compartments of the three cells shown; they are separated from the anode compartments A, A, A by the porous partitions E, E, E. Each of the cathode compartments is fed with a solution of cupric sulphate and ferrous sulphate supplied by pipes B, B, B, conveying the liquor through the series of cells. A portion of the copper in the liquor is deposited on each of the cathodes K, K, K. Seeing that the liquor as it enters the first cell contains more copper than when it leaves it, its specific gravity is higher at the point of entrance than at that of exit, and thus the decrease of the content of copper corresponds *pari passu* with the alteration of specific gravity, and the lighter liquor, poorer in copper, flows out through the U end of the second tube B in the first cell down to the bottom of the cathode compartment of the second cell C, where the process of elimination of copper and specific lightening of the liquid recurs. Therefore throughout the series of cathode compartments the deposition of copper proceeds step by step, the heavier, richer liquor

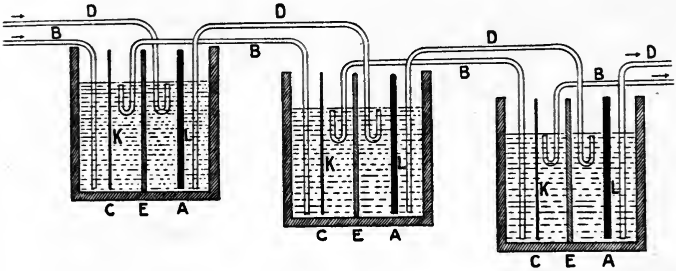

FIG. 13.

always entering at the bottom of the cell, and the poorer, lighter liquor flowing away at the top.

Precisely the converse holds good with the anode compartments A, A, A. The liquor from the last of the cathode compartments, nearly exhausted of copper, but containing all its iron as ferrous sulphate, flows into the first of the anode compartments by the pipe D, and is there oxidised at the anode L. The ferrous sulphate is converted into ferric sulphate, the solution of which is specifically heavier than that of the ferrous sulphate, and sinks in the anode compartment, increasing in its content of ferric sulphate and in specific gravity until it reaches the bottom, whence it flows by the pipe D into the next anode compartment. Thus the oxidation of the liquor is as systematic as is the reduction of copper from it, and the ultimate product on one side is a solution of ferrous sulphate containing a small residuum of cupric sulphate, and on the other a solution of ferric sulphate (still containing a small quantity of cupric sulphate) ready for extracting a fresh portion of roasted ore. The arrangement of pipes shown having upturned ends is merely a device, such as those which are shown in Figs. 8 and 9, pp. 50, 51, for allowing the flow of liquid through the tanks to be irregular, or to be stopped altogether, and started again without risk of any tank overflowing, or any syphon becoming empty and therefore unable to perform its functions when the flow of liquid begins again. The appended figure (Fig. 14) shows the arrangement on a somewhat exaggerated scale for the sake of clearness.

The tank B is on a lower level than the tank A, and thus liquid can flow through the syphon C. The original levels of the liquid in the tanks are represented by the lines L, L. The liquid in A flows into B until the level in each is altered, and becomes that represented by the lines L′, L′. On reaching these levels the syphon ceases to act, but the U-shaped bend remains full, and the syphon again begins to work when the level in A is raised by any fresh influx of liquid. Now suppose by some irregularity or accident the level in B falls again to L without there being any compensating influx from A. The liquid only falls in the short up-turned limb of the syphon to an equal extent, and on the resumption of a regular flow the short limb fills up again and the syphon resumes its office. The longer the U of the syphon the greater may be the irregularities of flow without throwing the syphon permanently out of action. This assumes that the pipe forming the syphon is made wide enough to allow the upturned end to fill quietly without enclosing air spaces, which, when the syphon started again, might cause a pocket of air at the top of the syphon and stop its working.

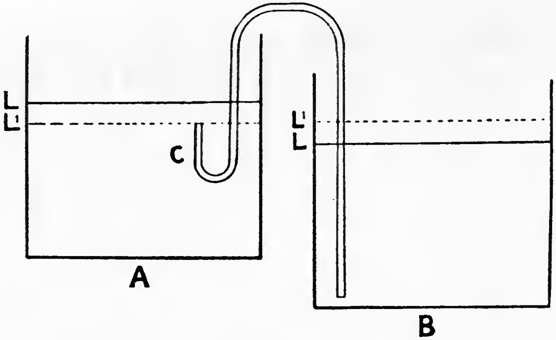

Fig. 14.

It will be noted that in the Siemens-Halske process the energy necessary to deposit copper from copper sulphate at the cathode is diminished by that afforded by the oxidation of ferrous sulphate to ferric sulphate at the anode. This saving of energy is secured by taking advantage of the fact that the ore, even when roasted, is not a completely oxidised body (for it contains copper as cuprous sulphide), and is capable of effecting the reduction of ferric sulphate to ferrous sulphate, thus providing a body capable of oxidation with the production of energy at the anode. A similar case is fully discussed and its quantitative relations are computed in the description of the Hoepfner process which is given in a succeeding section.

An estimate of the cost of a small plant for the Siemens-Halske process has been published (*J.S.C.I.*, 1892, 534). It may be given as an example of the items to be considered in calculations of this sort rather than as being of any intrinsic value, for, as will be seen presently, the Siemens-Halske process has not hitherto proved commercially successful.

The quantity of copper to be won is taken as one ton per 24 hours, using an ore containing 4—4·5 per cent. of Cu. The cost of the plant exclusive of buildings is reckoned at £5,765; crushing machinery, £1,557; leaching plant, £3,057—total, £10,379.

The cost of working per 24 hours is calculated thus:—

	£
Interest on plant (£10,379) at 5 per cent.	1·42
Depreciation at 10 per cent.	2·84
130 H.P.	3·12
Labour (15 men at 2*s*.)[1]	1·50
Interest on copper in baths	0·50
Fuel for heating extracting solution	0·50
General expenses and supervision	2·00
	£11·88

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[1] The estimate is German, wherefore the low labour charge.

Thus the winning of one ton of copper cost, exclusive of the cost of the ore, nearly £12. This expenditure is not immoderate, and would be smaller if a larger plant were employed. Nevertheless the process has not achieved success, for the reasons stated below.

The difficulties experienced in obtaining suitable permanent anodes and diaphragms have led to several modifications of the Siemens-Halske process.

In these the arrangement of electrodes and diaphragm has been horizontal instead of vertical, and the diaphragm has served not only as a separating membrane, but as a slow filter. This alteration is exemplified by the accompanying sketch.

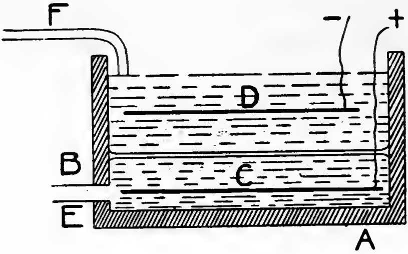

Fig. 15.

The vat A is separated into two parts by the horizontal filter B, of felt or asbestos. In the lower part is the anode C, and in the upper division is the cathode D. The anode may be built up of carbon plates or rods, while the cathode is a piece of copper sheet supported by a wooden framework (not shown). The leached liquor is fed in at F and drawn off at E, the rate of flow being so adjusted that it passes continuously through the filtering partition B, and is in contact with each electrode successively for a time sufficient to allow of the deposition of the bulk of the copper in the upper division and of the oxidation of the ferrous sulphate in the lower division, whence it is led back to the leaching tanks.

The circulation is thus from cathode to anode compartment of a single electrolytic cell, and not through all the cathode compartments of a number of cells and then through all the anode compartments of the same cells, as in the arrangement shown in Fig. 13, p. 71.

Several forms of apparatus having these characteristics, viz. the horizontal electrodes and the completion of the treatment of a given quantity of leaching liquor in a single cell, have been patented, but in spite of all these attempts no authentic account of a successful installation on a large scale has been published, and if a process of the kind is being worked it is kept secret.

THE HOEPFNER PROCESS

Two chief underlying ideas may be traced in this process. The first is to extract copper from its ores in which the metal exists as sulphide by a solvent which shall extract the copper from the *unroasted* ore. The second is to deposit copper from its cuprous salts instead of from its cupric salts. This latter idea may be profitably considered irrespective of any particular process. In the first place it is evident that cuprous chloride (Cu_2Cl_2) in which the copper is monovalent contains twice as much copper per unit weight of chlorine as does cupric chloride ($CuCl_2$). Therefore the number of coulombs necessary to decompose 134·5 grammes of $CuCl_2$ and yield 63·5 grammes of copper will decompose 198 grammes of Cu_2Cl_2 and will yield 127 grammes of copper. In other words, a current of one ampere acting for one hour will deposit 1·1827 grammes of copper from cupric chloride, and 1·1827 × 2 = 2·3654 grammes of copper from cuprous chloride.

It has been shown above that there is a substantial commercial advantage to be gained by using a high current density, because the quantity of copper turned out per unit of copper locked up and per unit of plant is thereby increased. The limiting current density is set by the difficulty of obtaining copper in a sound, coherent, and pure state when the current density exceeds a certain modest value, *e.g.* 10 amperes per square foot. Now assuming that *ceteris paribus* the same current density can be used with a cuprous as with a cupric solution,[1] it follows that with a given stock of copper, and with a given plant, twice as much copper can be reduced from the cuprous as from the cupric state with the same current. But it must not be assumed that twice as much copper can be reduced with the expenditure of the same amount of energy. This needs separate inquiry. Thus the heat of formation of one gramme molecule (134·5 grammes) of cupric chloride ($CuCl_2$) is 51·63 Cal. Hence to liberate 63·5 grammes of copper from cupric chloride requires 51·63 Cal., *i.e.* 215,125 joules. But the flow of 2 × 96,540 coulombs will deposit 63·5 grammes of copper from a cupric salt. Therefore these coulombs must be delivered at a pressure of $\frac{215{,}125}{2 \times 96{,}540}$ volts = 1·114 volts.

But the heat of formation one gramme molecule (198 grammes) of cuprous chloride (Cu_2Cl_2) is 65·75 Cal. Hence to liberate 2 × 63·5 grammes of copper from cuprous chloride requires 65·75 Cal., *i.e.* 273,958 joules. But the

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[1] This is an assumption, not a demonstrated fact. Like many other questions in the electrolytic winning of copper, this point is in need of experimental investigation.

flow of 96,540 coulombs will deposit 63·5 grammes of copper from a cuprous salt and 2 × 96,540 coulombs must flow to deposit 2 × 63·5 grammes of copper. Therefore the coulombs must be delivered at a pressure of $\frac{273,958}{2 \times 96,540}$ volts = 1·419 volts.

Thus, although it is true that a given current deposits twice as much copper from a cuprous as from a cupric solution, yet it requires per molecule of salt decomposed a higher voltage in the proportion of 1·419 volts to 1·114 volts. That is, the total energy required per unit weight of copper liberated from cuprous chloride is $\frac{\frac{1·419}{2}}{1·114}$ of that needed per unit weight of copper liberated from cupric chloride, *i.e.* approximately $\frac{16}{25}.$ Of course the same result is arrived at by considering directly the heats of formation of cuprous and cupric chloride, remembering that in the former each molecule contains twice the weight of copper present in a molecule of the latter. The foregoing calculation serves, however, to show the method by which computations of this kind may be made, and also to illustrate the fallacy of referring the efficiency of a given process solely to its output per coulomb (or, if over a given time, per ampere), ignoring the true efficiency, *i.e.* the output per unit of energy, this being stated in calories, joules, foot pounds or other convenient unit.

In the particular case now under discussion, the mere statement of the output per coulomb would imply that a process using a solution of cuprous chloride would be twice as efficient as a process using a cupric solution. In reality, however, it is about one and a half times as efficient, taking as a criterion the minimum possible consumption of energy. Its real claim to consideration (assuming practical difficulties to be overcome) is in the greater output of copper per unit of plant and of copper locked up, always provided that the maximum current density at which good coherent copper can be deposited is as high as that attainable with the use of cupric solutions.

These principles having being discussed, we may return to a consideration of the process illustrating them.

The Hoepfner process, as originally devised, was described by the inventor in a paper read before the Upper Silesian Society of Applied Chemistry, and transcribed into the *Zeits. f. Angewandte Chemie*, 1891, p. 160. The gist of this description, together with any necessary comments, may be given briefly here.

The cells are divided by a porous partition into anode and cathode compartments. Through all the cathode compartments of a given group of cells flows a solution containing cuprous chloride dissolved in a solution of sodium chloride or calcium chloride. Copper is deposited from this solution in double the quantity that would be deposited from a cupric solution by the same current. The liquor, having passed through the whole set of cathode compartments, flows away nearly free from copper. In similar manner a solution of cuprous chloride is supplied to the anode compartments. Now at the anodes chlorine appears in quantity corresponding with the copper deposited in the cathode compartments. This chlorine, however, does not become free, but combines with the cuprous chloride in the anode compartments to form cupric chloride. This reaction in itself tends to produce a current in the same direction as the current used for electrolysis, and thus the necessary minimum voltage is diminished. The minimum voltage for a cell having cuprous chloride in both anode and cathode compartments (the two being separated by a porous diaphragm) may be calculated. The calculation resolves itself into reckoning the voltage corresponding with the heat of combination of copper and chlorine to form cuprous chloride, minus that of cuprous chloride and chlorine to form cupric chloride;

i.e. $Cu_2 + Cl_2 = Cu_2Cl_2$.	65·75 Cal.
and $Cu_2Cl_2 + Cl_2 = 2\,\ddot{C}uCl_2$	32 Cal.
	33·75 Cal.

Therefore the total energy to be provided from without is 33·75 Cal. = 140,625 joules for 2 × 63·5 grammes of copper deposited from the cuprous chloride solution. Seeing that 2 × 96,540 coulombs must flow in order to deposit 2 × 63·5 grammes of copper from a cuprous solution, it follows that the current must have a voltage of $\frac{140{,}625}{2 \times 96{,}540}$ volt = 0·73 volt.

In the foregoing calculation such thermal changes as attend the removal of cuprous chloride at the cathode from its solution in brine or calcium chloride solution, and the production of cupric chloride (having a high heat of dissolution in water) in solution at the anode, have been intentionally neglected. Thus the main point stands out clearly, viz. that by taking advantage of the power of copper to form two chlorides the chlorination of cuprous chloride can be caused to yield energy in the cell, and thereby diminish substantially the quantity of energy necessary to be impressed from without.

The energy required to reduce again the cupric chloride to cuprous chloride, and thus economise the electrical energy which has to be expended in the cell, is afforded by the ore, which, being an unoxidised copper sulphide, is capable of acting thus. Therefore the saving of energy effected by taking advantage of the existence of two chlorides of copper comes ultimately from the ore itself. Just as a sulphide ore can be roasted in heaps by its own heat of combustion and without the aid of extraneous fuel, so can the same ore serve in great measure to go towards reducing copper which it contains to the metallic state. These energy considerations are quite elementary, but are often neglected or slurred over in dealing with electro-metallurgical questions.

The cupric chloride formed in the anode compartments during the systematic flow of a portion of the cuprous extract from the ore through these compartments is returned to the leaching tanks for extracting a fresh portion of the ore; there it acts on the cuprous sulphide in the ore according to the equation—

$$Cu_2S + 2\,CuCl_2 = 2\,Cu_2Cl_2 + S.$$[1]

It will be remembered that the liquor which has passed through the cathode compartments, though robbed of its copper, contains untouched the sodium chloride or calcium chloride used to keep the cuprous chloride in

[1] This equation has been disputed. Experiments in the author's laboratory have, however, shown it to be substantially correct. It must not be assumed, however, that a practicable process of leaching on these lines can necessarily be realised. Completeness of extraction depends largely on the fineness of the ore, the proportion of solvent to ore, and the temperature at which the extraction is conducted.

solution. Now, if complete reduction to cuprous chloride occurs (as it should) in the leaching vats, a quantity of cuprous chloride equal to that originally starting from the leaching vats will be regenerated. This will need the same quantity of sodium chloride or calcium chloride to retain it in solution as was requisite when the first solution was prepared. Therefore the liquor from the cathode compartments must be mixed with that from the anode compartments in order to provide sufficient sodium chloride or calcium chloride to hold the whole of the cuprous chloride in solution. To take a concrete case for the sake of clearness: Suppose a solution having a volume of 1 litre contains 2 gramme molecules of Cu_2Cl_2 and that this is kept in solution by 4 gramme molecules of NaCl.[1] Let half this solution pass through a cathode compartment and there deposit all its copper. The half litre of solution then contains 2 gramme molecules of sodium chloride. The other half of the solution passing through the anode compartments is there chlorinated, and after this change contains 2 gramme molecules of $CuCl_2$ and 2 gramme molecules of NaCl. Then passing to the extracting tanks, it is reduced to Cu_2Cl_2, fresh copper going into solution, and forms 2 gramme molecules of Cu_2Cl_2, which require *ex hypothesi* 4 gramme molecules of NaCl for their solution; but in the solution itself are only 2, hence the 2 bereft of copper in the cathode liquor must be supplied to make up the deficit.

It is evident that the process possesses some elements of elasticity of working. If it were found, as is likely, that impurities accumulated in the leaching solution to an inconvenient extent, the liquor from the cathode

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[1] Whether these solubilities are possible or not is immaterial as far as the argument is concerned.

compartments, thoroughly freed from copper, could be thrown away and replaced by clean water in which the requisite quantity of salt to make an effective solvent for the cuprous chloride had been dissolved. Thus purification could be attained with the expenditure only of the sodium chloride, and there need be no waste of copper, or necessity for working up a crude solution.

A subsidiary advantage claimed for the process is that cupric chloride is a solvent for silver contained in the copper ore; thus—

$$Ag_2S + 2\,CuCl_2 = Cu_2Cl_2 + 2\,AgCl + S.$$

The resulting silver chloride is sufficiently soluble in the solution of cuprous chloride in sodium chloride or calcium chloride, and from the solution the silver can be precipitated by well-known means, *e.g.* treatment with metallic copper, before the solution goes to the cathode or anode compartments. When the silver has been separated, removal of other impurities can be effected by precipitation with a limited quantity of lime. This, which is a common operation in wet metallurgical processes, can be easily carried out, because cuprous oxide is a strong base, and all ordinary impurities are precipitated before its salts are decomposed, when a base such as lime is added gradually.

The foregoing description is based on the facts set forth in Hoepfner's original paper. In the same document he proceeds to give an estimate of the cost of the plant and of the fuel required in a works using this method. These are here pretermitted, as they have not been realised in practice. The nature of the difficulties encountered may be gathered from the following abstract, appearing in the *J. Soc. Chem. Ind.*, 1895, p. 279, of a paper by E. Jensch (*Chem. Zeit.*, 1894, p. 1906).

"The Hoepfner process was used at Schwarzenburg from August, 1891, to March, 1892, and in the Giessen and Weidenau works. It was applied both to rich ores and mattes, and to cuperiferous pyrites from the Sulitjelma mines in Northern Norway, in which the copper per centage ranged from 9·5 to 12·25, and that of iron from 32·6 to 34·5. The ore was very finely crushed, so that 85 per cent. of the sample passed through a No. 200 and 96 per cent. passed a No. 100 sieve; but some little trouble was caused by the blocking of the meshes by the fine powder. The leaching was effected by means of a solution of cupric chloride in calcium chloride, which latter (instead of brine) becomes the solvent of the resulting cuprous chloride, the mixture being placed in revolving wooden drums of 900 to 6,600 litres capacity. The drums caused considerable difficulty by leakage, which began when the temperature of the liquid was raised by the admission of steam to hasten the reaction, and increased with the rise of temperature and the growing percentage of cuprous chloride, yet for obvious reasons lead and iron vessels could not be used. With the rich materials three or four extractions sufficed, but with the Sulitjelma ore, although the first extraction removed half of the copper, even ten or twelve leachings failed to extract the whole of the remainder, partly on account of the large percentage of iron present, partly owing to the increasing dilution of the liquid. At the temperature of the reaction, magnetic pyrites reacts with cupric chloride, giving equivalents of ferrous chloride, cuprous chloride, iron bisulphide and sulphur, while the resulting ferrous chloride reacts with another quantity of cupric chloride to give ferric and cuprous chlorides; and iron pyrites reacts directly with cupric chloride to give ferrous and cuprous chlorides and sulphur. For this reason an excess of cupric chloride must be used in the leaching solution. The slimes were filter-pressed at a temperature of 40° to 50° C. in order to avoid the retention of copper by them. The anodes were of paraffined carbon, the cathodes thin copper plates, experiments with coppered carbon cathodes having proved unsuccessful. Difficulties with the parchment paper diaphragms were also met with."

The copper obtained by the Hoepfner process is said to be of good quality, in spite of the fact that it is precipitated from a somewhat impure solution. A published analysis shows only traces of iron, arsenic, antimony and lead, nickel and cobalt amounting to 0·0012 per cent. and molybdenum 0·0023 per cent.

One of the most serious difficulties of the Hoepfner process has been the provision of refractory anodes and diaphragms. The patents taken out by Hoepfner in the years immediately succeeding the original promulgation of his process indicate this. He has suggested the use for anodes of ferro-silicon, *i.e.* iron containing sufficient silicon, *e.g.* 10—15 per cent. to constitute a silicide which is less readily attacked than iron and is still sufficiently conductive; for diaphragms he has advocated the use of mica plates joined together (this being necessary because the price of fairly large pieces of mica is high, and any piece over one foot square is practically unattainable) and perforated with numerous fine holes so that the liquids to be separated may be in electrolytic contact and yet be prevented from commingling freely. These almost desperate expedients indicate the heavy mechanical difficulties with which the process has had to contend. Having regard to all these things, the

Hoepfner process, in spite of its ingenuity and the soundness of the principles on which it rests, must be pronounced a failure up to the present.

Before dismissing the subject of winning copper directly from its ores by extraction with some solvent which can be regenerated and by electrolytic treatment of the resulting solution, a brief description must be given of an ingenious device due to Cohen (who has described it in the *Zeitschrift für Elektrochemie*, 1895, p. 25), by which he seeks to avoid the necessity for a diaphragm. The arrangement is shown in Fig. 16. There is no porous diaphragm; the cathode K is about half the length of the anode A, and the latter at its lower end is separated from the rest of the tank by the short vertical partition C. Cuprous chloride solution is fed in by the pipe B, and flowing down is partly robbed of its copper in passing over the cathode K. On reaching the anode A the cuprous chloride still remaining in solution is oxidised to cupric chloride, and its specific gravity is thus increased, wherefore it slides down the anode and collects in the sump E formed by the partition C. From this it is syphoned off by the pipe D, and is available for extracting another portion of the ore. The weak point of this arrangement is that the more completely the cuprous chloride is robbed of its copper (as is desirable) at the cathode, the smaller quantity of cuprous chloride remains in solution to be oxidised at the anode; under the best conceivable conditions only half the copper is deposited at the cathode, leaving an equal quantity to be oxidised from the cuprous to the cupric state at the anode. But, seeing that the upper parts of the two electrodes are not separated, more than half the cuprous chloride is likely to escape decomposition at the cathode and pass directly to the anode. It cannot be oxidised there by the action of the current, because the amount of chemical action at the anode is equivalent to that at the cathode. Therefore a considerable proportion of the cuprous chloride circulates idly through the extracting vats and electrolytic tanks. Moreover, it is highly doubtful whether the difference of specific gravity of the two solutions is large enough to ensure the cathode and anode liquids remaining fairly separate. Altogether the device is more ingenious than practicable.

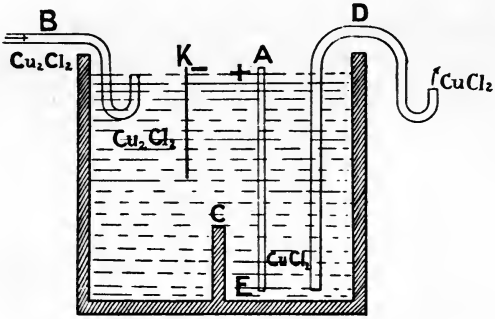

Fig. 16

The example of Hoepfner in using cuprous salts from which to deposit copper has been followed by Douglas, who proposes roasting sulphide ores to sulphate, extracting with a solution of sodium chloride, reducing the resulting cupric chloride to cuprous chloride by means of sulphur dioxide, and electrolysing the cuprous chloride (which may be as a paste if the quantity of sodium chloride is insufficient to keep it in solution) depositing copper at the cathode, and collecting the chlorine given off at the anode for use as such. There is no reason to suppose that this is more than a paper process.

From the foregoing description of the Siemens-Halske and the Hoepfner processes, the only methods which have been fairly tried on a manufacturing scale, it is evident that the electrolytic winning of copper, as distinct from its refining, has not yet been remuneratively accomplished. That it will be achieved in the near future is probable enough; meanwhile it presents an excellent field for invention. What is wanted is not so much a totally new device as a well-schemed plant, embodying perhaps nothing but what is common knowledge, but planned so as to be fairly permanent as a whole, and with its perishable parts easily and cheaply renewable.

LEAD

No process for the winning of lead from its ores by means of electrolysis has been devised. It is unlikely that any such process will be devised, because lead is an easily reducible metal, fusible at a low temperature, and of low price. Certain attempts have been made to refine crude lead, and these have met with a qualified success. It happens that the refining of lead by ordinary metallurgical processes has been brought so nearly to perfection that commercial lead, such as is used for the commonest purposes—plumbing, roofing and the like—is almost chemically pure, as may be seen from the following typical analysis:—

	Per cent.
Lead	99·9837
Copper	0·0014
Antimony	0·0037
Zinc	0·0016
Iron	0·0016
Silver	0·0080
	100·0000

Not only is the lead all but absolutely free from the commoner metals, but it contains only a small quantity —less than $\frac{1}{100}$ of 1 per cent.—of the most characteristic and valuable impurity, namely silver. In the sample, the composition of which is quoted above, there is 0·008 per cent. of silver, *i.e.* 5 ounces per ton. In many commercial samples of lead there is even a smaller amount, *e.g.* 2–3 ounces per ton. Thus it is evident that by existing methods of refining lead can be obtained of a quality good enough for all ordinary purposes, and at the same time free from the chief foreign constituent with recovering. From this it follows that any electrolytic process is not likely to achieve better results, and its only chance of adoption lies in the possibility of its being cheaper than the usual processes. It will be seen that the refining of lead stands on a totally different footing from that of copper (p. 35 *et seq.*). There a product (copper almost absolutely pure) is obtained which is procurable in no other way and for which there exists a large demand; with lead, on the other hand, the product can be at best only insignificantly more nearly pure, and can fulfil no demand not already fully satisfied by the ordinary metal of commerce. Therefore, whereas the extension of electrolytic copper refining and the ultimate extinction of dry processes are certain, the future adoption of electrolytic lead refining on any considerable scale is inherently improbable, unless an appreciable saving in cost of refining can be proved.

KEITH'S PROCESS

This process, although no longer in use, is worthy of brief description in that it illustrates the lines on which a refining process may be worked, provided the cost can be kept within reasonable limits. Crude lead containing 96–97 per cent. of Pb was used as the raw material.

The following analysis will serve to show the composition of lead of this class:—

	Per cent.
Lead	96·36
Antimony	1·07
Arsenic	1·22
Copper	0·31
Silver	0·55
Zinc, iron, etc.	0·49
	100·00

This crude lead is cast into plates to serve as anodes. These are enclosed in bags of muslin to retain the anode sludge containing the silver. The electrolyte consists of a solution of lead acetate or of lead sulphate dissolved in sodium acetate. The cathodes are thin sheets of pure lead, and on them the lead is deposited as loosely adherent crystals, which fall to the bottom of the depositing cell and are removed from time to time. The anode sludge remains in the muslin bags and is worked up for its silver. The lead crystals have to be squeezed into blocks and fused in the presence of a little charcoal and run into ingots. A certain amount of slagging and loss is apt to occur in this operation. Such loss can be minimised by adding the lead sponge to lead already molten, instead of fusing it *per se.* There is a certain limited demand for spongy lead for accumulator plates, and for this purpose the lead deposited electrolytically in a mass of loose crystals is well adapted. If, however, electrolytic lead refining is ever to be established on a large scale, this outlet would be much too small to take any considerable fraction of the lead produced, and some plan of fusing the metal and running it into ingots must be adopted.

One of the best attempts which have been made to refine lead electrolytically is that due to Tommasi. Like other methods, it has not yet reached a manufacturing status, but is nevertheless worthy of a brief description.

The electrolytic cell *d*, shown in vertical section (Fig. 17), contains two lead anodes *p*, *p*, which may be either cast plates or powdered lead packed in a perforated case.[1] Between the anodes is a large thin disc c (shown in vertical section in the figure, and therefore appearing as a line), made of copper or aluminium bronze and having

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[1] A device of doubtful utility.

its centre above the top of the cell. It is mounted on a spindle provided with a rubbing contact, and is made the cathode. The disc is rotated, and is alternately immersed in and withdrawn from the electrolyte. On each side of the disc is a scraper, which detaches the loose lead crystals deposited during the passage of the disc through the electrolyte and also aids in depolarising it. The finely divided lead falls into gutters, by which it is conveyed to a sieve. Here it is drained and washed. The lead is compressed and fused into ingots, a little charcoal being used to hinder oxidation. The electrolyte is said to be a solution of lead acetate and sodium or potassium acetate, to which certain substances are added to prevent the formation of lead peroxide at the anode. The nature of these substances is kept secret. It is probable that they are fairly cheap and easily oxidisable organic substances which serve to reduce any lead peroxide that may tend

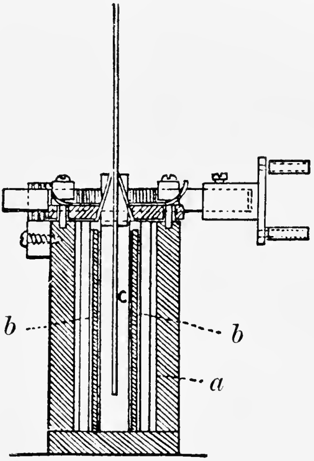

Fig. 17.

to be deposited. This tendency to deposit a portion of the lead as peroxide at the anode is a standing difficulty in lead refining. It is objectionable, not only because the lead is deposited in the wrong form at the wrong place, but also because it gives rise to a back E.M.F. which increases the voltage needed for the decomposition of the electrolyte. Supposing the formation of lead peroxide to be prevented from occurring by means other than the addition of reducing substances to the electrolyte, there will be no necessary consumption of energy in the transference of lead from the anode to the cathode. The only expenditure of energy required will be that needed to overcome the resistance of the electrolyte. In fact, the general conditions are identical with those obtaining in copper refining, and the remarks made on p. 39 apply equally here. Now it is evidently advantageous to keep the electrodes as close together as possible, so as to reduce the resistance of the cell. This is feasible with a revolving cathode, because the deposited lead is continually removed by the scrapers, and is thus prevented from forming irregular crystalline growths which would bridge the space between the electrodes. Tommasi calculates that with a distance of 2 cm. between anode and cathode, and using a current density of about 3 amperes per square diameter (say 27 amperes per square foot), the drop of pressure in each cell would be 0·75 volt, and that for an output of 84 tons of lead per day of 24 hours an installation of about 1,000 H.P. would be required. Making all the usual charges for labour, fuel, depreciation, and the like, the cost of the process per ton of refined lead is about 7*s*. By using water power this sum may be reduced to about 4*s*. Taking the cost of casting the anodes and working up the anode sludge for the recovery of silver and bringing the precipitated lead into marketable form at 2*s.* 6*d.* per ton of crude lead, the total cost will be 6*s.* 6*d.*–9*s.* 6*d.* per ton. This is to be compared with a working cost of 24*s.*, said to be incurred by the ordinary dry method of refining and desilverising. The low cost estimated for the Tommasi process can be covered by the value of even a small amount of silver, *e.g.* 4 ounces per ton, extracted. It must not be assumed, however, that the present dry process, even if requiring an expenditure of 24*s.* per ton of crude lead, cannot deal profitably with metal containing less than 12 ounces of silver per ton. The average content of silver in commercial refined lead, 2–3 ounces per ton, disproves this at once. The reason, of course, is that for most purposes the lead must in any case be refined, and the desilverising is an incident in the refining. Thus, the value of the silver need not be so large as to cover the cost of refining; the enhanced value of the refined lead is also to be reckoned when considering whether a lead poor in silver can be profitably treated. It is evident that the question is wholly one of cost, and, in deciding for or against the Tommasi process, detailed estimates, based on large scale experiments, would have to be compared with the actual works cost of a modern refining plant working on the Parkes or Pattinson system. As regards the production of spongy lead, there is, as stated above, some prospect of useful application of the Tommasi or some similar process. The cost of 1 ton of spongy lead will not be greater (assuming that the electrolytic process costs about as much as the dry method) than that of 1 ton of ordinary refined lead—say £11 10*s.* The cost of spongy lead obtained by any method of chemical precipitation, such as with zinc, which is sometimes employed, will be considerably greater, *e.g.* £50 per ton, both because the comparatively expensive acetate of lead is used and because the zinc acetate formed is of small commercial value. Any direct method of precipitation will include the impurities of the zinc in the spongy lead—an undesirable outcome when the lead is to be used for accumulator work, in which it is needed to be as pure as possible. To avoid the inclusion of these impurities it would be necessary to dissolve the zinc out of direct contact with the lead salt—in fact, in one compartment of a single voltaic cell, short-circuited. The lead would be deposited on the negative plate precisely as copper is deposited in a Daniell cell. In short, the lead would be produced electrolytically in the most expensive way. Its cost would make its use quite impracticable for all but very special purposes. On the other hand, at a price of about £11 10*s.* per ton there is no reason why spongy lead should not be used as the starting-point in manufacturing oxides of lead (litharge and red lead), and perhaps white lead (basic carbonate of lead). Should such an outlet be found, electrolytic lead may be profitably manufactured, irrespective of its utilisation as ordinary massive metal.

PROCESSES USING A FUSED ELECTROLYTE

Lead may be refined by electrolysis conducted with a fused salt of lead, instead of an aqueous solution of a lead salt, as the electrolyte. Difficulties caused by the deposition of the lead in a spongy state from an aqueous electrolyte naturally disappear when the electrolyte is fused and kept at a temperature above the melting-point of lead. It also appears that electrolysis can be conducted successfully with a far higher current density in a fused electrolyte than in one which is aqueous. This allows the apparatus to be smaller for a given output of lead—a matter of considerable importance. Of ordinary salts of lead, the chloride is most generally suited for use as a fused electrolyte. It melts at 498° C. = 928° F., and does not vaporise largely until considerably above this temperature. It is relatively cheap, not unduly corrosive and is a good conductor. The use of a fused electrolyte for lead refining must, of course, be so arranged that both the crude lead acting as anode and the refined lead collecting on the cathode may be kept fused, that fresh crude lead may be added, and the separated pure lead may be removed continuously or from time to time, preferably without interrupting the working of the plant. An ingenious apparatus has been designed by Borchers to meet these requirements. It does not appear that this apparatus has ever been tried on a manufacturing scale; nevertheless, it illustrates certain principles and ideas sufficiently well to warrant a brief description. The chief features of the apparatus are shown in the diagrammatic sketch given on the opposite page.

A cast-iron vessel A, shown in cross section, is divided electrically by the insulating joint B. The left-hand side of the vessel (which serves as the anode) is not vertical, but has a slope sufficient to allow a series of grooves in its face to retain melted lead and to allow this lead to flow down the side of the vessel terrace-fashion in a continuous stream. The lead is put in through a hopper (not shown) at the top, and is drawn off by an inverted syphon (not shown) at the bottom. The electrolyte filling the vessel is a mixture of potassium chloride and sodium chloride in molecular proportions, to which has been added lead oxychloride. The vessel is set in the flue of a furnace, so that its contents may be kept fused. The only sensitive part is the insulating joint, and this is water-cooled, so that it is protected from the electrolyte by a crust of solidified salt. The part of the vessel on the side of the insulating joint opposite the anode serves as the cathode, and in it the refined lead is deposited and collected. This lead is drawn off by an inverted syphon in manner similar to that used for the anode side. Using this apparatus, Borchers has been able to employ as high a current density as 10 amperes per square decimetre (= 93 amperes per square foot) even when the lead was rich in bismuth and it was sought to refine it and separate the bulk of it from this valuable impurity. If the quantity of bismuth be small, the enormous current density of 60 amperes per square decimetre can, it is said, be adopted without impairing the purity of the lead produced or endangering the apparatus. Borchers also states that even with these high current densities the requisite voltage is only 0·5 volt, and that thus 10 pounds of lead can be refined by an expenditure of energy of 1 H.P. hour. Taking this as costing 1*d*. for comparatively small installations, one finds that the cost

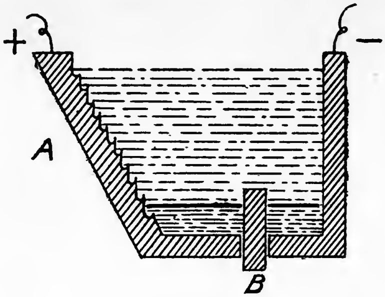

FIG. 18.

of refining is about £1 per ton as far as the requisite energy is concerned. It must be noted that it is by no means clear that this process is adapted for dealing with argentiferous lead. Probably with a moderate current density the silver would remain unattacked and be concentrated in the residual anode lead. The distribution of other metallic impurities common in crude lead, and having to be provided for by any scheme of refining, is also uncertain. Thus, speaking generally, it may be justly said that, ingenious as is the apparatus, it and its action require close and extensive study before it can be considered as an improvement on existing methods of lead refining.

GOLD AND SILVER

THE ELECTROLYTIC EXTRACTION OF GOLD FROM ITS ORES

Gold almost always occurs as free metal in ordinary ores; its extraction, therefore, consists in acting on it with an appropriate solvent which will not attack appreciably the non-auriferous part of the ore. It is on this account that the oldest of all extraction processes, that of amalgamation, has been, and still is, largely and successfully employed. Mercury is an excellent solvent for gold, and does not dissolve the oxides and sulphides of base metals or the earthy gangue which accompany the gold. The reason why a process of amalgamation is not always the best that can be used for extracting gold is that the gold may be covered with a film of sulphide or oxide of some other metal, which may prevent its being brought into full contact with the mercury, or it may be so finely divided that it may float in the water carrying the powdered ore, and may thus equally escape contact with the mercury. Further, devices to mix the mercury intimately with the pulp of ore and water so as to catch this finely divided gold are very apt to convert the mercury itself into a "flour" so difficult to restore to its normal condition that it is carried away and lost. These and other difficulties make the use of mercury as a solvent less ideal for the extraction of gold than would at first sight appear. Free chlorine will dissolve gold, and is used in a number of processes of "chlorination," which consist essentially in treating the finely powdered ore with water into which chlorine gas is led or in which it is generated by the action of sulphuric acid on bleaching powder. The objections to these processes are that other metals than gold are dissolved, and that the quantity of chlorine required is hugely in excess of that strictly necessary to dissolve the gold. Potassium cyanide solution in the presence of oxygen will dissolve gold, and is utilised in enormous quantity and with the most complete practical success for treating ores, especially those of the type found in the Rand goldfields of South Africa. The success which has attended the use of potassium cyanide is largely due to its property, when used in sufficiently dilute solution, of dissolving gold rather than other soluble matters; this selective action tends to prevent waste of the solvent. Even with cyanide, however, the amount of solvent required, compared with that corresponding chemically with the weight of gold to be dissolved, is colossal.

Reflecting on the facts set forth in this preamble, inventors have for years endeavoured to enhance the solvent powers of the solvent which they have selected by some electrolytic method. In many cases the methods suggested are quite empirical and indeed wholly useless. Thus it has been proposed to use an ordinary process of amalgamation, and to make the mercury the cathode of an electrolytic cell. The most that could be expected of such a proceeding is that the surface of the mercury might be kept clean, and therefore in a better condition to dissolve gold; the operation, if effective, is similar to the addition of a little sodium to the mercury, which is frequently practised, and tends to prevent the mercury "sickening," *i.e.* becoming coated and unfit to act as a solvent. There are obviously great difficulties in devising a workable electrolytic process for the extraction of gold from its ores. Bearing in mind the fact that an ordinary paying gold ore may average 2 ounces per ton, *i.e.* 0·005 per cent., and that many paying ores are poorer than this, it is evident that it is useless to make the ore the anode in a suitable electrolyte (say a chloride) and hope to cause the gold to dissolve. Such a proceeding is impracticable, because no definite electrical connection can be made with the minute particles of gold, relatively very few and distributed through the whole mass of gangue. Thus the solvent action of the current cannot be centred on those particles which alone it is desired to dissolve. Therefore a practicable electrolytic process must consist in leaching out the ore with a solvent, depositing the gold therefrom and revivifying the solvent, and returning the solvent to extract a fresh batch of ore. The solvent may be actually prepared electrolytically, or it may be an ordinary chemical bought *ad hoc.*

ELECTROLYTIC GOLD RECOVERY

It may be said at once that there is only one electrolytic gold process in actual operation on a large scale, viz. the Siemens-Halske process. Even in this the *extraction* of the metal is accomplished by purely chemical means, a solution of potassium cyanide being used. It is the recovery of the metal from the solvent which is electrolytic. There is no reason in the nature of things why a similar electrolytic recovery process should not be applied to the treatment of liquors obtained by the extraction of gold from its ores by means of chlorine; the gold could be deposited without doubt. Simpler methods of chemical precipitation, *e.g.* with ferrous sulphate or charcoal, are, however, generally preferable.

The process of electrolytic recovery is specially applicable to the liquors from cyanide extraction for the following reason: By the electrolytic process recovery can be effected from very weak cyanide liquors which cannot be treated equally completely with zinc—the usual chemical precipitant; such weak liquors are much more economical for extraction; thus electrolytic recovery presents a considerable advantage. In short, it is the desirability of extracting gold ores with weak cyanide liquors and the necessity of devising some means for recovering the gold from these liquors which have led to the invention of the Siemens-Halske process and its modifications.

The Siemens-Halske process is carried out in a simple form of apparatus. The cyanide liquor which has been used for extracting gold from the ore, containing 0·05 per cent. (or less) of potassium cyanide and about 5 to 6 pennyweights of gold per ton, is electrolysed between iron anodes and sheet-lead cathodes. A low current density, *e.g.* 0·06 amperes per square foot, suffices, and even with this the current efficiency is extremely small. This is of little consequence, as the cost of the energy required is a mere trifle compared with the cost of the cyanide and labour in handling the ore. In fact the process is simply one for the cheap, efficient and convenient recovery of gold from its dilute solutions in potassium cyanide, and must not be judged by standards applicable to ordinary methods of depositing metals electrolytically. The weak point in the process is the difficulty of providing satisfactory anodes. It appears that in weak alkaline liquids carbon is attacked and disintegrated; platinum might serve, but its cost is excessive. Iron is used, as mentioned above, and is attacked to some extent. By the action of the cyanide it is dissolved and converted into double cyanides of iron, *i.e.* Prussian blue. To prevent this from contaminating the electrolyte, the iron anodes are enclosed in linen bags; the Prussian blue has a small commercial value. It may be reconverted into cyanide by treatment with alkali to form ferrocyanide and fusion of this body with sodium to yield cyanide, if such a series of operations be found remunerative at the present low price of cyanide. Whether this recovery be practised or not, the iron goes to waste and forms a tangible item of expense. Estimates of cost of working the process have been made and published. Their details are of importance in a work on gold extraction processes, but would be out of place here. It is sufficient to say that the cost of working the whole process of extraction and recovery is about 3*s.* per ton, out of which the cost of working the electrolytic part of the plant amounts to about 8*d.* The chief portion of this 8*d.* is expended in replacing the lead cathodes and iron anodes, the cost of power being a minor item.

It is well to make clear, and to repeat if necessary, that the electrolytic recovery of gold is a mere auxiliary to the cyanide process of gold extraction—a very useful auxiliary, but still only a subsidiary part of the process. The great advantage of the electrolytic over other processes of recovery is, as has been said above, its ability to precipitate gold from solutions weak in cyanide. This allows extraction to be performed with much weaker solutions, *e.g.* 0·05 per cent. instead of 0·5 per cent., than can be effectively employed when recovery is performed by means of zinc as the precipitant of the gold.

Modifications of the Siemens-Halske process have been devised. Thus Andreoli uses anodes of lead peroxide and cathodes of iron. The lead peroxide is said to be unattacked, and the iron cathodes are periodically stripped of their deposit of gold by immersing them in a bath of fused lead, the gold dissolving therein. The stripped plates are returned to the bath. When the lead is sufficiently enriched it is cupelled and the gold is recovered.

A process of combined extraction and recovery of gold from its ores which presents certain features of interest is that known as the Haycraft process. In this the ore is placed in a cylindrical iron vessel filled with brine and provided with a vertical shaft carrying arms from which depend carbon anodes. At the bottom of the vessel is a layer of mercury which is made the cathode. The vessel is filled with a solution of common salt, which is heated and the ore is mixed therewith, the whole being kept stirred by the revolution of the agitator carrying the anodes. It is stated that the coarser particles of gold, which are susceptible of ready amalgamation and are not easily dissolved by chlorination, sink through the electrolyte, arrive at the mercury (which is kept clean and active by its being a cathode), and are then caught. The finer gold, and that which does not easily amalgamate, is acted on by the chlorine liberated at the anodes and is dissolved as gold chloride. In course of time, as the liquid is kept agitated, this gold chloride reaches the cathode and is there decomposed, the gold being deposited in the mercury. When once caught it cannot be redissolved by the chlorinated electrolyte because it forms part of the cathode. Gradually, therefore, the ore is robbed of its gold, which is transferred to the mercury. The exhausted ore is run away together with the solution, is allowed to settle, and the solution is returned to be used with a fresh batch of ore. There is nothing in this process which is absurd or obviously impracticable, and yet it is doubtful whether it can be successfully worked. The wear of the anodes exposed both to the attack of chlorine and to the abrading action of the ore would be apt to be considerable. Some loss of mercury due to the metal being mixed with the ore by the agitation intentionally performed, and carried away with the spent ore, might be expected. Even if these difficulties were found not to be serious, it is not clear that the process possesses any distinct advantage over an ordinary amalgamation process, followed by chlorination or cyanide extraction of the tailings.

Another process of combined extraction and recovery is that known as the Pelatan-Clerici. As far as published descriptions are intelligible, the process seems to be a kind of blend of an amalgamation process, a chlorinating and a cyanide extraction method. Its merits do not appear to be commensurate with its complexity.

THE ELECTROLYTIC REFINING OF GOLD

Besides these processes for extracting gold, the electrolytic refining of gold is practised to a limited extent. This term refining applies to gold already tolerably free from impurities, and does not refer to the electrolytic parting of gold from silver or its recovery of gold-silver-copper alloys, which will be dealt with anon. The method of refining gold containing platinum practised by the Nord Deutsche Affinerie of Hamburg is said to consist in using the crude gold as anodes in a solution of gold chloride and receiving the deposited gold on cathodes made of thin sheets of the pure metal. It is evident that a process thus described would not be workable. In the first place, platinum or palladium contained in the anodes would dissolve as well as the gold in a bath of gold chloride. It might prove possible to prevent their deposition on the cathode by working with a low current density, but with a low current density the rate of refining would be low, and the weight of gold locked up in the baths would be so large that the expense of interest on the value of the metal would make the process too costly. Further, if the current density be increased in a neutral solution of auric chloride, chlorine is evolved at the anode without causing its equivalent attack. If, however, HCl or an alkali chloride be present the dissolution of the anode proceeds regularly. Apparently a chloride of the form $AuCl_4H$ (from $AuCl_3$ and HCl) is a necessary constituent of the electrolyte, the ions of which may be regarded as $AuCl_4$ and H. Applying this observation, it is found that, when an ample supply of hydrochloric acid is present in the electrolyte, a current density at the anode of 10 amperes per square dm. (about 90 amperes per square foot) may be used without causing evolution of chlorine at the anode. The electrolyte should contain 25–30 grammes of gold per litre and the voltage should be kept low, *e.g.* 1 volt, to avoid the deposition of impurities dissolved from the anode. Under these conditions the gold is deposited in a crystalline adherent condition. As in ordinary metal refining by electrolysis, certain of the impurities dissolve and are not deposited on the cathode and certain others remain undissolved and constitute an anode sludge. The usual impurities in gold of the class which is suitable for electrolytic refining are platinum, palladium, osmium and iridium (in the form of osmiridium), and silver. Of these the platinum is dissolved, but is not redeposited. It can, therefore, be allowed to accumulate in the electrolyte until the liquid contains enough to give, with ammonium chloride, a precipitate of ammonium platino-chloride, $(NH_4)_2PtCl_6$. Palladium is also dissolved, but is not precipitated by ammonium chloride. It can be recovered by precipitation with potassium iodide as the black palladous iodide PdI_2. Osmiridium remains undissolved and unattacked in the anode sludge, and silver is converted into silver chloride, which is slightly soluble in the electrolyte, containing as this does both hydrochloric acid and auric chloride. The bulk of the silver chloride remains undissolved, but the small quantity in solution suffices to yield a little silver at the cathode, which is deposited together with the gold. The proportion is, however, quite small, so that the gold ultimately obtained is 999·8 fine. A certain amount of gold is left in the anode sludge. As the process of electrolysis goes on the bath becomes poorer in gold from the gradual replacement thereof by the impurities, such as platinum and palladium, and fresh auric chloride has to be added to maintain a proper concentration of the electrolyte. It is found that the electrolysis does not proceed smoothly with the formation solely of auric chloride at the anode and the exact deposition of its gold at the cathode. Besides auric chloride, aurous chloride (AuCl) is formed at the anode. This in great measure breaks up at once thus:—

$$3\,AuCl = AuCl_3 + 2\,Au.$$

The gold is deposited at its place of origin, the anode, and forms part of the anode sludge, as mentioned above. A part, however, of the aurous chloride escapes immediate decomposition and diffuses through the electrolyte, ultimately arriving at the cathode, where it is decomposed and deposits its gold together with that from the auric chloride, which forms the chief constituent of the electrolyte. It would seem at first sight that it would be advantageous to form as much aurous chloride as possible, because a given current would deposit three times as much gold as it would if auric chloride were formed. The considerable decomposition of the aurous chloride which takes place and the consequent appearance of two-thirds of its gold in the anode sludge make the formation of the lower chloride undesirable. The use of a high current density is found to restrict the proportion of aurous chloride.

THE PARTING OF GOLD AND SILVER

Gold as obtained from its ores commonly contains a certain proportion of silver (from 10 to 50 per cent.). It may be separated therefrom by various methods of parting. One of the older processes is to fuse the gold-silver alloy with enough silver to lower the proportion of gold to 33 to 25 per cent. of the whole alloy. This alloy, being comparatively rich in silver, can be attacked satisfactorily by nitric acid, which dissolves the silver and leaves the gold untouched. A cheaper method is to part by boiling with sulphuric acid; in this case the gold should not exceed one-sixth of the whole alloy to allow free and complete attack by the acid. The same method of parting is, of course, applicable to auriferous silver even poorer in gold. These older chemical methods have now a formidable rival in the shape of an electrolytic process of parting.

If an alloy of gold and silver containing two or three times as much silver as gold is made the anode in an electrolyte of nitric acid, the silver will be dissolved and the gold left as a residual sludge at the anode. The method is equivalent to parting with nitric acid, but has this advantage, viz. that the nitric acid is not consumed. By the ordinary chemical method, not only is nitric acid used (permanently) to form silver nitrate, but also another portion of nitric acid is reduced in the course of the dissolution of the silver, thus:—

$$4\,Ag + 6\,HNO_3 = 4\,AgNO_3 + N_2O_3 + 3\,H_2O.$$

In this case two molecules of nitric acid over and above those necessary to form silver nitrate are needed for every four atoms of silver. In electrolytic parting nothing of the kind occurs. The nitric acid is only a convenient medium serving to dissolve the silver at the anode and to provide silver nitrate to be decomposed at the cathode where the silver is deposited. If the electrolysis is properly conducted, and the solution kept rich enough in silver so that hydrogen is not evolved at the cathode, no reduction and loss of nitric acid can occur. The economy which results is sufficient to cover the cost of power and plant, and incidentally reinstates nitric acid as a parting menstruum preferable to sulphuric acid, which had displaced it.

Application of this idea has been made by Moebius, whose system is used by the Deutsche Gold- und Silber-Scheideanstalt vorm. H. Rossler at Frankfort-on-Main. The Moebius apparatus consists of a set of wooden tanks containing cast anodes of the silver-gold alloy about $\frac{1}{4}$ to $\frac{3}{8}$ inch in thickness and thin sheet silver cathodes.

The anodes are enclosed in bags of filter cloth stretched on a wooden frame, the object of this arrangement being to retain the finely divided gold which separates as sludge, and to prevent it from mingling with the silver collected at the cathode. The cathodes are placed between the prongs of a wooden fork, which can be passed over their surface from end to end; the arrangement is shown in the figures.

C is the cathode of thin sheet silver attached to a stout copper rod D, which serves as its electrical connection. E is the wooden fork made of a couple of laths connected by a cross-piece, and carried by a roller F, running on the wooden rail H. The fork, one prong of which is on each side of the silver sheet, can thus be passed from one side of the vat to the other, clearing off in its passage any loose silver crystals which may be adhering to the cathode.

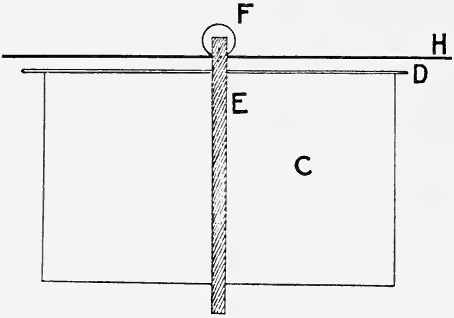

Fig. 19.

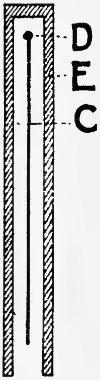

Fig. 20.

The silver crystals thus swept off fall into trays at the bottom of the vat. These trays are wooden frames covered with filter cloth, so that, when lifted from the vats, they retain the silver crystals and let the electrolyte run through. By these devices all risk of short-circuiting by the growth of silver crystals from cathode to anode is avoided; all chance of contamination of the silver with the anode sludge is also removed, and the recovery of the silver in a form easy to wash and melt into ingot form is accomplished.

The vats used are 12 feet × 2 feet, and are divided into seven compartments, each constituting a cell in which are three anodes and four cathodes. The anodes are not cast in a continuous sheet extending from one side of the cell to the other, but are composed of strips placed in the manner shown in plan in the drawing.

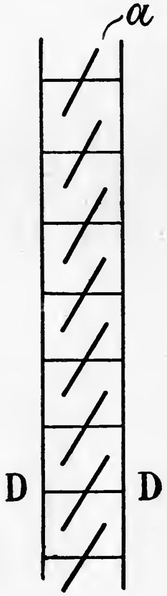

Fig. 21.

The anodes *a* are suspended on arms resting on the conductors D, D, the whole contrivance being enveloped in a bag of filter cloth as aforesaid. Fairly narrow strips of metal serving as anodes are advantageous, because the inevitable irregular dissolution of the metal composing the anode would be apt to break large fragments off a wide plate, whereas from a narrow plate pieces relatively small would be separated. Therefore the consumption of the anode material, and consequent purity of the anode sludge, will be greater with small anode elements than with large. The electrolyte used is dilute nitric acid, which soon becomes silver nitrate. It is advisable to keep the solution acid with nitric acid, so as to avoid the deposition of copper (occurring as an impurity in the silver-gold alloy constituting the anodes) with the silver at the cathodes. This may be done by making the current density greater at the anodes than at the cathodes, or by regulated addition of nitric acid. In either case a certain amount of nitric acid will be used up in the production of cupric nitrate, but the loss is infinitesimal compared with the consumption which occurs when "parting" with nitric acid is practised. In the section on the refining of copper it has been pointed out that the turnover of metal should be as large as possible compared with the stock of metal held, to minimise the interest which must be reckoned on the capital thus locked up. With precious metals this necessity becomes acute. Therefore as high a current density as possible must be employed. In practice a current density as great as 28 amperes per square foot is used, but is diminished as the proportion of copper to silver in the electrolyte increases. It is obvious that any waste of current caused by the use of a high current density is more than counterbalanced by the reduction of interest charge. The purity of the gold left as an anode sludge is not necessarily perfect. The following analyses indicate the nature and amount of the impurities:—

	Per cent.	Per cent.	Per cent.
Gold	99·954	99·947	99·955
Lead	0·036	0·043	0·030
Bismuth . . .	0·010	0·010	0·015
	100·000	100·000	100·000

If the electrolysis has been carefully conducted, the proportion of nitric acid maintained, and the current density diminished as the content of the electrolyte in copper increased, the deposited silver will be sensibly pure. The silver and copper can be ultimately recovered from the electrolyte when it has become so loaded with copper as to be no longer fit for use by ordinary chemical means. Thus the silver may be precipitated by copper plates or as chloride, and the copper in a crude form by iron. This process of recovery, however, will not need to be put into use until a large amount of silver-gold alloy has been worked up, unless, indeed, the alloy is unusually rich in copper, and therefore the waste of electrolyte will be relatively small.

The Moebius apparatus has been modified in the following way. The electrodes are arranged horizontally, the anode being separated from the cathode by a porous diaphragm. The cathode is a thin sheet of silver travelling over rollers, as shown in the figure. It deposits its silver on another travelling band, from which it is scraped at a point outside the vat. This arrangement does away with the necessity for taking out at periodical intervals the trays containing the silver crystals. The general scheme of the apparatus is shown in the figure.

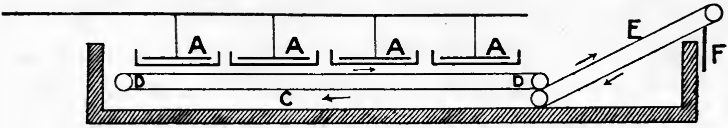

Fig. 22.

The anodes A are suspended in frames covered with filter cloth immediately above the travelling cathode C, which runs on rollers D, D. At the right-hand end of its course the cathode brushes against the travelling belt E, running in the opposite direction. On this the loose silver is deposited, and by it is conveyed outside the electrolytic tank, and is swept off by the scraper F into any suitable receptacle. One sees again here the care taken to build up the anode of small units so as to prevent the wasteful breaking up which would occur with a large plate. This point has already been dealt with (see above).

THE ELECTROLYTIC REFINING OF SILVER

The method and apparatus above described are adapted to the refining of auriferous silver as well as to the parting of gold from silver. It stands, in fact, in a position similar to that of the ordinary electrolytic process for refining copper (*q.v.*), in that the residue of gold left as an anode sludge goes a great way towards paying the cost of the refining operation. So here the recovery of a little gold will be profitable, even though much silver has to be transferred from anode to cathode in order to win it. A case of the kind is afforded by the plant of the Pennsylvanian Lead Company at Pittsburg, which is used for refining silver obtained in the usual routine of refining lead. The crude silver contains about 2 per cent. of impurities, *e.g.* lead, bismuth, and copper. The plant is of the older type, with fixed cathodes and travelling scrapers. A current density of 18 amperes per square foot is used, and an output of 88 ounces of silver per H.P. hour is obtained; the pressure required is about 1·2 volts. The plant consists of fourteen tanks, each divided into seven cells, *i.e.* in all 98 units. Of these about 84 are usually running, a certain number having to be left standing for cleaning and repairs. The gross capacity of the plant is 40,000 ounces of silver per day of 24 hours, and the actual output is about 33,000 ounces. The tanks are of wood, 10 × 2 feet × 22 inches deep, each cell being 2 feet long (across the tank) and 1 foot 5 inches wide.

There are four cathodes and three anodes in each cell. The cathodes are 22 × 13 inches and are of thin sheet silver. The anodes are 18 × 10 inches and about ½ inch thick. It is found that such stout anodes (each weighing 13–15 kilos) are, on the whole, less advantageous than are anodes about one-tenth this thickness, such as are used at Frankfort. The importance of the electrolytic refining of silver may be gathered from the fact that in 1895 the output in the United States was 10,000,000 ounces, or about one-seventh of the whole. An installation of the newer form of the Moebius process (see above) has been adopted by the Guggenheim Smelting Company, Perth Amboy, New Jersey. In this there are 48 tanks each 14 feet 3 inches × 16 inches wide × 7 inches deep. The material refined is similar to that used by the Pennsylvanian Lead Company, viz. silver containing 98 per cent. of Ag and 0·3–0·8 per cent. of gold, the balance being casual impurities. The electrolyte is a solution containing 0·1 per cent. of free nitric acid, 4–5 per cent. of Cu, and about 1 per cent. of silver. It may be assumed that the presence of the copper is inevitable but not essential, inasmuch as this metal would naturally dissolve from an impure anode, and could have no sensible influence on the course of electrolysis until its quantity became sufficient to cause it to be precipitated with the silver. A certain amount of nitric acid is used up, mostly for the dissolution of the copper and partly probably by reduction at the cathode. The quantity thus consumed is 1½ pounds per 1,000 ounces of silver treated—an almost negligible loss. The anodes are comparatively small units, viz. 15 × 3½ × ½ inches, and are in separate frames, as shown in the figure above. The silver belt constituting the cathode is 31 feet long and 15 inches in width. Its upper side is smeared with graphite to prevent too close an adherence of the deposited silver, so that the metal may be readily removed by the scrapers. These were first of hard rubber, but are now "rush-wood brushes." A current of 220 amperes at 90 volts suffices for the treatment of 24,000 ounces of silver per 24 hours. Each tank needs a pressure of 1½–2 volts. The cost of the process is reckoned at $\frac{1}{16}$*d.* per ounce of silver refined, and the capital expenditure for a plant capable of dealing with 30,000 ounces of silver per 24 hours at £1,200. It is interesting to note that the silver which is almost pure is melted down with a little scrap copper, because English buyers decline to recognise a higher approximation to purity than 998 fine. This little incident neatly illustrates the intense conservatism of the metal trades in this country, a trait familiar to all who have daily dealings therewith.

There is little to be said concerning the electrolytic treatment of silver other than what has been given in the foregoing descriptions. The usual wet methods of silver extraction from the ore, by which the silver is converted into chloride and leached out by means of brine or sodium hyposulphite, might well be found to lend themselves to an electrolytic recovery process. At present the silver is precipitated as metal, by bringing its solution into contact with copper, or as silver sulphide. No attempt seems to have been made to precipitate it electrolytically.

The alloy of zinc and silver obtained in the Rössler modification of the Parkes process, may be separated into its constituent metals by electrolysis in a solution of zinc sulphate, the zinc being deposited and the silver remaining as an anode sludge. This process is strictly analogous to the refining of argentiferous copper in a sulphate solution.

REFINING OF GOLD, SILVER, AND COPPER ALLOYS

It will be understood from what has already been said that the principle of separating copper, silver, and gold by the selective action of the current in a nitric acid bath can be applied generally to alloys having a large range of composition, provided the proportion of gold is moderate. With an alloy rich in gold, difficulty is encountered because of the imperfect solubility of the anode and its irregular consumption. Various inventors, notably Borchers and Dietzel, have devised apparatus in which the alloy is granulated and is caused to move relatively to the electrolyte, so that the anode sludge may be separated as it is formed. By these means it is hoped to overcome the obstacles mentioned above, but the processes in question do not appear to have been taken into commercial use. It is probably preferable so to dilute the refractory alloy, by fusing it with copper or silver as may be necessary, so that it may be regarded as an auriferous copper or an auriferous silver, and may be refined accordingly by electrolysis in a sulphuric acid or nitric acid bath. The difficulties inseparable from the treatment of metal in a granulated state and used as an anode will thus be avoided. Dietzel has worked out a process, which has now been in use for some years by the Allgemeine Gold- und Silber- Scheideanstalt at Pforzheim which consists in dissolving the gold, silver and copper alloy (about 5 per cent. Au, 35 per cent. Ag, and 50 per cent. Cu), as anodes in an electrolyte containing free nitric acid, prepared by the passage of a stream of copper nitrate over the cathodes in the same cell. The silver thus dissolved is precipitated chemically by the action of copper scrap in an adjacent vessel, and the regenerated copper nitrate is returned to the electrolytic apparatus. A current density of about 15 amperes per square foot is used, and a pressure of 2·5—3·0 volts. For the success of this process, it is evidently necessary to arrange a flow of copper nitrate solution over the cathode, sufficiently copious to prevent the diffusion of silver nitrate from the dissolution of the anode back to the cathode, where a portion of the silver would be deposited together with the copper.

NICKEL

Within the last few years the refining of nickel by electrolytic means has become commercially practicable. The electrolytic winning of the metal from its ores is not yet accomplished. The metallurgy of nickel is complicated and difficult, and the ordinary processes of obtaining it are comparatively expensive. Thus there is a field for its direct electrolytic production, but this field has not been cultivated vigorously and successfully.

Regarded metallurgically, nickel stands between copper and iron, presenting similarities to both. It is like copper in the comparative stability of its sulphide, and like iron in the relative difficulty of its reduction from oxide, in the high fusing-point of the metal when reduced, and in its tendency to unite with carbon and silicon, giving a crude metal analogous to cast iron. Nickel, whether obtained as a crude cast metal or from a matte of copper sulphide and nickel sulphide or from an arsenical matte, *i.e.* a speiss, is invariably impure, as is shown by the following analyses:—

	Per cent.	Per cent.
Nickel	98·39	98·68 [1]
Copper	—	0·76
Iron	0·10	0·30
Carbon	1·10	—
Silicon	0·13	0·19
Sulphur	0·26	0·07
	99·98	100·00

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[1] In these analyses the figure for nickel probably includes the

Such crude nickel may be conveniently refined electrolytically. On the other hand, alloys of nickel and copper containing approximately equal parts of the two metals, produced relatively easily by dead-roasting sulphide mattes of nickel and copper and reducing the mixed oxides, are not readily refined electrolytically. The refining of such mixtures would be best attempted by dissolving the mixed oxides in sulphuric acid, precipitating the copper electrolytically in acid solution, neutralising and depositing the nickel in similar manner. But in both cases the process is one of electrolytic reduction, and not merely of transferring the metal as such from anode to cathode; the energy required and the consequent cost would therefore be high even were there no technical difficulties, which is not to be lightly asserted.

No complete and authoritative account of the processes of nickel refining as carried out in the United States and in this country has been published. Thus it appears that nickel, not as mere plating but in thick sheets, is being deposited by Messrs. Thomas Bolton & Sons at Cheadle, and that a similar operation is accomplished by the Balbach Smelting and Refining Company in New Jersey, but in both cases details of the process are not forthcoming. Processes have been devised by Hoepfner, Rickets, and others, but have not been brought into use and exhibit no idea sufficiently novel or illustrative to warrant their description. But, although there is a dearth of positive and detailed information concerning plants actually at work, there exists a considerable store of knowledge relating to the conditions necessary for the

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percentage of cobalt which is present in most nickel ores, the only notable exception being the silicate ores of New Caledonia.

successful electro-deposition of nickel, from which can be deduced the chief precautions which must be observed in working on a manufacturing scale.

Before this matter is dealt with it may be said that there is no difficulty in depositing nickel (using nickel anodes) in thin films, as in plating. The art of nickel plating (*q.v.*) is thoroughly well understood, and a good and adherent coating of nickel can be obtained if proper care is exercised; bad nickel plating is common, but it need not be. But in refining nickel the metal must be deposited in sheets of reasonable thickness, *e.g.* ¼ to ½ inch. When it is attempted to continue the deposition of nickel in an ordinary plating bath, so as to produce not a mere film but a stout sheet, it is found that as soon as a very small thickness is exceeded the metal detaches itself from the cathode and curls up in thin flakes. These are too thin to collect and melt to an ingot with economy and ease, and thus it is impracticable to work a nickel-refining plant by simply continuing the operations of the plater. These difficulties are evident even in the most careful work, as the following paragraphs will show.

Pure electro-deposited nickel was prepared by Bischof and Thiemann, as the material to be used by Winkler in his determination of the atomic weight of the metal. In similar manner they deposited cobalt destined for the like purpose.

For the deposition of nickel the purest procurable nickel sulphate was used as the raw material. 200 c.c. of a solution of this salt, containing 32·84 grammes of Ni per litre, was mixed with 30 grammes of ammonium sulphate, 50 grammes of ammonia of specific gravity 0·905, and 250 c.c. of water. This solution of the double sulphate of nickel and ammonium, containing excess of ammonium sulphate and of ammonia, was electrolysed with a current density of 0·5 ampere per square decimetre and a pressure of 2·8 volts. An insoluble anode (of platinum) was used and the deposited nickel was received on a nickel cathode, platinum not being used for this electrode because of the difficulty frequently experienced in detaching deposited nickel from a platinum surface. When the nickel had attained a certain thickness it separated spontaneously from the cathode and curled up in thin leaves precisely as it is observed to do in ordinary plating, where the materials are not perfectly pure and the same scrupulous care in manipulation is not aimed at. The product was white, lustrous, and free from any discoloration such as might be produced by local oxidation; on heating the metal in hydrogen its weight was unaltered, proving the absence of oxide.

A similar experiment on the preparation of pure cobalt was made. A solution of the sulphate was prepared containing 11·64 grammes of Co per litre. 100 c.c. of this solution was mixed with 30 grammes of ammonium sulphate, 30 grammes of ammonia of specific gravity 0·905, and 500 c.c. of water. This solution was electrolysed with a current density of 0·6 ampere per square decimetre and a pressure of 3 volts. The cathode was of platinum, and the cobalt formed on it a coherent and fairly stout sheet, which was bright on the side in contact with the platinum and had a grey matte surface on the other. The cobalt when ignited in hydrogen lost 0·23 per cent. of its weight, corresponding with a content of 0·55 per cent. of the hydrated oxide $Co_2O_3\ 2\ H_2O$. A second experiment gave similar results, save that the deposited cobalt was received on a nickel cathode (instead of one of platinum) and stripped spontaneously from it precisely as did the nickel in the former trial.

It may be noted as a point of interest that these two metals, which may be accepted as sensibly pure specimens of nickel and cobalt respectively, differed slightly but distinctly in colour, the nickel having a slight yellowish tint, while the cobalt was of a bluish-white tone.

Another exact and important study of the electrolytic deposition of nickel, which has moreover a direct bearing on the manufacturing employment of such a process, has been made by Dr. F. Foerster. From his researches it appears that nickel can be deposited in thick coherent plates if the electrolyte be kept at a temperature between 50° C. and 90° C. The electrolyte used was a solution containing 145 grammes per litre of commercial nickel sulphate, corresponding with 30 grammes per litre of metallic nickel. The level of the liquid and its concentration were maintained constant throughout the experiment, and the electrolyte was kept well mixed and agitated. A stout nickel plate was used as the anode; it was enclosed in parchment paper to retain the anode sludge. The cathode was a thin nickel plate from which the deposited metal could readily be detached. The preliminary experiments were made with electrodes having an effective surface of 80–100 square cm., and the experiment was continued until 25–40 grammes of nickel had been deposited. It was found that with a current density of 0·5—2·5 amperes per square decimetre and at a temperature of 50° C.—90° C. good coherent deposits, bright grey or tin white in colour, were obtained. The higher the current density, the brighter and smoother was the deposit. Thus with 0·5 ampere per square decimetre, and using a solution containing 100 grammes of Ni per litre, kept at a temperature of 80° C., the deposit had a rough surface and was dull grey in colour; with a current density of 2–2·5 amperes per square decimetre the deposit was silver white and could be obtained in plates 0·5–1 millimetre in thickness. Frequently it was noticed that the deposit exhibited certain rugosities, produced by the circumstance that a stream of hydrogen had been given off for some time at particular spots, and thus had caused a local irregularity in the current density. This trouble could be avoided by stirring the electrolyte so that the evolution of hydrogen did not persist at any given point for an appreciable time. A larger scale experiment was made under similar conditions, and as much as 0·5 kilo of electrolytic nickel was prepared. In this case the cathode had an area of 2 square decimetres; the electrolyte contained 100 grammes of Ni per litre and was kept at 60° C. The current density employed was 1·5–2 amperes per square decimetre.

The nickel deposited was particularly tough; the thickness of deposit is not stated, but from the weight given and the area of the cathode it can be calculated as slightly smaller than 3 mm., say $\frac{1}{8}$ inch. A plate of such thickness could be melted down without serious loss, though for manufacturing purposes an even more substantial deposit is desirable. Nevertheless the achievement of Dr. Foerster is remarkable, and may well embody the only secret worth guarding in the electrolytic refining of nickel as now practised with much mystery in this country and elsewhere. Armed with this knowledge, an enterprising manufacturer should have no great difficulty in refining nickel electrolytically with commercial success.

An important piece of collateral evidence supports the belief that the electrolytic nickel now available as a marketable commodity is prepared by processes substantially identical with that set forth above. Dr. Foerster found that iron and cobalt, the characteristic impurities of commercial electrolytic nickel, were also present in his own product. The study of the degree of purification effected by the electrolytic refining of nickel is particularly instructive, and should suffice to dispose of, once for all, the ridiculous belief that a metal prepared by electrolysis is necessarily and *ipso facto* of unusual purity. The anodes used by Dr. Foerster had the following composition :—

	Per cent.
C	0·40
Si	0·02
Cu	0·10
Fe	0·43
Co	0·14
Mn	0·02
Nickel (by difference)	98·89
	100·00

Of these all but the iron and cobalt were absent from the electro-deposited nickel, which contained as impurities 0·3 per cent. of iron and from 0·1 to 0·3 per cent. of cobalt. How considerable is the tendency for iron and cobalt to be deposited together with nickel is shown by the fact that an electrolyte containing 0·087 gramme of iron and 0·82 gramme of cobalt per 100 grammes of nickel contained, after it had been used for refining, 0·034 gramme of iron and 0·064 gramme of cobalt, being thus actually impoverished in these impurities, which were deposited in the first 100 grammes of nickel thrown down on the cathode, the metal containing as much as 0·38 per cent. of iron and 1·6 per cent. of cobalt. On continuing the electrolysis a further deposit of 400 grammes of nickel was obtained, containing 0·20 per cent. of iron and 0·57 per cent. of cobalt, these figures corresponding closely with those for the anode used in this particular experiment, viz. 0·27 per cent. of iron and 0·60 per cent. of cobalt. Of these two impurities the iron alone is objectionable for most purposes. Both it and cobalt can be eliminated by adding to the electrolyte an organic acid, such as tartaric acid, and electrolysing with a low current density (0·3–1 ampere per square decimetre), whereby the iron is deposited, the nickel remaining in solution. On increasing the current density above 1 ampere per square decimetre the nickel is deposited. Such a method, although it might be employed to purify an electrolyte periodically, could not well be used for the continuous refining of nickel, *i.e.* the transference of the metal from an anode of the crude material to a cathode whereon it was to be deposited pure.

When a solution of nickel chloride was used instead of the sulphate, the results were less favourable, the deposit stripping at the ordinary temperature and a basic salt being deposited on the cathode when the electrolyte was used hot. A better effect was obtained by using a solution containing about 2·5 grammes of free hydrochloric acid per litre. Another trouble when using the chloride solution is that the envelope of parchment paper round the anode is quickly attacked ; it is better to dispense with this diaphragm and to trust to the natural tendency of the residue of the anode to stick together, which it does fairly well if not disturbed by the stirring of the solution. Regarding the attack of the envelope round the anode an interesting observation was made. When the parchment paper was replaced by linen, so much organic matter went into solution that the electrolyte had a caramel-like smell, and yielded metal containing 0·6 per cent. of C, and of dark colour, brittle, and tending to curl off the cathode. When once the electrolyte was thus spoiled it continued to yield bad deposits, even after the organic envelope had been removed, and had eventually to be thrown away.

The successful attempt recorded above to deposit nickel in plates of fair thickness from solutions of its sulphate when a nickel anode was used and the process was therefore one of refining and not of winning, prompts the belief that it may be practicable to deposit nickel similarly from a sulphate solution, using an insoluble anode. Should this be feasible, nickel could be extracted by leaching out a roasted matte containing nickel sulphate, and, after removal of impurities likely to be deposited together with the nickel, electrolysing this sulphate solution with carbon anodes and thin sheet nickel cathodes. Experiments made with a solution of nickel chloride gave unsatisfactory results, because the carbon anodes gradually dissolved and contaminated the electrolyte so considerably that the deposited nickel soon became grey and brittle. On account of this action, and because of the chlorine finding its way to the cathode to some extent, the output was not more than 70 per cent. of that calculated from the current. A sulphate solution was not tried, but it is probable, from the known behaviour of carbon anodes in sulphuric acid, that an equally serious attack and consequent dissolution of carbonaceous matter would occur. Anodes of lead peroxide would possibly serve, but have not yet been tried. It is of course evident that, as in the electrolysis of a solution of nickel salt with an insoluble anode energy must be supplied, not for the mere transport of the nickel but for its reduction to metal, the expenditure of electrical energy per unit weight of nickel deposited will be greater than that necessary simply for its refining. This question has been discussed fully with regard to copper (p. 67), and need not be recapitulated here. It may be noted in passing that in this industry, as in other electrolytic manufactures, carbon electrodes of high quality are much needed; those at present made are generally inferior to good retort carbon.

COMMERCIAL ELECTROLYTIC NICKEL

In 1896 the Balbach Smelting and Refining Company, of Newark, New Jersey, began working up crude nickel bought from the Orford Copper Company, which is engaged in smelting the nickel ore from Sudbury, Ontario. The composition of the crude nickel and that of three samples of the electrolytically refined metal are given below.

CRUDE NICKEL.

	Per cent.
Ni	95·00
Cu	0·55
Fe	0·75
Si	0·25
C	0·45
S	3·00
	100·00

REFINED.

	I.	II.	III.
	Per cent.	Per cent.	Per cent.
Ni . . .	99·48	99·17	99·20
Cu . . .	0·10	Trace	0·14
Fe . . .	0·48	0·66	0·58
S . . .	0·29	0·03	0·03
	100·35	99·86	99·95

The content of cobalt (which was probably present) is not given. The presence of iron in considerable quantity recalls the fact that Dr. Foerster found that metal to be retained persistently when crude nickel containing iron is refined electrolytically. The process used is kept secret. It may be either electrolysis in sulphate solution, renewed as the impurities (notably iron) accumulate, or, as suggested by Titus Ulke, a cyanide method. In this case iron and cobalt would tend to form complex stable cyanides, while nickel would form ordinary double cyanides readily decomposed on electrolysis. Against this idea must be set the fact that a cyanide bath is never used in nickel plating, and it is doubtful whether a satisfactory deposit can be obtained therefrom. A sample of electrolytic nickel, made by Messrs. Gustav Menne & Co., of Siegen, Germany, was found to contain 0·12 per cent. of lead, an impurity due to the fact that it had been prepared by the electrolysis of a solution leached from a complex matte and not from a crude nickel free from such extremely alien impurities. In quality it was inferior to the American product.

A plant has been put down by the Canadian Copper

Company, of Cleveland, Ohio, to refine bessemerised matte of the composition:—

	Per cent.
Ni	40·0
Cu	43·4
Fe	0·3
S	13·8
	97·5

This matte also contains precious metals, viz.: Ag, 0·0218 per cent.; Au, 0·0003 to 0·0006 per cent.; and Pb, 0·00155 per cent. The method proposed is as follows: The matte may be used as such, or may be worked up to a copper-nickel alloy. It may be remarked that, having regard to general experience in the use of matte anodes, successful refining of a matte with even relatively little sulphur is unlikely. It may be assumed, therefore, that an alloy of about 50 per cent. copper and 50 per cent. nickel would be the raw material. This is cast into anodes and electrolysed in a bath of copper sulphate acid with sulphuric acid. The electrolyte is kept at a temperature of 30° C. = 86° F., and is well circulated throughout the process. A current density of 2·2 amperes per square decimetre is used at the beginning of the operation, and is dropped to 0·8 ampere towards the finish. Copper is dissolved and redeposited, while nickel and a little iron remain in solution. As the electrolysis proceeds and the anodes are used up, the electrolyte gets poorer in copper, and on this account the diminution of current density becomes necessary. When the bulk of the copper is deposited nickel tends to be thrown down, (if the voltage is high enough). The rest of the copper can be recovered, and the electrolyte thus freed from copper by electrolysing with a small voltage and low current density, using an anode of nickel unalloyed with copper; but in practice it is cheaper to precipitate the copper with sulphuretted hydrogen. The solution then contains nickel together with a little iron as sulphates, and can be electrolysed with insoluble anodes to recover nickel. It is to be noticed that the published account, as is usually the case, stops short just at the interesting part. The point is, how best may nickel be deposited from a sulphate solution, using an insoluble anode? The answer is not forthcoming from the description made public.

COBALT

No cobalt is prepared electrolytically on a commercial scale. The foregoing pages contain references to such experiments on its deposition as are likely to be of value if its electrolytic preparation should need to be undertaken. There is no immediate prospect of any requirement of this kind, because metallic nickel is for most purposes as well suited as cobalt and is greatly cheaper. With the present relative abundance of the two metals the use of cobalt is almost wholly confined to those purposes, *e.g.* the preparation of smalt and of glazes, in which the unrivalled blue of its silicate is turned to account. The only case in which the metal itself is preferable to nickel is in plating (*q.v.*), the cobalt being stated, with some authority, to give a better coating than does nickel.

TIN

ALMOST the sole source of tin is the native oxide SnO_2. This body is relatively heavy, and can be separated from the ores containing it by mechanical processes of concentration. The reduction of the oxide thus separated from the gangue can be effected without difficulty by means of carbon. The resulting tin can also be refined to a degree of purity sufficient for most purposes by ordinary dry methods. Thus it comes about that there is little prospect of superseding the existing method of winning tin by any electrolytic process. In the first place, stannic oxide is insoluble in any agent that could be used for leaching the ore. Thus mechanical concentration is inevitable. Given the concentrated ore, its reduction to tin by carbon is by far the simplest method of dealing with it. The only stage of the process in which electrolytic means might be usefully employed is in refining the crude tin. No serious attempt to do so appears to have been made, although there is reason to experiment in this direction, because commercial tin is often comparatively impure (containing 0·5–1 per cent. of foreign metals), and because in the manufacture of certain of the alloys of tin (notably gun metal) a pure metal would be distinctly preferable to one containing miscellaneous alien substances. Nevertheless, as a matter of fact, electrolytically refined tin has no industrial existence.

The case is somewhat different with scrap tin plate.

Articles such as household utensils, cans and boxes for preserved goods and the like are usually made of what is known colloquially as "tin," by which is meant tinned iron. The manufacture of tin plate, *i.e.* sheets of iron coated with tin, consumes the major part of the world's output of tin. The metal is applied in as thin a film as possible, because it is relatively expensive, but the aggregate quantity thus used is very large. It has long been an object with inventors to devise a means whereby the tin from used tin plate may be recovered. The advantages to be derived from an efficient process of recovery are palpable. The used tin plate (as "tins" and the like) is a waste product; the tin to be recovered (amounting to about 5 per cent. of the weight of tin plate) has a fairly high price, *e.g.* £60–£80 per ton;[1] and the iron stripped of tin has a certain market value. The value of the iron is smaller now than heretofore, because ordinary tin plate is made from ingot iron ("mild steel"), whereas puddled iron of good quality was formerly used. In spite of this the scrap clean and free from tin would be saleable. If imperfectly stripped and retaining some tin its value would be smaller, because of the possible incorporation of this tin with the iron (to its detriment) on melting the latter.

In practice the prospect of remunerative treatment of tin scrap is less bright than would appear from this statement of fact. In the first place, the raw material (old "tins") is hardly worth special collection, and must usually be retrieved from dust bins and rubbish heaps. The supply is apt to be uncertain. Their recovery is therefore somewhat expensive. Next, the

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[1] The fluctuations in the price of tin are large, owing chiefly to speculative manipulations of the market.

recovered tins are covered with miscellaneous dirt, and have to be completely cleaned before treatment. Thirdly, they are bulky and troublesome to handle. Fourthly, they are extremely inconvenient to strip electrolytically. Thus it has come about that most of the methods which have attained even a qualified success have been concerned with the treatment of the scrap, consisting of the cuttings from new tin plate left as a waste material from the manufacture of vessels for tinned goods. These are clean and of such a shape as to be capable of being packed in a space which is not excessive, and as they are a factory bye-product, and do not need collection, one cause of expense disappears.

Various methods have been proposed for treating tin scrap. The scrap may be made the anode in an electrolyte of dilute sulphuric acid, and the tin may be received on lead or copper cathodes. Unfortunately, the tin dissolves less readily than the iron, and as soon as the latter is exposed its dissolution proceeds rapidly, and the bath becomes full of ferrous sulphate, which is of low commercial value. The exposure of the iron also tends to protect the remaining tin, and the iron scrap is left imperfectly stripped, and therefore of smaller value than if clean. The tin is deposited from acid solutions in a spongy or pulverulent form, and its fusion to form an ingot involves loss. Some market may, however, be found for various salts of tin, notably stannous chloride (made by dissolving the tin in hydrochloric acid), which is used as a mordant. A more rational method is to make the tin scrap the anode in a solution of caustic soda, in which the metal is soluble, forming sodium stannate; the iron remains substantially unattacked. The stannates are, however, somewhat unstable, and are easily decomposed by carbonic acid, so that solutions exposed to the air are apt to deposit tin as oxide. This tendency and their poor conductivity have apparently prevented their successful use. It may be noted that it is possible to strip tin plate both by acid and alkaline solvents without the aid of a current, and that, if the purely chemical method fails, there seems to be no valid reason why an electrolytic method should serve better. The difficulties of collection, cleaning, and handling mentioned above probably account for the comparative failure of all methods of recovery, and the remunerative utilisation of old "tins" and tin scrap is likely long to be a pet problem for the professional inventor.

Attempts have been made to recover the tin from tinned lead scrap. The lead sheet is often provided with a coating of tin by covering thicker lead plate with tin and rolling this down to the required gauge. Such tinned lead sheet is used largely for bottle capsules. Recovery of tin from these is easy, because, unlike iron, lead is electro-negative to tin, and, on making the scrap tin the anode in an electrolyte of sulphuric acid, the tin dissolves, leaving the lead unattacked. Both tin and lead are thus readily separated and recovered. To the difficulty of collection referred to above is to be ascribed the failure to base an industrial process on these principles.

ANTIMONY

The chief ore of antimony is its sulphide, which is usually reduced to metal by dry metallurgical processes. These processes are relatively simple, not unduly expensive, and suffice to produce a metal of sufficient purity for most purposes. It is clear, therefore, that the need for an electrolytic process is not great. The chief advantages that can be claimed for a process of this kind are the possibility of treating ores too poor to pay when smelted by the ordinary methods and the feasibility of reducing the metal by water power in inaccessible districts where fuel is scarce. Such plain economical considerations are too often overlooked when electrolytic methods are invented or discussed.

At present only one process has succeeded in producing metallic antimony on a commercial scale. It is worked by Siemens & Halske, and the details of manufacture are not publicly known. There is, however, a patent of the same firm dealing with the same matter, and it is probable that this patent describes and protects the process now being worked. The leading principles of the patented process are as follows: Antimony ore containing the metal as its sulphide (Sb_2S_3) is leached with a solution of sodium sulphide. The antimony sulphide dissolves, leaving the siliceous gangue. The solution containing the antimony is then passed through the cathode compartments of a series of electrolytic cells, and is deposited on iron cathodes. The anode compartments contain a solution of common salt in which are carbon anodes; chlorine is given off at these, and is utilised for the manufacture of bleaching powder or chlorate. The solution passing from the cathode compartments consists chiefly of sodium sulphide containing little or no antimony, and is used to leach a fresh portion of ore. The object of thus working with a porous diaphragm and producing a bye-product (chlorine) is to avoid the oxidation of the leaching solution, viz. the sodium sulphide, which is inevitable if the electrolysis is conducted in an undivided cell and the sulphide solution comes in contact with the anode.

The antimony prepared by the Siemens-Halske process is in the form of plate about 2 mm. in thickness and having a ridgy and warty surface, the appearance of which recalls in some measure that of some samples of electrolytic copper. The metal is nearly pure, and can, if necessary, be further refined by the ordinary process of dry refining, which consists in fusing the metal with a flux composed of crude potash melted with antimony sulphide. This flux contains potassium sulphide, which removes from the antimony any residual antimony sulphide, forming a thioantimonite. For most purposes, however, the antimony is pure enough in the state in which it is deposited. The following analyses show the quality of the unrefined electrolytic antimony, of the same metal after refining, and of refined antimony prepared by the ordinary dry process:—

	Unrefined electrolytic antimony.	Refined electrolytic antimony.	Refined antimony made by dry process.
	Per cent.	Per cent.	Per cent.
As	—	—	Trace
S	0·288	0·0001	0·1000
Fe	0·008	0·0046	0·0100
Pb and Cu . .	Trace	0·0084	0·0303
Na	0·014	—	—
Sb	99·690	99·9869	99·8597
	100·000	100·0000	100·0000

It will be seen that unrefined electrolytically prepared antimony is almost pure, save for a little sulphur, doubtless arising from the fact that the metal is deposited from a solution rich in that element. Also, that refined electrolytically prepared antimony compares favourably with that made by the ordinary dry process. It is noteworthy that antimony of good quality which has been cast in ingot form shows its crystalline character by a well-marked stellate appearance. This appearance is known as the "star" of antimony, and is usually accepted as an index of purity. It is evident that in the case of electrolytically prepared antimony, stripped direct from the cathodes and not melted and cast, this "star" is absent; it is replaced by the peculiar warty surface referred to above, which may also be taken as an indication of the source of the metal and as a guarantee of good quality. Although the Siemens-Halske process is the only method by which antimony has been successfully prepared on a commercial scale, other methods have been devised and to some extent worked out. Of these Borchers' process may be mentioned. Borchers has studied the conditions of precipitation of antimony from solutions of its sulphide in sodium sulphide, and has designed a plant as the result of his experiments. It does not seem, however, to have been tried on a manufacturing scale. Using solutions of antimony sulphide (Sb_2S_3) in sodium sulphide (Na_2S) with and without caustic soda,[1] and working without a diaphragm, he found that the whole of the antimony could be deposited, but that at the anode there was not merely a separation of sulphur (and consequent formation of polysulphides), but an oxidation of the sodium sulphide to thiosulphate (hyposulphite). On account of this action the sodium sulphide solution would decrease in effectiveness as a solvent for fresh portions of antimony sulphide, and the cyclical working of the process would be impaired. A point would soon be reached at which the sulphide solution, exhausted of its antimony, could no longer dissolve a fresh quantity, and it would have to be replaced by a new supply of sodium sulphide. Another difficulty of the process is the fact that the antimony is deposited in the form of powder, and has to be collected and fused before it is marketable. Having regard to these fundamental defects inherent in the method, a discussion of the merits of the plant proposed to work it is evidently superfluous.

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[1] Two to three per cent. of common salt was added to improve the conductivity of the electrolyte.

ZINC

Zinc is a metal the winning of which by electrolysis presents peculiar advantages. Its refining, on the other hand, can be best accomplished by non-electrolytic processes.

The commonest ore of zinc is blende (zinc sulphide), from which zinc can be extracted by the usual metallurgical methods only after the ore has been roasted and a crude zinc oxide produced. This oxide, on heating with carbon, is reduced, yielding metallic zinc. To effect the reduction a temperature of about 1,300° C. = 2,372° F. is required; the boiling-point of the reduced metal is, however, only 930° C. = 1,706° F. From this it follows that, when a mixture of zinc oxide and carbon is heated to a temperature sufficiently high to reduce the oxide to metallic zinc, the metal is generated as vapour, and cannot be directly run down to a regulus, as can less volatile metals, *e.g.* copper and iron. In consequence of this the winning of zinc by ordinary metallurgical methods is always effected by distilling a mixture of the oxide and carbon (powdered coke or non-caking coal) in retorts of refractory fireclay. (The bearing of this disquisition on the electrolytic winning of zinc will be seen immediately.) The reduction of zinc oxide to zinc is represented by the equation—

$$\mathrm{ZnO} + \mathrm{C} \rightleftarrows \mathrm{Zn} + \mathrm{CO},$$

and absorbs 56 Cal per gramme equivalent of zinc obtained. This quantity of heat has to be supplied to the charge through the walls of the retort, and even the best methods of heating for this purpose are so wasteful that the quantity of fuel used vastly exceeds the calculated minimum.

Another large cause of expense is the renewal of the somewhat costly and fragile retorts in which the distillation is conducted. From a consideration of these facts it is evident that there is ample room for an economical method of winning zinc from its ores, whether by electrical or other means.

Recognition of this circumstance induced the Brothers Cowles about the year 1882 to attempt to distil zinc in an electric furnace (see section on aluminium, consisting essentially of a fire-brick box into which projected two carbon electrodes. These were surrounded by the charge of carbon and ore to be reduced, and between them an arc was formed. The principle underlying this endeavour is perfectly sound in that by means of an apparatus of this kind it is possible to apply heat, not through a refractory envelope, but in the very heart of the charge to be heated, which may be surrounded by a non-conducting box of the most massive and efficient design, so as to confine the heat to the real seat of operations. But though the heat is economically used it is applied in a costly form, viz. as electrical energy, and at the present time no successful attempt has been made to manufacture zinc in this manner. The question of the practicability of realising the original idea of the Brothers Cowles might well repay investigation.

Putting this aside as a matter for inquiry and not an accomplished process, one finds that already there exists a growing industry in the production of electrolytic zinc. Zinc is a metal so electropositive, and needing so much energy for its reduction, that when aqueous solutions of its salts are electrolysed there is a tendency to produce hydrogen instead of zinc at the cathode. Moreover, from most zinc solutions the metal is deposited in a spongy and incoherent condition, unless special conditions, *e.g.* as regards acidity and current density, are fulfilled. These circumstances have rendered the device of a workable method for depositing zinc electrolytically peculiarly difficult.

As mentioned at the beginning of this chapter, zinc is not *refined* electrolytically. In the event of a demand for especially pure zinc arising, it could at once be met with ease by the fractional distillation of ordinary commercial zinc *in vacuo*—a process which can be accomplished at a temperature but little above the softening-point of glass, *i.e.* at a barely visible red heat. The description of electrolytic processes for zinc will, therefore, relate chiefly to those concerned with the winning of the metal from its ores.

PRINCIPLES OF ELECTROLYTIC DEPOSITION OF ZINC

Several conditions must be carefully observed in order to obtain a coherent deposit of zinc. Many inventors and investigators have laid down precautions more or less empirical, but their instructions need not be considered, because the whole subject has been investigated in the most thorough manner by Mylius and Fromm (*Zeits. f. anorganische Chemie*, 1895, p. 144), and from the data which they have established by small scale experiments the working conditions in manufacture can be deduced.

It must not be supposed that such knowledge can be translated at once to the works with a certainty of immediate success; nothing but close study of the actual working of a process on a commercial scale will suffice; nevertheless the guiding principles which must be regarded are established, and each manufacturer must apply them for himself. This may seem cold comfort to the technologist, but it is all he can expect to get, for, as a matter of fact, the few processes for the electrolytic reduction of zinc which are working successfully are guarded as secrets in the details. It is not to be supposed that in these there is any great divergence from what is common knowledge, but it is fair to conclude that by attention to numerous small points of working the manufacturers using these processes have been able to apply remuneratively the principles about to be discussed, and it is manifestly unreasonable to expect them to make public what has been acquired at the cost of much time, money and labour.

The chief difficulties in the electrolytic deposition of zinc from a solution of its sulphate are:—

(1) The evolution of hydrogen at the cathode instead of the deposition of zinc there.

(2) The precipitation of the zinc in a spongy condition.

As might be predicted, the evolution of hydrogen is most apt to occur when the electrolyte is poor in zinc, for in that case there are likely to be too few zinc ions at the cathode at any given instant, and the current is thus occupied in the liberation of hydrogen from the water or sulphuric acid which is relatively abundant in the neighbourhood of the cathode. The electrolyte should, therefore, be fairly concentrated, *e.g.* should contain at least 10 per cent. of the crystallised salt

$ZnSO_4 7 H_2O$. Next, it should be neutral or slightly acid. If unduly acid, hydrogen as well as zinc will be liberated at the cathode. Thirdly, a high current density should be used, *e.g.* 1–2 amperes per square decimetre, *i.e.* about 9–18 amperes per square foot. With a concentrated electrolyte the current density may be considerably increased and good adherent deposits may be obtained. Fourthly, the electrolyte must not be basic, *i.e.* it must contain no zinc oxide over and above that necessary to form a neutral salt. Neutral zinc salts dissolve small quantities of zinc oxide, and from such solutions spongy zinc is precipitated. It must also contain no oxidising impurity. These last two conclusions were arrived at by Mylius and Froman from a systematic study of the character of the spongy zinc which is often deposited. It has been suggested that the formation of this spongy zinc is caused by the presence of a hydride (ZnH_2). There is no evidence of this, and against it is the fact that the spongy deposit always contains zinc oxide or a basic salt of zinc, which can be detected and isolated by dissolving the metallic zinc in mercury. The quantity of oxide thus left is under 1 per cent., but is sufficient to produce sponginess. When to a solution of a zinc salt a small quantity of an oxidant, *e.g.* hydrogen peroxide or zinc nitrate, is added, such a solution on electrolysis yields spongy zinc; under identical conditions of temperature, concentration, current density and the like, a solution free from these oxidising impurities gives a normal deposit of coherent reguline zinc. Curiously enough the presence of a small quantity of arsenic or antimony in the electrolyte will cause the formation of spongy zinc; the *rationale* of their action is obscure, but the observation is important in that it indicates that the electrolyte must be carefully purified for the successful deposition of zinc on a commercial scale. The fact that the presence of zinc oxide induces the deposition of spongy zinc explains why a basic electrolyte is peculiarly apt to produce an unsatisfactory deposit; also, seeing that a strong solution of a neutral zinc salt, such as the sulphate, will dissolve more zinc oxide than will a weak solution, it may be expected that in a strong solution a slight excess of base will be less detrimental than in a weak solution. Experiment shows that that is the case.

Foerster and Günther have made a study of the conditions necessary to be observed in order to obtain a good coherent deposit of zinc from solutions of its chloride. This study forms a useful supplement to the work of Mylius and Fromm, cited above. The electrolysis of zinc chloride in aqueous solution may prove applicable in metallurgical practice, and a knowledge of its principles cannot be neglected. As in the case of the sulphate, the chief difficulty is in obtaining the metal in a reguline and coherent condition. There is an inconvenient tendency to form spongy deposits. In the experiments about to be described, Silesian zinc of exceptional purity, containing not more than 0·03 per cent. of lead and 0·05 per cent. of iron, was used as the anodes. The cathode was a piece of polished sheet zinc. A solution of zinc chloride was used as the electrolyte, and was tried neutral, acid, and basic in turn.

It being established that the production of spongy zinc is primarily caused by the presence of zinc oxide, it appears probable that deposition of zinc of good quality is more likely to be attained with a solution of zinc chloride than with one of zinc sulphate, because zinc oxide is more soluble in the former, and is therefore less likely to make its appearance at the cathode and impair the quality of the zinc there precipitated. This is borne out by experiment, for a solution of zinc chloride containing 54·6 grammes of Zn per litre when electrolysed with a current density of 1·4 amperes per square decimetre continued to give a good deposit until the electrolyte became so basic as to form a precipitate of zinc oxychloride. This occurred when there was present for every 14 molecules of $ZnCl_2$ 1 molecule of ZnO in solution. An obvious advance on this is to use a slightly acid solution of zinc chloride to hinder the formation of a basic chloride. But when the electrolyte is acid, hydrogen as well as zinc appears at the cathode, current is wasted, and the deposit becomes uneven because of the local irregularities of current density, due to bubbles of hydrogen, causing spots and patches on the surface to be inaccessible to the electrolyte while they persist there. A device which has been employed by Mylius and Fromm can be resorted to for the repression of this hydrogen. It consists in placing a small independent anode near the cathode and passing by its means into the electrolyte a current sufficient to evolve enough chlorine to combine with the objectionable hydrogen. By adopting this plan a good deposit of zinc can be obtained in a slightly acid solution of zinc chloride. This observation is specially worthy of remark, because it probably explains the attempts that have frequently been made, as in the Ashcroft process (*q.v.*), to obtain good deposits of zinc by the use of an oxidising agent. These attempts have occasionally succeeded, although usually based on erroneous assumptions, *e.g.* that the sponginess of the deposited zinc was due to the pressure of a zinc hydride. We now see the true reason, viz.

that the use of an oxidant in regulated amount allowed an acid electrolyte to be used (thus avoiding the deposition of a slightly oxidised, and therefore spongy, zinc), while at the same time suppressing the hydrogen, which is liable to cause local irregularities of current density, and therefore rough, warty deposits.

As might be premised from the work recorded above, a basic solution of zinc chloride, if not containing so much oxide as to make it turbid, may give good deposits at first; as the process goes on it becomes more basic and spongy zinc begins to be formed.

In these experiments it was noticed that before the electrolyte became so basic as to be turbid the deposit began to change in character, forming long growths (apparently of compact reguline zinc) from the edges of the cathodes.

It must not be supposed that zinc oxide[1] in the electrolyte is the only material capable of causing the formation of spongy zinc. Various foreign metals in the electrolyte have the same effect, and on this account the industrial electro-deposition of zinc, especially from solutions obtained by leaching out complex ores, will always be a somewhat delicate operation, requiring care and skilled supervision.

The energy required to reduce zinc sulphate electrolytically to metallic zinc can be readily computed. The decomposition represented by the equation—

$$ZnSO_4Aq = Zn + H_2SO_4Aq + O$$

requires for its realisation the expenditure of 106 Cal, *i.e.* 106 Cal must be provided for winning 65 grammes

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[1] Later researches throw doubt on the belief that a spongy deposit is necessarily caused by zinc oxide, for in a solution containing excess of caustic alkali, and therefore capable of dissolving zinc oxide, spongy zinc may form.

of zinc. This corresponds with 2,564 H.P. hours per ton; therefore the theoretical output of zinc per H.P. year (365 days of twenty-four hours each) is 3·42 tons.

Now the critical voltage for the decomposition of zinc sulphate (calculated from its heat of formation in manner similar to the example already given) is 2·25 volts. To obtain the output per H.P. year given above it would be necessary to work at the critical voltage. But in practice a voltage of about twice this, viz. 4·5 volts, would probably be required. Further, having regard to the tendency for the current to reduce hydrogen instead of zinc, the current efficiency is not likely to be more than 80 per cent.; the voltage efficiency is 50 per cent., therefore the energy efficiency is $\frac{80 \times 50}{100 \times 100}$ per cent. = 40 per cent. It follows that the output per H.P. year is not likely to exceed 1·368 tons. With cheap water power, costing say £2 10*s.* per H.P. year, the cost of energy for refining 1 ton of zinc is £1 16*s.* 6*d.* With steam power at ¼*d.* per H.P. hour, *i.e.* £9 16*s.* per H.P. year, the cost for 1 ton of zinc would be £7 3*s.* 3*d.* The selling price of zinc being about £20 per ton, it is clear that the cost of electrolytic reduction by steam power would be a large part of the whole value of the product, and that the margin for such heavy expenses as roasting, extracting, maintenance of plant—to say nothing of the cost of the zinc in the ore—is inconveniently small. It is only where very cheap water power is available that the electrolytic winning of zinc *per se* may be practised with a fair prospect of success. The case is somewhat different where the zinc is, as it were, a bye-product. Processes falling under this head will be dealt with below.

PROCESSES FOR THE PRODUCTION OF ELECTROLYTIC ZINC

Usually these processes have been designed to produce zinc as a bye-product of some other manufacture, and not for the winning of zinc from its ores as the principal object. One of the chief causes of the various attempts which have been made to invent a workable electrolytic process for zinc is the growing necessity of treating mixed sulphide ores, consisting of blende and galena (zinc sulphide and lead sulphide) so intimately associated that their separation by any method of mechanical "dressing" is well-nigh impracticable. Such ores are also difficult to smelt by the ordinary processes, and many plans have been proposed to treat them by wet extraction methods.

THE SIEMENS-HALSKE PROCESS

Ore consisting essentially of lead sulphide, zinc sulphide and gangue, and containing about 20 per cent. of zinc, 30 per cent. of lead, and 20 ounces of silver per ton, is roasted at a low red heat so as to oxidise the sulphides and convert them into oxides and sulphates.

It is desirable that the temperature should be kept low, in order that a large proportion of the sulphides should be converted into sulphates instead of oxides.

This requires a long time and much stirring of the ore. Altogether this stage of the process, which sounds simple enough, is rather difficult and expensive. The roasted ore is extracted with dilute sulphuric acid (about 10 per cent. strength), and the zinc is dissolved as sulphate, leaving the lead (also as sulphate) as an insoluble residue. This is melted by the usual dry methods. The bulk of the silver, which is always present in ores of this class, is also left with the lead, though some may go into solution. Of course the value of the silver is an important part of the whole value of the ore, and its careful extraction and recovery are necessary to make the process remunerative.

The solution of zinc sulphate needs to be purified from iron, copper, and other foreign metals by ordinary chemical methods, such as limited precipitation with lime and chloride of lime. The preparation in this manner of a tolerably pure solution of zinc sulphate is by no means an easy matter. These non-electrolytic parts of the process are the cause of quite as much difficulty as the electrolysis itself. When a satisfactorily pure solution of zinc sulphate has been obtained it is electrolysed, lead anodes being used and thin zinc cathodes. The conditions, stated above, necessary for obtaining a good coherent deposit of zinc must be carefully observed. In this process zinc is not merely transferred, it is actually reduced from the solution of its sulphate, and the electrolyte becomes more acid as the reduction proceeds. When the acidity is so great as to cause the evolution of an unduly large amount of hydrogen at the cathode, the solution is run off and used again for extracting wasted ore. Thus there is in circulation a large quantity of a solution of zinc sulphate acid with sulphuric acid, which is alternately robbed of a portion of its zinc and again supplied with an equivalent amount. But in each cycle of operations the solution acquires impurities from the roasted ore, and these must be eliminated before it can be used again as an electrolyte. The process has been tried by the Smelting Company of Australia, at Illawarra, in New South

Wales, but no information as to its success has been published. Its weak points are sufficiently indicated in the foregoing description.

THE ASHCROFT PROCESS

This process is designed to work up refractory sulphide ores of the same grade as those intended to be treated by the Siemens-Halske process (*q.v.*). The ore is finely ground and is roasted to convert the sulphides of zinc and lead into oxides and sulphates.

The difficulty and expense attending the thorough roasting of this class of ore have already been spoken of. The remarks then made apply equally here. The solvent used is ferric chloride, which is used up and replaced (not regenerated) in the manner about to be described. In the first place the roasted ore is leached with a solution of ferric sulphate and chloride; zinc sulphate and chloride are formed and ferric hydroxide is precipitated. The extracted residue of lead sulphate, gangue, and ferric hydroxide is smelted in the usual manner, the oxide of iron aiding as a flux. The solution containing zinc is first passed over scrap zinc to precipitate any silver which may be in solution, and is then circulated through the cathode compartments of a series of electrolytic cells and there deposits a portion of its zinc. On cathodes of sheet zinc the good and coherent quality of the deposit of zinc is said to be promoted by allowing the solution to be slightly basic. Now, seeing what has been said above (p. 145) on the bad influence of basic salts of zinc on the quality of the metal deposited, it is fairly evident that it is unlikely that this method of working can be successful. Only about one-third of the total quantity of zinc in solution is deposited during the passage of the electrolyte through the cathode compartments, and the liquor then passes to the anode compartments, which are separated from the cathode compartments by a porous partition of cloth. The level of the electrolyte in the anode compartments is kept lower than that in the cathode compartments in order to prevent the liquid from passing from the anode to the cathode compartment through the diaphragm. This is because the anode liquid contains iron salts, which would interfere with the deposition of the zinc if they found their way into the cathode compartment. In some of the anode compartments are iron anodes, which dissolve in proportion as zinc is deposited in the cathode compartments, forming ferrous sulphate (or chloride). In the remaining anode compartments, viz. those through which the liquor passes out of the group of electrolytic cells, the anodes are of carbon instead of iron. At these insoluble anodes the ferrous salts previously formed at the iron anodes are oxidised to the ferric state, and the liquor becomes capable of acting again as a leaching agent for a fresh portion of the ore. It will be seen that the process is comparatively complex. The solvent action of the solution of ferric salts is by no means particularly vigorous, and anything approaching complete extraction of the ore is difficult to attain. The precipitation of the iron by means of the zinc oxide in the roasted ore is difficult to effect completely, and if iron be left in solution the deposition of the zinc is interfered with. The plan of depositing zinc from a slightly basic solution is (as has been shown above) based on an erroneous view, and is likely to hinder rather than help. The renewal of the leaching liquor by the dissolution of iron anodes and the subsequent oxidation of the ferrous salts thus produced necessitates the use of a diaphragm to prevent commingling of the anode and cathode liquors. The theoretical advantage gained is that the comparatively cheap energy rendered available by the dissolution of the iron aids in the deposition of the zinc by reducing the voltage required for this purpose.

Whether as much as is gained by this is not lost by the increased resistance of the electrolyte and diaphragm is a nice point. That these difficulties are not imaginary is shown by the fact that the sulphide corporation which worked the Ashcroft patents spent large sums of money without bringing the method to a successful issue. Great efforts were made to put the process on a working basis, and the history of these attempts is contained in a paper by Mr. Edgar A. Ashcroft, which was read before the Institute of Mining and Metallurgy in June, 1898. The gist of this paper, as far as is necessary for a comprehension of the difficulties encountered in the treatment of mixed sulphide ores, is given in the ensuing paragraphs.

THE ASHCROFT PROCESS AS WORKED AT COCKLE CREEK

The ore treated proved to be poorer than was anticipated, containing about 20 per cent. of lead, 25 per cent. of zinc, and 10 ounces of silver per ton, instead of 30 per cent. of lead, 30 per cent. of zinc, and 45 ounces of silver per ton, as was expected. Thus, ore containing metals with a gross assay value of only £7 18*s.* per ton was available instead of ore worth £13 8*s.* Seeing that all calculations of profit had been made on the latter, the ultimate failure of the process is not surprising.

The ore is dried, ground in Krupp ball mills to a fineness such that it will pass a 60 × 60 mesh sieve, and roasted in a long reverberatory furnace with a terraced hearth, so that the roasting can be done systematically and the ore well turned and rabbled as it descends from the higher steps at the far end of the hearth to the lower steps nearer the bridge.

The roasting is conducted at as low a temperature as possible, in order that the product may be sulphate rather than oxide. The operation is carried out by hand labour, but would probably be better effected in a mechanical roasting furnace. The roasted ore is reground and its zinc leached out by means of "sulphuric acid, with or without ferric sulphate." In the paper from which these facts are taken it is not specifically stated that the use of ferric salts as leaching agents has been abandoned, but the general tenor of the description conveys the impression that this is the case. In fact it may fairly be assumed that, at least in the later stages of the trial, the roasted ore was simply extracted with a solution from the cathode compartments of the cells, containing free sulphuric acid, and of course zinc sulphate. The characteristic reaction on which the claim of the process to be considered novel is based, thus disappears.

The leaching is done in large wooden vats with agitators, and the solution is kept at about 80° C. = 176° F. When the bulk of the free acid is neutralised and the greater part of the zinc in the ore is extracted, the mixture is filter-pressed, the residue sent to the smelting furnaces for reduction to argentiferous lead, and the solution of crude zinc sulphate purified in order to make it fit for electrolysis. Iron is always present, and is peroxidised in the anode compartments and precipitated when the electrolyte, partially depleted of zinc, is used to leach out a fresh portion of ore. Manganese is also present, and is considered very objectionable. It is stated that its removal by means of bleaching powder and other oxidising agents is too costly, and therefore it is allowed to accumulate until its influence becomes excessive, when a portion of the liquid is removed and replaced by dilute sulphuric acid or a fresh extract from the ore. The fraction of the liquid thus taken out of the cycle of operations may be worked up for zinc by evaporation to dryness, decomposition of the zinc sulphate by heating (the $SO_2 + O$ evolved being reconverted into sulphuric acid), and reduction of the crude zinc oxide thus obtained by the usual process of distillation with carbon. It is stated that sufficient purification of the liquor to be electrolysed can be effected by allowing it to fall in cascade over cast-iron scrap or borings, and that this (apart from the periodical necessity for removing a fraction on account of the accumulation of manganese) is the only operation necessary between the leaching vats and the electrolytic cells. In spite of these attempts at simplification, the electrolytic separation of zinc by this process has not yet proved to be successful.

THE HOEPFNER PROCESS

Numerous processes for the electrolytic winning of zinc have been devised and patented by Hoepfner. One of these has been worked on a semi-manufacturing scale (about 100 H.P. being used) at Früfurt in Germany. The raw material is an iron ore containing about 10 per cent. of zinc. This is roasted and extracted with sulphuric acid; the solution is treated with common salt in order that the zinc may ultimately be obtained as chloride. The liquor is purified from manganese by the use of caustic soda and bleaching powder, and from lead and copper by means of zinc dust. The purified solution is cooled to 25° F., the sodium sulphate crystallised out, and the resulting solution of zinc chloride is electrolysed. The anodes are gas carbon, and the cathodes are revolving zinc plates. They are separated by diaphragms of nitrated cellulose. A pressure of 3–7 volts per cell is required, and a high current density as much as 36 amperes per square foot may be used. The electrolyte is circulated independently through the anode and cathode compartments. The products are zinc, which is obtained on the revolving cathodes in a coherent state, and chlorine, which is used for making bleaching powder.

Another process devised by Hoepfner is being worked by Brunner, Mond & Co. in this country. As far as the electrolysis is concerned, it is generally similar to that described above, the electrolyte being a solution of zinc chloride. The adoption of a process of this kind by an alkali works becomes intelligible when it is considered that the electrolyte (zinc chloride) is obtained by acting on zinc oxide (roasted zinc ore) with calcium chloride solution and CO_2; calcium carbonate is precipitated, and zinc chloride goes into solution. It is said that this reaction works smoothly. The zinc obtained may be regarded as a bye-product, covering the cost of the ore and part of that of the process, the real object of the alkali maker (using the ammonia-soda process, and therefore not obtaining hydrochloric acid as a bye-product, as does the Leblanc maker) being to recover chlorine from his waste calcium chloride liquors. The plant at Brunner, Mond & Co.'s works is about to be increased to 1,200 H.P. The output is estimated at 4 kilos of zinc per horse power per day. (*Cf.* p. 148).

THE DUISBERG PROCESS

A process which is successfully producing zinc on a commercial scale is that devised by Dieffenbach and worked at Duisberg in Germany. The details of the process are kept secret, but it appears that the electrolyte is a solution of zinc chloride. It is probable that such an electrolyte will prove better than one of zinc sulphate, partly because the carbon anodes last better in a chloride solution, partly because chlorine is a valuable bye-product. The success of the process at Duisberg may be gathered from the statement that the output is 90 tons of zinc per month and that the plant is being increased.

ELECTROLYSIS OF FUSED ZINC CHLORIDE

The use of fused zinc chloride instead of aqueous solutions of the chloride and other salts of zinc has attracted the attention of inventors. No working process has resulted from their efforts, but the apparatus, devised by Borchers (shown in fig. 23), will serve as an example of the attack of the problem on rational lines.

A leaden vessel A having a grooved rim is used to contain the fused zinc chloride. The rim is filled with zinc chloride in the fused state and the cover D placed in position. Water is turned into the trough C surrounding the grooved rim, and the zinc chloride is thus caused to solidify, sealing the cover. A sheet of zinc B bent to the shape of the vessel is used as the cathode, and the carbon rod E as the anode. F is a pipe serving to carry off the chlorine, and G is a plug closing a hole through which fresh zinc chloride can be introduced from time to time. At the beginning of electrolysis the main quantity of zinc chloride in the vessel A is fused by the application of external heat; afterwards it can be kept fused by the heat generated by the passage of the current, provided a sufficiently high current density be used. The two weak points in the process are the difficulty of preparing zinc chloride in quantity anhydrous and sufficiently pure to serve for the preparation of electrolytic zinc, and the fusibility of the leaden vessel. Lead melts at 325° C. = 617° F. and zinc chloride fuses at 262° C. = 504° F., so that the margin of safety is not large.

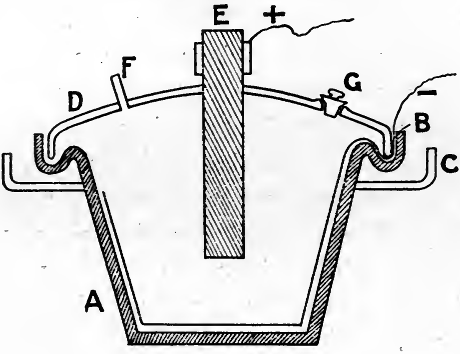

Fig. 23.

WORKING UP "ZINC AMALGAM" FROM THE PARKES PROCESS

One of the most effective methods of desilverising lead consists in treating the molten metal with an immiscible solvent, viz. zinc.[1] The zinc floats on the surface of the

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[1] A full description of this elegant process can be found in any good metallurgical text-book.

lead and is periodically removed. During its contact with the lead to be desilverised, the zinc absorbs not only silver, but also a certain amount of lead. It also oxidises to some extent. Thus it comes about that the "zinc amalgam," as the crust of zinciferous matter floating on the bath of lead is termed, is a loose, friable mass, varying considerably in composition according to the conditions of working. Its composition ranges from 55 to 77 per cent. of lead, 12 to 40 per cent. of zinc, 2·5 to 5 per cent. of silver, with various other metals and oxides. The ordinary metallurgical method of working up this complex alloy consists in liquating the excess of lead (which is returned to the desilverising pots), and distilling the residual mixture of zinc, silver and oxide of zinc with a little charcoal. The zinc already present as metal and that reduced from the oxide by the charcoal distils off, and crude silver remains, which is purified in the usual way. It is proposed to improve on this process by refining the alloy electrolytically, the object being to dissolve out the zinc and to leave the lead and silver. This is not altogether easy, because the alloy is too brittle and contains too much oxide to be cast into plates. Also the quantity of soluble material (zinc) which is to be extracted is small compared with the quantity of insoluble material (lead and silver). Thus, any form of anode will become crusted with this insoluble material, and its dissolution will be hindered thereby. A better grade of "zinc amalgam" is said to be produced when the desilverising of the lead is conducted with zinc containing a small percentage of aluminium, in that it contains a smaller proportion of lead. But even in this case the product contains much lead, dissolves slowly, and cannot be cast into serviceable anodes. It must therefore be treated in fragments, lying loose on a plate, or contained in a metallic basket serving as the anode. Such a receptacle may be made of lead. A solution of zinc sulphate should serve as the electrolyte, and the conditions for the deposition of zinc in a coherent form should be maintained as nearly as possible like those which have been already laid down as suitable for the winning of zinc (p. 142 *et seq.*). After a time the outer parts of the fragments of zinc-lead-silver alloy will become robbed of their zinc and converted into a spongy mass of argentiferous lead. A kernel of unattacked zinc-lead-silver alloy will remain. The dissolution of the zinc from this will be slow, partly because its conductive connection with the plate or basket serving as the anode is impaired by the formation of a film of lead sulphate on the spongy lead. A remedy for this state of things is the removal of the partly spent fragments, the liquation of the coating of argentiferous lead from the core of zinc-lead-silver alloy, and the retreatment of the kernels thus isolated. This is a cumbrous and costly proceeding, and is not likely to conduce to the success of the process.

Somewhat sketchy information is extant concerning the treatment of " zinc amalgam " containing aluminium. It is said that this can be successfully worked up in an electrolyte consisting of a strong solution of the chlorides of zinc and magnesium, and that the zinc is collected on revolving disc cathodes, as in the Hoepfner process (see above). The zinc obtained is substantially pure, and the lead and silver left as anode sludge contain but little zinc, and can be cupelled at once to recover the silver.

Summing up, one may say that the electrolytic treatment of zinc is in a backward state. For that purpose which promises most reward—the winning of zinc from its ores, especially from mixed sulphides—no satisfactory process has yet been devised. For the mere purification of zinc already won from its ores—which is comparatively easy—there is not, nor can be, any demand which is not easily supplied by the simple method of redistillation. In the case of the one crude product from which zinc may be advantageously separated by electrolytic means—"zinc amalgam"—there are many difficulties in treatment. A moderate success must be chronicled in "cold galvanising," *i.e.* coating iron and steel with zinc electrolytically deposited. This is dealt with in the section allotted to the art of electro-deposition.

SECTION III

Winning and Refining Metals in Igneous Solution

ALUMINIUM

ALUMINIUM differs from all other metals used as such in the arts, in that at the present time it is produced solely by electrolytic methods. Ordinary metals—copper, zinc, silver, etc.—which are employed not for their chemical peculiarities, as are sodium and magnesium, but on account of their physical and mechanical properties, are obtained partly or chiefly by other than electrolytic means. Aluminium alone is manufactured exclusively by electrolysis. Thirty years ago this was not the case; aluminium was then made wholly by methods which were purely chemical. Even twenty years ago no serious attempt had been made to manufacture aluminium by an electrolytic process.

The reduction of aluminium from its oxide by smelting the latter with carbon is impracticable at ordinary furnace temperatures.[1] The cognate metal iron can be reduced with ease, and this is done daily in the blast furnace. If we substitute Al_2O_3 for Fe_2O_3 and heat it with carbon no metal is obtained. It is only at the extremely high temperature of the electric arc (about 3,500° C. = 6,332° F.) that reduction occurs. Even then, if alumina be heated in contact with carbon, it is not Al but the carbide Al_4C_3 which is obtained.

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[1] The equation $Al_2O_3 + 3\,C = Al_2 + 3\,CO$ requires the addition of 305 Cal for its realisation.

If a metal with a great affinity for oxygen is used instead of carbon, *e.g.* manganese or magnesium, reduction equally fails to take place. But if another compound of aluminium, namely the chloride, be used instead of the oxide, metals of this class will reduce aluminium therefrom. The original chemical method of Deville is based on this fact. Anhydrous aluminium chloride is prepared by heating a mixture of alumina and carbon in a stream of chlorine. By adding sodium chloride to the mixture, the double chloride $Al_2Cl_6\,6\,NaCl$ is obtained, and this is the substance used in the old Deville process. When this double chloride is heated with sodium it is reduced according to the equation—

$$Al_2Cl_6\,6\,NaCl + 6\,Na = Al_2 + 12\,NaCl.$$

Instead of the double chloride, the double fluoride $Al_2F_6\,6\,NaF$ (cryolite) may be treated with sodium for the production of Al. Any process of this kind involves, in the first place, the manufacture of sodium. Deville's process remained costly until cheap sodium was produced by Castner, who made the metal by reducing caustic soda by means of an intimate mixture of carbon and iron. It will be observed that the large amount of energy necessary to sever aluminium from oxygen is provided in this chemical process in two stages. In the first aluminium chloride is produced, the heat of combination of which is 322 Cal, as against 392 Cal for the oxide. In the second a metal (sodium) reducible by carbon and having a high heat of combination with chlorine is manufactured. This, being caused to react with the aluminium chloride, accomplishes what it could not do had it been applied to aluminium oxide. Thus ultimately almost all the energy needed to reduce alumina has been obtained from carbon in two stages, each being ineffective alone. Now one of the great advantages of electrolytic methods is that the energy needed for their execution can be supplied at any desired pressure. The critical pressure for the electrolytic decomposition of alumina is 2·82 volts, and this is, of course, well within working limits. Seeing that this value is considerably higher than the critical pressure corresponding with the electrolytic decomposition of water, it is clear that the reduction of aluminium cannot be accomplished in aqueous solution; it must be carried out in a fused electrolyte. The realisation of these conditions in practice constitutes the modern electrolytic method of aluminium manufacture, which has completely ousted the Deville process and its modifications depending on purely chemical procedure.

ELECTROLYTIC REDUCTION OF ALUMINIUM

The process on which the world's supply of aluminium now depends consists in the electrolysis of alumina. Alumina, having a very high fusing-point, is conveniently dissolved in a fused salt of aluminium, *e.g.* the fluoride or the double fluoride of aluminium and sodium. This is accomplished by several processes, which will be described in turn.

THE HÉROULT PROCESS

This process as at present worked is the type of all successful processes for the production of pure aluminium as distinct from aluminium alloys. There are several other processes, known by the names of their devisers, which profess to be distinct from the Héroult, but the distinction if it exists is in law rather than in fact.

The Héroult process is that worked by the Aluminium-Industrie-Aktien-Gesellschaft at Neuhausen in Switzerland and by the British Aluminium Company at Foyers in Scotland, the two largest manufacturers of aluminium in Europe. It is noteworthy that in the original patents the preparation of aluminium bronze rather than of aluminium was contemplated, and that all the accounts of the process apply to the production of the alloy. There is, as a matter of fact, no published account of the Héroult furnace as now used for the manufacture of pure aluminium. The general arrangement, however, may be understood from the following description.

The claim in Héroult's German patent is for the continuous electrolysis of aluminium compounds between a carbon anode and a cathode consisting of a bath of a metal, *e.g.* copper, in a state of fusion, the whole being contained in a crucible provided with a tapping-hole. The process as actually carried out embodies more than this. As stated above, the electrolyte consists of alumina dissolved in cryolite or in an artificial mixture of aluminium fluoride with sodium fluoride. This electrolyte is kept fused, not by heat externally applied, but by heat generated by the passage of the current. The waste which thus occurs, in that costly electrical energy is used for mere heating, is more than compensated for by certain practical advantages. These are, first, that whereas any method of external heating would require the transmission of every unit of heat through the walls of the containing vessel, the electrical method applies the heat precisely where it is needed; secondly, that whereas in external heating the fused electrolyte would be in contact with the walls of the containing vessel and would dissolve and destroy any material but platinum, with electrical heating the walls remain cool and may be thickly lined with a congealed crust of the electrolyte itself; thirdly, that the temperature of the electrolyte is more readily controllable by altering the current and distance between the electrodes than by regulating an external heating apparatus. It may be safely said that one of the chief features of the Héroult process is this method of maintaining the electrolyte in a fused state. The original Héroult apparatus designed for the electrolysis of alumina in contact with a copper cathode is shown in the above figure.

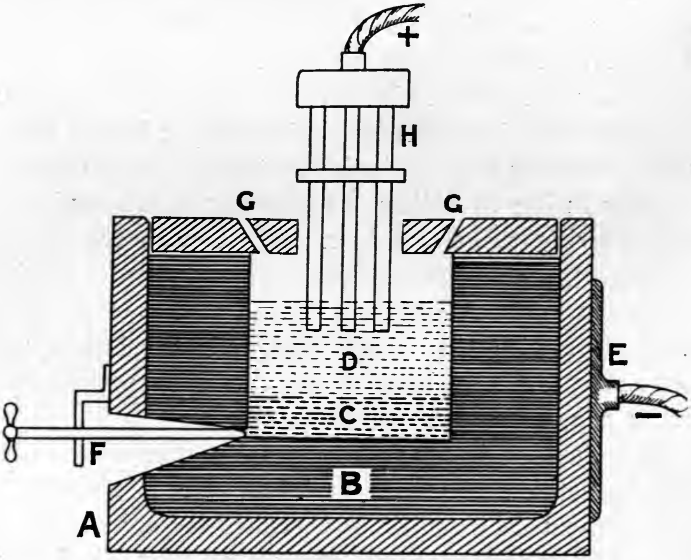

Fig. 24.

A is an iron box, lined with carbon plates B. The central cavity contains melted copper C and the electrolyte (alumina dissolved in cryolite) D. The copper is made the cathode of the cell, electrical connection being obtained by the cable E clamped to the wall of the iron box. The tapping-hole F is closed by a rod arranged to act as a screw-valve, as shown in the figure. The cell is provided with a cover of carbon, having two holes, G, G, through which alumina may be fed and having a central hole large enough to clear the anode H, which is built up of carbon plates suitably clamped together.

The furnace is started by placing copper in the lower part, bringing the anode in contact with the metal, thereby fusing it, adding the electrolyte, and gradually withdrawing the anode from contact with the copper —both copper and electrolyte are maintained in fusion by the current. Aluminium is separated at the cathode and alloys with the copper, the product being tapped off at intervals. Fresh alumina and copper are fed in at G, G, as may be required.

This furnace is apparently equally well adapted for the production of pure aluminium, for if that metal be substituted for copper at the start and alumina alone be fed in, the sole cathode product will be aluminium, which can be tapped off as it accumulates. Nevertheless no authentic description of the Héroult furnace now actually in use for the manufacture of aluminium, has ever been published. It has been suggested that the walls of the furnace are thinner, and are cooled by air or water so as to solidify a crust of the electrolyte inside them to protect them. This is probable enough, and there is no reason why such an arrangement should not be workable. If it were used contact would need to be made by a conductive rod of carbon, or preferably of iron, with the pool of melted aluminium at the bottom of the cell. The whole arrangement is shown diagrammatically below.

A is a wrought-iron box with hollow sides through which water can be circulated by the pipes B and C. It is unlined save for the coating of solidified electrolyte (cryolite or other double fluoride of aluminium formed and maintained by the coolness of its walls). D is a steel plug with a mushroom head passing into the lower part of the cell. It makes a mechanical fit with the bottom of the iron box, and its junction therewith is protected by a layer of solidified electrolyte. Its head projects into the bath of melted aluminium. Above this is the fused electrolyte E, into which dips the carbon anode F. The cell is covered by a fireclay slab G. It is evident that if found preferable this slab could be replaced by a hollow iron

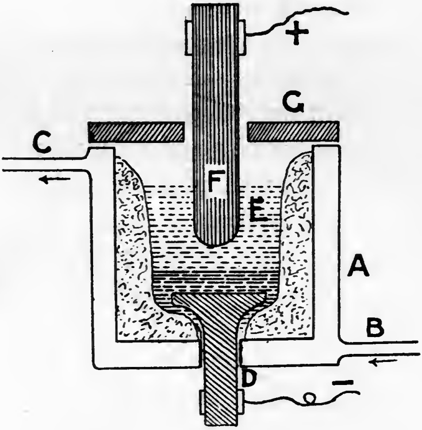

Fig. 25.

lid, cooled by circulation of water so that it would protect itself against the electrolyte splashed up on to it from the bath. Such details as feeding and tapping arrangements are intentionally omitted from the illustration.

In the Héroult process the source of the aluminium is alumina. The cryolite or other double fluoride of aluminium and sodium serves only as a solvent for the alumina. The case may be likened to that of the electrolysis of zinc chloride dissolved in water, where the water acts simply as a solvent, the products being zinc and chlorine. The products are, therefore, aluminium at the cathode and oxygen at the anode. The anode, being of carbon, is attacked by the oxygen there produced and yields carbon monoxide. If this attack be considered as an integral part of the process of electrolysis, the critical voltage for the Héroult process will be that corresponding with the equation—

$$Al_2O_3 + 3\,C = Al_2 + 3\,CO,$$

which requires 306 Cal, corresponding with a pressure of 2·2 volts. This reduction of voltage from the 2·82 requisite for the electrolysis of Al_2O_3 with an unattackable anode is, however, dearly bought by the consumption of expensive carbon anodes. This corrosion of the anode is a serious item of expense, as will be seen when the whole cost of the process is considered below. The reason is that although chemically carbon in any form would suffice for combination with the oxygen, yet for working conditions it is necessary that the carbon should be of the best electrode carbon, mechanically fairly strong, sound and homogeneous, of good conductivity and nearly free from ash. The ash, consisting chiefly of silica, alumina, and oxide of iron, will dissolve in the electrolyte and eventually contaminate it to such an extent that the aluminium produced will be no longer pure, but will contain silicon and iron, both objectionable impurities; ultimately the collection of impurities in the electrolyte will compel its renewal or purification, the former being probably the more practicable proceeding. For the production of pure aluminium it is necessary also to use a moderate current density; if a certain maximum be exceeded, sodium and fluorine will appear at the cathode and anode respectively. The extreme chemical activity of fluorine makes it highly objectionable, because of its corrosive action on everything with which it may come in contact, while the occurrence of sodium in the aluminium causes the metal to be easily oxidised, the oxidation taking place locally and leading to serious deterioration.

Provided a proper supply of alumina be maintained there should be no risk of decomposing NaF, for its heat of combination is approximately 100 Cal, corresponding with a critical voltage of 4·3 volts as against 2·82 for the decomposition of Al_2O_3, or 2·2 volts of the oxidation of the carbon anode is assumed to act as an auxiliary source of electrical energy. This diminution of voltage (supposing it to occur) by no means compensates for the cost of the carbon electrodes; it would be better to work with insoluble electrodes, *e.g.* of platinum, were that feasible.

The Héroult process was first put to work at Neuhausen in 1888, 300 H.P. being used. In the following year the right to use 4,000 H.P. was acquired. The plant put down consisted of two turbines of 600 H.P. each and one of 300 H.P. The turbines were arranged horizontally, their vertical shafts carrying the dynamos at their upper end. This simple and compact arrangement has since been adopted at the great power house at Niagara, and in many situations is the best that can be desired. A further increase has since been made by putting down five more turbines, each of 610 H.P. driving dynamos, each of which gives 7,500 amperes at 55 volts. The whole installation suffices for the production of 2,500 kilos of aluminium per day of 24 hours, or for a working year of 300 days, 750 tons. There has been a further increase of plant lately, and the output has risen to 1,800 tons per year. This rapid development has been equalled by other installations, and at the present time the world's output of aluminium cannot be far short of 7,000 tons per year. Considering the comparatively limited and special uses of the metal, it is remarkable that this quantity should find a market.

The Héroult process is in use at Foyers, in Scotland, where 3,000 H.P. are available, corresponding with a capacity for an output of 4,000 pounds per day, *i.e.* 535 tons per year of 300 days. The raw material for this works is obtained from bauxite at Larne, in the north of Ireland. The preparation of pure alumina is necessary as a preliminary stage in all modifications of the Héroult process, and a description of the method may be usefully given.

The bauxite has the following average composition:—

	Per cent.
Alumina	56
Ferric Oxide	3
Silica	12
Titanic Acid	3
Water	26
	100

The material is crushed so as to pass a quarter-inch mesh sieve, and is gently roasted in a revolving calcining furnace, the temperature being regulated so as to destroy any organic matter and ensure that all iron shall be present as Fe_2O_3, and nevertheless not to render the alumina insoluble. The roasted material is powdered so as to pass a sieve having 30 meshes per linear inch, and is digested with a solution of caustic soda of specific gravity 1·45 at a pressure of 70–100 pounds per square inch. After digestion for two or three hours the solution is diluted to a specific gravity of 1·23 and is passed through filter presses, and afterwards through cellulose filters consisting of sieves carrying a layer of cellulose pulp, the whole contrivance somewhat resembling the laboratory apparatus known as a Gooch crucible. By this double filtration a satisfactorily clear liquor is obtained. In former processes for the manufacture of alumina, the alkaline aluminate was decomposed with CO_2 and the alumina was thus precipitated. The disadvantages of this process, apart from the cost of the CO_2, are that any silica present in solution is also thrown down and contaminates the alumina, and moreover the alkali is converted into carbonate, and has to be recausticised before it can be used again for extraction. By Bayer's process, which is that now in use, the caustic solution of alumina is treated with a small portion of alumina precipitated in a previous operation; it is thereby caused to deposit about 70 per cent. of its dissolved alumina if the solution is well agitated and the precipitation allowed to continue for about 36 hours. The clear liquor is drawn off and the alumina washed in a filter press and dried to some extent by a blast of air, being then roasted at about 1,100° C. = 2,012° F. in order to render it both anhydrous and non-hygroscopic. The latter quality is necessary, as otherwise the alumina would absorb water during storage and would not be fit to feed into the electrolytic cell.

The caustic soda solution, diluted but retaining a portion of its alumina, is concentrated in a triple-effect vacuum evaporator to its original specific gravity of 1·45, and is then ready for the extraction of another portion of bauxite. It will be seen that the caustic soda serves merely to pick out the alumina from its accompanying impurities, and to deposit it, as it were by the word of command, in a pure state.

Both silicon and iron are objectionable impurities in aluminium, and great pains are therefore taken to exclude both from the raw material (alumina). This necessity for the careful purification of ore (alumina) differentiates the manufacture of aluminium from that of any metal prepared by ordinary smelting processes, and adds considerably to the cost of manufacture. Indeed, the cost of the alumina necessary to produce 1 pound of aluminium may be $\frac{1}{3}$ to $\frac{1}{4}$, the total manufacturing cost of the aluminium.

THE HALL PROCESS

This is a process presenting many similarities to the Héroult. The raw material is purified alumina; it is dissolved in a fused bath of aluminium fluoride and sodium fluoride mixed in about the proportions $Al_2F_6 2 NaF$. The sodium fluoride may be replaced by calcium potassium or lithium fluoride. In the various patents by which the process is disclosed the electrolyte is to be kept fused by external heating. If this is actually practised difficulties will certainly arise from the attack of the containing vessel by the electrolyte. It has been pointed out above (p. 169) that protection for the containing vessel may be best secured by a congealed coating of the electrolyte itself, and this is only possible when the heating is internal, *i.e.* is produced by the passage of the current. If then the heating is internal, the Hall process is practically identical with the Héroult.

An official description of the Hall process has been published by Hunt, the President of the Pittsburg Reduction Company, which uses the Hall process at New Kensington, Pennsylvania, and at Niagara Falls. At each place it has 1,600 H.P., with an output of about 2,000 pounds per day of Al. It is intended to increase the Niagara works considerably.

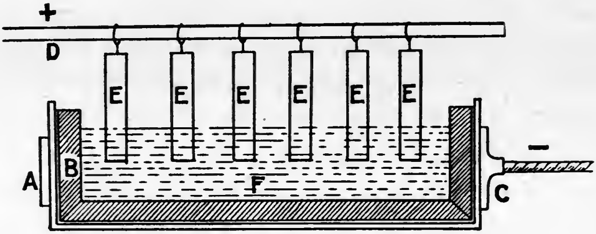

FIG. 26.

The vessel (A, see Fig. 26) containing the electrolyte is an iron trough lined with carbon plates B. It is made the cathode by connection with the dynamo by the copper strip and cable C. From a copper rod D the carbon anodes E, E are hung, and dip into the electrolyte F. They can be lowered as they are consumed. It is stated that the carbon lining is not sensibly affected, and that both it and the iron pot last a long time. This is very dubious if the heating is external. Under such conditions the electrolyte would soak through the carbon and be likely to attack the iron.

The following details have been published by the inventor of the process. The chief raw material (alumina) costs about 2½*d.*–3*d.* per pound, and can be obtained in the requisite purity from various chemical manufacturers in the States, who prepare it from cryolite. It is, of course, hydrated and substantially free from all impurities save soda. Cryolite, costing about 3*d.* per pound, can be obtained from the same manufacturers. Hydrofluoric acid (necessary for the preparation of the aluminium fluoride) can be bought in quantity of the required quality at 2*d.*–2½*d.* per pound. Carbon for lining the electrolytic cells is prepared from good coke or retort carbon and tar baked in the usual way; the cost is about 1½*d.*–2*d.* per pound. The electrolyte is prepared by treating a mixture of alumina, cryolite and fluorspar with hydrofluoric acid in a lead-lined vessel. The mass is dried, fused in the carbon-lined steel troughs described above, and electrolysed. After some hours, when the mixture is thoroughly fluid, alumina is fed in, and then functions as the electrolyte proper, as in the Héroult process. The separated aluminium collects at the bottom of the carbon-lined cell, care being taken to keep the electrolyte specifically lighter than the fused metal. This can be aided by the addition from time to time of the double fluoride Al_2F_6 2 KF. The general rules to be observed in the manufacture of aluminium by this (or, indeed, by any cognate) process have been laid down by Hunt, whose authority has been cited above.

(1) The solvent, with its dissolved alumina, must be fusible at a moderate temperature.
(2) The solvent must dissolve alumina freely, *e.g.* must take up at least 20 per cent. at the working temperature.
(3) The critical voltage for the solvent must be higher than that for the alumina.
(4) The specific gravity[1] of the solvent at its working temperature must be lower than that of aluminium at the same temperature, so that the metal may collect at the bottom of the cell.

The same writer supplements Hall's earlier account in several respects. Thus the solvent may be formed of various fluoride mixtures and yet comply with the conditions laid down above. The solvent most commonly used is one of 677 parts by weight of aluminium fluoride, 251 of sodium fluoride, and 234 of calcium fluoride. The ingredients may be fused in separate vessels or in the electrolytic cell by the passage of the current. It should

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[1] The specific gravity of solid aluminium is not higher than 2·7, and that of cryolite is about 3. When these materials are fused, however, the alteration of their specific gravities is very considerable, and the relation of the specific gravities is reversed. Richards has published an interesting table which shows why it is possible in the Héroult and similar processes to keep the separated aluminium at the bottom of the bath.

	Specific Gravities.	
	Fused.	Solid.
Commercial aluminium	2·54	2·66
Commercial Greenland cryolite	2·08	2·92
Cryolite saturated with alumina	2·35	2·90
Cryolite mixed with aluminium fluoride in the proportion required by the formula Al_2F_6 2 NaF	1·97	2·96
This mixture saturated with alumina	2·14	2·98

be noted that this is not in accordance with the general tenor of Hall's patents, in which fusion is effected by heat externally applied. When the solvent is fused, alumina to act as the electrolyte is fed in in the proportion of about 20 per cent. of the weight of the solvent, and this proportion is maintained as electrolysis proceeds. The bath is kept below 982° C. The separated aluminium is baled out from time to time.

The descriptions of the Héroult and the Hall processes which have been given above show their principles and mode of working to be substantially identical. It may be accepted without much hesitation:—(1) that the electrolyte in each case is alumina dissolved in a fused mixture of aluminium fluoride and the fluoride of the metal of an alkali or alkaline earth; (2) that the bath in each case is kept fused by the heat generated by the current itself; (3) that carbon anodes are used; (4) that the cathode in actual working is or soon becomes a pool of liquid aluminium. The chief point on which full information is lacking is the nature of the containing vessel, having regard to the necessity for protecting it from the action of the fused electrolyte. The most reasonable and probable design has been given on page 171.

THE MINET-BERNARD PROCESS

This process is the only other method of preparing aluminium which need be referred to. According to the patent taken out jointly by Minet and Bernard, the electrolyte is a mixture of aluminium fluoride and sodium chloride, fused in a metal vessel by heat externally applied. The vessel may act as cathode, or a separate carbon cathode may be used; the anode is of carbon. When the vessel is made the cathode a portion of its substance is dissolved by the separated aluminium, and the metal obtained is only fit for the production of alloys. For pure aluminium a carbon cathode is requisite. It will be seen that the whole arrangement is very crude, and meets none of the difficulties which have been discussed above. The Minet-Bernard process is said to be in use at one works; if this be true the process must have been considerably modified, and, it may be fairly assumed, on the lines which have been laid down in considering the Héroult process.

OTHER METHODS

The method of production of aluminium by the electrolysis of alumina dissolved in a fluoride bath is not without certain drawbacks. In the first place, the bath is highly destructive of most materials that can be used as containing vessels, and thus makes necessary the use of various devices, which have been described above, to prevent it from acting thereon. Secondly, expensive carbon anodes are necessary, and these are consumed by the oxygen of the electrolyte (alumina). Thirdly, these same anodes inevitably contain ash, consisting largely of silica and oxide of iron, impurities which dissolve in the bath and eventually contaminate the alumina. It is therefore not surprising that other methods should be worth considering.

Before the advent of a practicable electrolytic method, many attempts were made to devise a chemical process cheaper than the chemical method of Deville. The key to all possible processes is this: alumina cannot be reduced to aluminium at ordinary furnace temperatures by carbon or any other practically available reducing agent. Its heat of combination is too high, viz. 392 Cal. The reduction must therefore be effected in two stages, as in Deville's process, where the anhydrous chloride is first produced (heat of combination 322 Cal), and then this in turn is reduced with sodium. In like manner the anhydrous sulphide may serve as an intermediate step. Al_2S_3 has a heat of formation of 124·4. The heat of formation of manganese sulphide is about 45 Cal, so that the equation—

$$Al_2S_3 + 3\,Mn = Al_2 + 3\,MnS$$

should be possible, as it would evolve $3 \times 45 — 124{\cdot}4$ Cal, *i.e.* 10·6 Cal. Unfortunately pure manganese cannot be produced by any ordinary smelting operation, the material obtained always containing a good deal of iron, silicon and carbon. Thus direct reduction of aluminium sulphide by any ordinary chemical process is hardly to be looked for; the sulphide itself has, however, certain merits as a material for electrolytic reduction.

In the first place, its critical voltage is 0·89 volt, as against 2·82 for Al_2O_3. Secondly, its anode product is sulphur, which does not combine with carbon until a high temperature has been reached; the carbon anode should therefore remain unattacked. These obvious merits have induced sundry inventors to devise processes in which the sulphide, instead of the oxide, of aluminium is to be employed. The great obstacle in the way of this class of process is the manufacture of aluminium sulphide. Al_2S_3 is decomposed by water yielding Al_2O_3 and H_2S, and consequently cannot be prepared by any wet method. The reaction—

$$Al_2O_3 + 3\,C + 3\,S = Al_2S_3 + 3\,CO$$

requires the addition of 211 Cal in order to bring it about. This may be met in some measure by using CS_2

instead of C and S independently (CS_2 being an endothermic substance), and bringing into the reaction a store of energy previously acquired. If the equation—

$$2\ Al_2O_3 + 3\ CS_2 = 2\ Al_2S_3 + 3\ CO_2$$

is possible, it would still require 100·5 Cal per gramme equivalent of alumina converted into aluminium sulphide; if the reaction took the form—

$$Al_2O_3 + 3\ CS_2 = Al_2S_3 + 3\ CO + 3\ S,$$

there would still be lacking 168 Cal. These facts show clearly enough that the first necessity for processes proposing the electrolysis of aluminium sulphide is an improved method of manufacturing that substance. According to the patents of Bucherer it can be obtained by the joint action of sulphur and carbon on alumina in the presence of sulphides of the alkali metals, double sulphides of the form—

$$Al_2S_3\ 3\ Na_2S$$

(thio-aluminates, in fact) being produced. The only additional source of energy heat which makes this proceeding more hopeful than that expressed by the equation—

$$Al_2O_3 + 3\ C + 3\ S = Al_2S_3 + 3\ CO$$

is the combination of Na_2S with Al_2S_3, and this is likely to yield but little energy.

Assuming that aluminium sulphide is produced, it can, according to Bucherer, be dissolved in fused sodium chloride and electrolysed as in the Héroult process. The fusion of the mixture may be effected either by the current or by external heating, the former for choice, because fused sodium chloride attacks any material available for a containing vessel. It is said that the Aluminium-Industrie-Aktien-Gesellschaft at Neuhausen (the company which first exploited the Héroult process) is trying a sulphide method, but no information as to its working has been made public.

THE COST OF PRODUCTION OF ALUMINIUM

From the foregoing pages it will seem that under even favourable conditions the amount of energy needed for the reduction of a given weight of alumina to aluminium is very large, viz. 272,222 joules per gramme equivalent, *i.e.* 4·5 grammes. Therefore an apparatus working with theoretical efficiency would produce 88·8 grammes of aluminium per H.P. hour, *i.e.* 4·7 pounds per H.P. working for 24 hours. It is certain, however, that this theoretical efficiency is never approached. The current efficiency is not likely to be higher than 50 per cent., and the voltage required will be not less than double the critical pressure, 2·8 volts. The energy efficiency will therefore be 50 per cent. × 50 per cent. = 25 per cent., and the output per H.P. hour not greater than 22·2 grammes, or say ¾ ounce. This agrees with estimates made by Bochers, based on small manufacturing experiments, and with the most reliable figures which have been published concerning processes actually at work on a large scale. It may be taken from these facts that a plant of 1,000 H.P. (net, delivered at the terminals of the electrolytic cell) will manufacture 194 tons of aluminium per year of 365 days of 24 hours each. This is not a large quantity of metal, and it is easy to see that an aluminium factory to have a fair output must be in a position to use several thousand H.P. In fact, in this, as in many electro-chemical industries, 1,000 H.P., large as it seems from a mechanical point of view, is a convenient unit to think in. The capital cost of a water-power plant must include the expenditure for dams, conduits, turbine pit, turbines with buildings, and land necessary for their accommodation. It will obviously vary greatly according to the circumstances of each case. If much civil engineering is required, *i.e.* if the water has to be impounded and a new and artificial outlet and course have to be provided for it, the capital expenditure may be very large. But if the prospect of the undertaking's success is to be good, the total outlay for this work and for the power plant should not exceed £50 per electrical H.P. That is, a capital outlay of £250,000 will be necessary for a single plant of 5,000 H.P., which, though certainly a good size, is by no means colossal, seeing that it is capable of producing no more than 1,000 tons of aluminium per year, the power being used continuously. Such a plant will yield power at the rate of about £4 per electrical H.P. year, allowance being made for interest, depreciation and running charges. This corresponds with £4,000 for 194 tons of Al, *i.e.* £20 12*s.* per ton, or 2·2*d.* per pound. The market price of aluminium is about 1*s.* per pound, whence it appears that the cost of power, though a considerable item, is not so large as to make it certain that a source of cheap power can be profitably used for the manufacture of aluminium, irrespective of other considerations, such as cost and accessibility of raw material.

Probably the largest item of cost in the manufacture of aluminium is the price of the alumina. About 2 pounds of anhydrous alumina are needed to produce 1 pound of aluminium, and the present price of alumina of good quality made from bauxite is 2*d.* per pound. The next large item is the cost of the carbon electrodes. The calculated consumption of carbon is 66⅔ per cent. of the weight of aluminium produced, but in practice it usually amounts to 100 per cent. Taking the cost of carbon electrodes at 2*d.* per pound, the expenditure on this score is as great as that necessary for power. The approximate minimum cost of manufacturing aluminium may be set forth as follows:—

	Per pound of Al produced.
Power	2· 2*d.*[1]
Alumina	4· 0
Carbon electrodes	2· 0
Labour superintendence, interest on and repairs to furnaces	2· 0
	10· 2*d.*

This estimate is so little below the market price of aluminium (1*s.* per pound) that it is probable that some of these items have lately decreased in cost. For example, alumina may well come down to £10 per ton (say 1*d.* per pound), and carbon electrodes to a like figure. The minimum cost of aluminium would then be 7·2*d.* per pound, and its selling price may fall to 9*d.* per pound. At that price it is one and a half times the price of copper weight for weight, and less than half its price bulk for bulk, so that it can be freely used as an industrial metal of moderate price.

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[1] An estimate for the Hall process shows similar figures:—

	Per lb. of Al produced.
Power	2· 1*d.*
Alumina	6· 3
Carbon electrodes	1· 6
Miscellaneous	0· 6
	10· 6*d.*

USES OF ALUMINIUM

There are three distinct directions in which aluminium is chiefly used:—

(1) As a reducing agent. Vast quantities are employed as an addition to steel when it is about to be cast to reduce and remove any entangled oxide, to cause the metal to pour quickly and to produce sound castings. It is sometimes used as an addition to copper and copper alloys for a like purpose. In this case the proportion added is small—ounces per ton—and the aluminium, having done its work, passes from the metal, and may leave no recognisable trace in the finished material. The aggregate amount thus used is very large, although individual doses are minute.

It is also used to reduce refractory oxides, such as that of chromium, and thus yield the metal in a pure state.

(2) As an industrial metal for small ware and structures where lightness and resistance to corrosion are required. The specific gravity of commercial aluminium ranges from 2·67 to 2·70. The metal can be worked as freely as brass, save that it is not readily soldered. All kinds of small articles for daily use—boxes, travelling cups and flasks, cooking vessels and such like—are made in large quantities, and are now cheap enough. Specially light boats may have their fittings of aluminium, or even be built of it entirely; aluminium motor car bodies and engine cases are also made.

(3) As a constituent of alloys. Aluminium added to copper gives alloys of great strength and high

mechanical utility. Similar good alloys are obtained when aluminium is added to brass. The quantities used range from 1 to 10 per cent. of Al. Another series of aluminium alloys is made by adding 1 to 10 per cent. of alloying metals, such as copper, nickel and tungsten, to aluminium itself. Alloys of this class are almost as light as aluminium, and a good deal stronger. They may often be substituted with advantage for unmixed aluminium, and used for the purposes already mentioned under section 2.

IMPURITIES OF COMMERCIAL ALUMINIUM

On account of its method of production by the electrolysis of alumina, which is never quite pure, and by reason of the introduction of additional impurities from the carbon anodes, commercial aluminium almost invariably contains small quantities of iron and silicon. If too high a current density has been used or the bath allowed to become poor in alumina sodium may also be present. Thus commercial aluminium rarely contains more than 99 per cent. Al. A great deal of that put on the market is no better than 98 per cent., and a crude metal of 96 per cent. or lower is manufactured for reducing purposes. The following analyses show the nature and amount of the usual impurities in the better grades of aluminium :—

	I.	II.	III.
Al	99·59	99·00	98·45
Si	0·25	0·87	1·29
Fe	0·16	0·13	0·10
	100·00	100·00	99·84

One of the impurities mentioned above, viz. sodium, is particularly objectionable, because the sodium, which is present in minute specks and spots segregated from the mass of the metal, oxidises readily and causes injury and corrosion. Even when oxidised it continues to cause corrosion, for the caustic soda produced itself acts on the aluminium surrounding it.

MAGNESIUM

Magnesium, like aluminium, is a difficultly reducible metal which can be most economically manufactured by electrolysis. Formerly magnesium chloride was reduced by means of sodium, but the metal thus obtained had to be purified by distillation. As magnesium boils at about 1,000° C. = 1,832° F., this operation is somewhat difficult and costly, and its avoidance is accomplished by the use of the electrolytic process, which, if properly conducted, yields a metal sensibly pure.

Magnesium chloride is the raw material. It is obtained in the double salt carnallite ($KCl\,MgCl_2\,6H_2O$) from the saline deposits of Stassfurt. Whereas an aqueous solution of magnesium chloride, when evaporated to dryness, is largely decomposed, yielding magnesia and hydrochloric acid, one containing also the chloride of an alkali metal can be dehydrated without decomposition. The anhydrous double chloride is fused and electrolysed between a carbon anode and an iron cathode. The process presents analogies to that for the manufacture of aluminium, but differs in the fact that the electrolyte is not the oxide of the metal dissolved in its fused halogen salt, but is the halogen salt itself. The essential parts of an apparatus for the electrolytic reduction of magnesium are shown in the accompanying drawing (Fig. 27) of one devised by Graetzel, which, in more or less modified form, is a type of the plant now employed.

A is a cylindrical steel vessel, made a cathode by the cable B. It is closed by an air-tight cover C, through which passes an entrance pipe D, conveying a gas, *e.g.* nitrogen, or furnace gases free from oxygen; the surplus gas passes out by the pipe D. E is a porcelain cylinder open at the bottom, and having slits in the sides. This contains the carbon anode F, and carries a pipe G for the escape of the chlorine generated at the anode. The vessel A is filled with carnallite, which is kept fused by heat externally applied. The products of electrolysis are magnesium and chlorine. The first floats on the fused carnallite, and is protected from oxidation by the atmosphere of nitrogen or other inert gas supplied through D. The chlorine liberated at the anode can pass freely away, and is hindered from casual entrance into the outer vessel by the porcelain cylinder E, which, nevertheless, permits free flow of the current and of the electrolyte itself. As is usual in the electrolysis of the fused salts of difficultly reducible metals, the design of

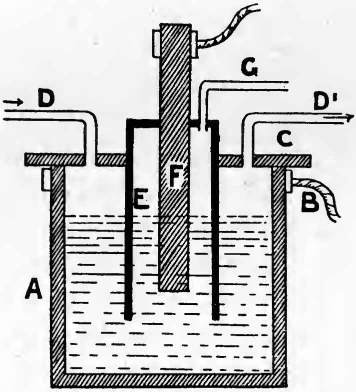

Fig. 27.

an apparatus which will yield the metal is comparatively simple; the device of one which will be fairly permanent in actual manufacture is less easy. In that shown above no attempt is made to protect the walls of the outer vessel from the action of the electrolyte; should this action be found severe, recourse must be had to the method described under Aluminium, viz. the cooling of the walls to form a protective crust. In this case the vessel itself could not be the cathode, and an independent cathode, as in the aluminium apparatus, would be necessary; also the electrolyte would be kept fused by the current, and not by heat externally applied.

It was noted above that the magnesium, as it was reduced, collected on the surface of the electrolyte. This is far from convenient, and necessitates, both in the present apparatus and in one of the aluminium type, an envelope for the anode, to hinder union of anode and cathode products. In the case of aluminium, although the solid metal is specifically lighter than the solid electrolyte, yet when both are fused the metal is the heavier. This convenient relation does not obtain with magnesium and carnallite. It is possible that it might occur for some other feasible electrolyte, but exact data are lacking. The demand for magnesium is too small to warrant much technical investigation for the device of a perfect process. What is needed can be made, and its cost of production is a secondary matter.

The heat of combination of $MgCl_2$ is 151,000 Cal. The critical voltage for its electrolysis is therefore 3·26 volts. The heat of combination of $KCl + MgCl_2$ to form carnallite is probably so small as not to affect this value appreciably. In practice a high current density is used, *e.g.* 100 amperes per square foot of cathode surface, and the voltage is correspondingly higher, in spite of the fact of fused carnallite being a good electrolytic conductor. There are certain details in the process which have been studied by Oettel, and are of interest in that they indicate the sort of difficulty not obvious from a consideration of the principles of a process, but prominent enough when it is put to work. In order to collect the magnesium which floats on the electrolyte, it is desirable that it should run together into large buttons. Minute globules are difficult to collect and oxidise in proportion to their surface, which is relatively great. The cause of the failure of the metal to agglomerate in the desired manner is usually the formation of a thin skin of magnesia on the globules of metal, which prevents their mutual contact, much as dirt and oxide on mercury will prevent it from running together. This magnesia comes from the electrolysis of $MgSO_4$, present as an impurity in carnallite, the products of electrolysis being MgO and SO_2 and O. This explanation is not completely convincing, for it might well be supposed that MgO would dissolve in considerable quantity in fused carnallite, and would thus be harmless. Once dissolved it would be as readily reduced as $MgCl_2$, its heat of combination being nearly the same. A more likely cause seems to be the presence of oxygen in the gas used as a neutral atmosphere for the cathode compartment. This would act on the small globules of metal as they rose from the cathode and swam on the surface of the electrolyte; it would coat them with a film of MgO, and prevent their coalescing. Even if magnesia is fairly soluble in fused carnallite, it would not be promptly removed from these globules because they are not fully immersed in the electrolyte. The removal of this film may be accomplished by adding fluorspar (calcium fluoride) to the melt; in like manner a mass of magnesium globules mixed with carnallite, such as will be obtained by ladling out the contents of the cathode compartment, may be caused to come together by adding fluorspar and heating. A clear melt and magnesium stripped from any coating of magnesia will result. Melted magnesium in bulk, and not in globules, can be handled without fear of its taking fire, or even oxidising largely, if it be kept not much above its melting-point, viz. 750° C. = 1,382° F.; if the temperature be allowed to rise to a good red heat, combustion will occur.

The production of magnesium is more interesting as illustrating many principles of electrolysis applied to fused salts than important from a commercial point of view. The latest statement from what is the chief and perhaps the only factory now making the metal, viz. the Aluminium and Magnesium Works at Hemelingen, is to the effect that the demand for magnesium is decreasing. This may well be due to the preferential use of aluminium as a reducing agent; even for flash-lighting, for which magnesium seems especially suitable, aluminium has been proposed as a substitute. Almost the only other purpose for which magnesium is employed is as an addition to nickel to cause it to cast well. Here it doubtless acts as a reducing agent, and removes entangled oxide. As it does not alloy with nickel, the surplus magnesium does not appear in the finished casting. An alloy of magnesium with aluminium has lately been prepared which is said to be not easily corrodible; no other useful alloy of this metal has yet been obtained.

SODIUM

Reference is made to the electrolysis of fused sodium salts, and the production of sodium, in the chapter on Alkali and Chlorine (*q.v.*). In the processes there dealt with, however, the production of sodium is incidental, and the metal itself is not isolated; it serves only as an intermediate stage in the formation of caustic soda or sodium carbonate. When the metal sodium is the desired end-product, other methods than those there described become necessary.

Sodium was formerly manufactured by distilling sodium carbonate with charcoal, the reaction being—

$$Na_2CO_3 + C_2 = Na_2 + 3\,CO.$$

This process needed a very high temperature, was costly in fuel and destructive of retorts, and was superseded by the Castner process (a purely chemical method, not to be confused with the Castner electrolytic process for sodium, which is about to be described).

In this process caustic soda was used instead of sodium carbonate, and the reducing agent was a mixture of iron and finely divided carbon made by heating together oxide of iron and tar. The function of the iron is to weigh down the carbon and keep it immersed in the fused NaOH.

The reaction—

$$4\,NaOH + C_2 = Na_2CO_3 + Na_2 + 2\,H_2 + CO$$

requires 106 Cal, instead of 186 Cal requisite for the reduction of sodium carbonate formerly practised, and moreover takes place at about 800° C. = 1,472° F. instead of at about 1,500° C. = 2,732° F. These advantages more than compensate for the use of the dearer raw material, caustic soda, in place of sodium carbonate.

At the present time all chemical methods for the manufacture of sodium are obsolete. It is produced exclusively by electrolysis, the sole process employed being one devised by Castner, the inventor of the chemical method described above. It is noteworthy that the alkali metals were first isolated by the electrolysis of caustic alkalies by Davy, and that the same process is now the only method of commercial importance.

THE CASTNER PROCESS

As stated above, the raw material of the Castner electrolytic process for the manufacture of sodium is caustic soda. This substance, in its commercial state, always contains water (up to about 10 per cent.), and fuses more readily in consequence. As the water is driven off the melting-point rises, but never exceeds a low red heat. It is to this fusibility of caustic soda that the success of the Castner process is in a large measure due. The requisite temperature is manageable, and the apparatus is not rapidly destroyed, as it is when fused salt, for example, is used as the electrotype. Further, the gas evolved at the anode is oxygen, not chlorine, and it is therefore possible to use iron anodes, which are little attacked by oxygen in alkaline liquids at moderate temperatures. A diagrammatic view of the Castner apparatus is given in Fig. 28. A is a cylindrical steel crucible with an opening at the bottom through which the iron cathode B passes. The crucible is set in a flue, so that the body of it is heated while the neck C remains cool. The caustic soda which fills the crucible consequently solidifies in the neck C, and protects the joint made between the cathode and the crucible. The anode D, which may be a cylinder with vertical slits to allow free flow of the electrolyte, surrounds the upper part of the cathode. This upper part is encircled by a cylinder of wire gauze E, depending from the collecting pot F. As electrolysis proceeds, fused sodium floats from the cathode and collects on the surface of the fused caustic soda in the pot F. It is hindered from straying into the anode compartment by the wire gauze, through which it cannot easily pass on account of its high surface tension. The extreme fluidity of caustic soda and the ease with which it wets all surfaces allow that body, on the other hand, to pass freely through the gauze.

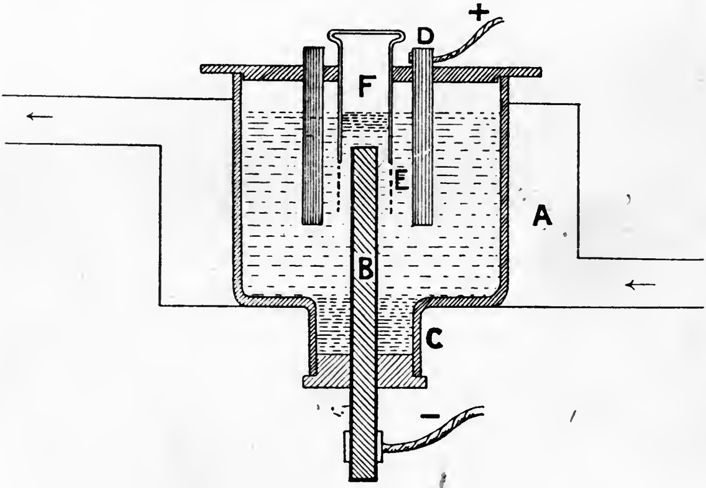

FIG. 28. Chem. process.

From the collecting pot the sodium can be baled from time to time. This pot is, of course, full of hydrogen, which serves to protect the sodium from chance oxidation. In actual work small quantities of hydrogen occasionally ignite; thus a succession of small and harmless explosions usually accompanies the process of electrolysis.

It may be said that the world's supply of sodium is provided by this process, which is at work at Oldbury, at several works in Germany, and at Niagara. At the last-named place the Electro-Chemical Company use about 700 H.P., supplied from the main power house at the Falls. The output possible for such a plant may be calculated. The heat of combination of NaOH is 102 Cal. The critical pressure necessary for its electrolytic decomposition is, therefore, $\frac{425{,}000}{96{,}540}$ volts = 4·4 volts. Assuming that this voltage could be used and that theoretical current efficiency could be attained, the output of 700 H.P. would be 102 kilos Na per hour, *i.e.* 732 tons of Na per year of 300 days of 24 hours. In practice the joint current and pressure efficiency is not likely to be greater than 50 per cent., whence it follows that a plant of this size would turn out about 360 tons of sodium per year. The quantity is small, but probably ample for the requirements of the market. Sodium is used only for a few special purposes, such as the manufacture of sodium peroxide, the production of cyanides, and for "quickening" mercury in gold amalgamation; in the larger industries it has as yet found no place. In the future it may possibly be used as a compact, amenable and portable form of energy.

Potassium could doubtless be manufactured in the same manner as sodium, but as it has no industrial use it need not be dealt with here. Small quantities are prepared for scientific purposes, probably by the older chemical processes.

The third member of the alkali group, lithium, has no industrial use as a metal.

SECTION IV

Winning and Refining Metals and their Alloys in the Electric Furnace

Carbides, Borides and Silicides

THE ELECTRIC FURNACE

THE high temperature attainable in the electric furnace has not merely served to produce certain metals and alloys less easily won by older means, but has allowed of the preparation of many substances not previously known—at least in an industrial sense. When the formation of a given product needs a temperature exceeding 2,000° C. = 3,632° F. there is no choice in the matter, because ordinary processes of combustion cease at or below that temperature. By pouring electrical energy through refractory electrodes into a box made of a material which conducts heat badly, the temperature in the interior of that box can be raised to that of the arc (computed at 3,500° C. = 6,332° F.), and reactions unknown at ordinary furnace temperatures proceed freely. For the further discussion of the principles of this method of heating, see Section I., p. 24. For the purpose of the present section it is sufficient to realise that by the use of the electric furnace it is possible to attain temperatures far above those which can be reached in any other way, and this without contact with any foreign matter other than the electrodes and the walls of the refractory box forming the furnace.

Probably the earliest attempt to use this peculiar advantage of electrical heating was in the manufacture of zinc by the process devised by the Brothers Cowles, who heated a mixture of zinc ore and carbon in an electric furnace, the zinc being reduced, distilled and collected (see p. 141). This process was not successful, because the temperature necessary for the reduction of zinc is not high enough to make ordinary furnace heating ineffective. Wasteful as it is of heat, it is nevertheless cheaper than electrical heating when the temperature aimed at is moderate.

The same inventors adapted their furnace for the production of aluminium bronze. As this furnace is the type and forerunner of many modern electric furnaces a sketch of it in its simplest form may be usefully given.

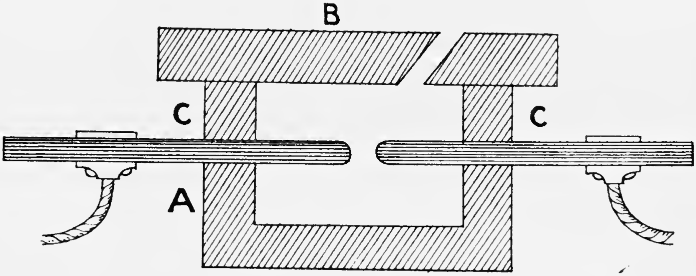

Fig. 29.

A firebrick box A, fitted with a cover B having a hole for the escape of gases, is pierced with two openings one at each end, through which pass large carbon electrodes. These are coupled by heavy copper clamps to cables of large section. A large current may thus be passed into the box and a powerful arc formed. The substance to be heated—in this case a mixture of alumina and carbon—is packed round the electrodes and fills the box. This form of furnace has been modified in various ways, but its type remains fixed. It is merely a device for heating by an enclosed arc.[1] The Cowles furnace has now only a

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[1] There need be no actual arc; passage of the current through a

historical interest, but it was in many ways so well conceived and carried out that a short account of its more developed form may be given.

In this furnace, which was one of the latest forms in use shortly before the Cowles process for the manufacture of aluminium bronze was given up, the electrodes consist of bundles of large carbon rods and are inclined. The rods C, C are set in massive metal caps, which are of copper if a copper aluminium alloy is to be produced and of iron if ferro-aluminium is to be made. This is because the electrodes and their holder get very hot and the latter towards the end of the run may melt, mingling with the charge. The caps are connected by rods with the cables D, D. The holders slide in the tubes E, E, and are moved forward as required by the screws F, F, which pass through nuts attached to the rods and bear against the flanges of the guide tubes. A heavy fireclay cover with vents for the escape of gas completes the apparatus, which is throughout very simple and massive. The disposition of the charge is important. The brickwork constituting the body of the furnace is, of course, lined with firebrick, but this is by no means sufficiently refractory to resist

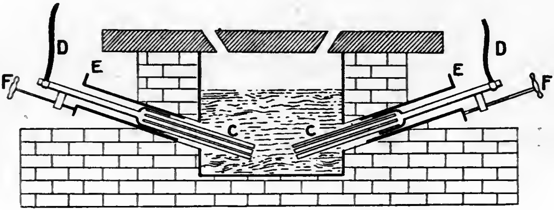

Fig. 30.

high resistance, such as that of a thin carbon rod or of the heated charge itself, will equally determine the production in the midst of the furnace of as high a temperature as that of the arc proper.

the high temperature which prevails in the furnace. It is, therefore, protected by a lining of broken charcoal. Lest this should become graphitic and agglomerate at the high temperature of the furnace it is previously dipped in milk of lime, so as to leave a film of lime on each particle. Thus satisfactory isolation of the heated charge from the walls of the furnace is secured.

The form of alumina usually employed in the Cowles process is corundum (crystallised aluminium oxide); the first charge consists of 15 kilos of corundum and 30 kilos of granulated copper, with enough carbon to make the mixture conductive. To subsequent charges the slag from previous operations is added; this material is well worth working up, seeing that it contains about 30 per cent. of aluminium and 25 per cent. of copper, both present chiefly as metal. The charge is covered with coarsely powdered wood charcoal and a current of 3,000 amperes at a pressure of 50 volts turned into the furnace. This pressure is maintained as nearly as possible throughout the run, the electrodes being drawn back as the resistance of the charge decreases. About ten minutes after the current has been switched on, the air and moisture in the materials will be expelled, and the reduction of the alumina begins according to the equation—

$$Al_2O_3 + 3\,C = 3\,CO + Al_2.$$

The CO escapes at the vent holes and is burned under a chimney. The burnt gases, which may contain many mineral particles volatilised or carried away mechanically, are passed through a depositing flue. After two hours the electrodes are about 1·1 metres apart and the charge is worked off. The run is stopped and the electrodes are drawn back as far as possible into their protecting iron tubes so as to hinder their useless oxidation. When the charge is drawn it is found to consist partly of unused charcoal, together with slag and unreduced alumina, and, as the desired product, a mass of crude aluminium bronze containing 14 to 20 per cent. of Al. From this, after analysis, alloys of determined composition, *e.g.* 10 per cent. aluminium bronze, 5 per cent. aluminium brass, and the like, can be prepared. It is found that even with proper working up of the slag not more than two-thirds of the aluminium originally present in the corundum is recovered as metal. The output per H.P. hour is poor, being in the case just cited about 7·5 grammes; in later practice at Milton in England as much as 25 grammes per H.P. hour was obtained. The theoretical output can be readily calculated. Thus the reaction—

$$Al_2O_3 + 3\,C = 3\,CO + Al_2$$

needs the expenditure of 305 Cal for its realisation, that is to say, 305 Cal are required for the production of 54 grammes of Al. Now 1 H.P. hour = 646 Cal, whence it follows that it should produce 114 grammes of Al. An actual output of 25 grammes per H.P. hour, therefore, represents an efficiency of only 22 per cent. Apart from this low efficiency, the expenditure necessary for wood charcoal and electrodes is considerable, so that the process is comparatively costly. Further, the product is not of particularly good quality, for in the tumultuous sphere of reaction all oxides are reduced, and such impurities as iron and silicon tend to appear in the crude aluminium bronze. Thus it came about that as soon as the Héroult process and its congeners had been got to work successfully the Cowles process for the production of aluminium bronze was superseded. At present it is generally preferable to prepare such alloys from the pure metals, but of course the alloys themselves could, if desired, be made in the Héroult furnace (p. 169) by using a cathode of copper or other metal to be alloyed with the aluminium. Indeed, the Héroult process was originally designed for the direct production of such alloys.

The chief interest of the Cowles process lies in the fact that on its account a highly practicable form of electric furnace was devised; also that it took advantage of the tendency of aluminium to alloy with certain metals rather than to form a carbide. If it is attempted to prepare unalloyed Al by the use of the electric furnace, the chief product will be Al_4C_3. In addition to this tendency to form carbide, there is another obstacle to the production of pure aluminium in the electric furnace. Moissan has shown that alumina even when liquid is not reduced by carbon, and that both bodies must be vaporised and their vapours very strongly heated before the alumina is reduced; the product then consists of aluminium mixed with aluminium carbide. It is only when a metal is present capable of alloying freely with Al—and preferably, as in the case of copper, with the evolution of heat—that a carbonless product is obtained. According to the Cowles patents the original intention of the inventors was to form such an alloy and then remove the alloying metal, recovering pure Al. But such removal is impracticable, and the process naturally evolved itself into one for the production of alloys.

The systematic and scientific study of the capabilities of the electric furnace is due almost entirely to Moissan. His investigations are far in advance of any industrial application which they have yet received, and afford accurate data for the manufacture of such of the various carbides, silicides and borides as may from time to time be found commercially important. In view of this it is desirable that an outline of his work should be given here, in order that the applications already made may be the better understood.

The starting-point of his researches was the study of the crystallisation of carbon, with especial regard to the production of the octahedral or diamond form of crystals. For this purpose it was necessary to cause a metal containing carbon in solution to solidify in such a manner as to exercise great pressure on the carbon at the moment of its crystallisation. In order to saturate the chosen metal with carbon it was requisite to heat the metal far above ordinary furnace temperatures. Thus various forms of furnace were devised, in which the substance to be heated was kept apart as far as possible from the electrodes and from all other foreign bodies. The difficulty of finding a substance of which to construct the body of the furnace was considerable; eventually lime was chosen. A typical furnace is shown in Fig. 31. The body A is made of blocks of lime scooped out in the

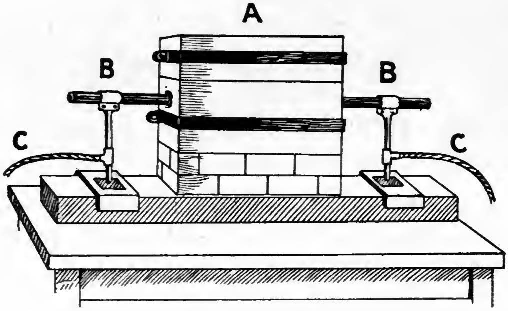

Fig. 31.

middle to form a small cavity, into which the electrodes B, B project. The cables C, C are attached at the bottom of the clamps, so that they may not be burned by the torrent of flame which may burst out from the holes into which the electrodes pass. As will be seen, it consists essentially of the same parts as those of the furnace diagrammatically represented on p. 204. The chief difference is in the materials of the walls of the furnace, which in the former case are of firebrick and in the present instance of lime. The lime is not only enormously more refractory than the firebrick, but is also a vastly worse conductor. With the aid of this apparatus Moissan was able to bring about novel reactions and to prepare substances previously unknown industrially.

By the use of this furnace with a small hearth on which the energy represented by an output of 100 H.P. can be expended, every known oxide can be reduced or volatilised. Lime, magnesia, alumina and zirconia melt and volatilise freely. Carbon boils, and its vapour can be used to reduce refractory oxides also in ebullition. The chief conclusions to be drawn from Moissan's work having an industrial significance are as follows:—

The stable form into which carbon, whether amorphous or crystallised as diamond, tends to pass is graphite. Under ordinary conditions carbon does not melt, but passes directly into the gaseous state; if subjected to high pressure, as it may be by suddenly cooling a liquid, *e.g.* iron, in which it is dissolved, it may be liquefied and then may crystallise as diamond.

Lime, magnesia, molybdenum, tungsten, vanadium and zirconium may be fused. Silica, zirconia, lime, aluminium, copper, gold, platinum, iron, uranium, silicon, boron and carbon may be volatilised. The oxides among these substances may be deposited in a crystalline form. Oxides usually regarded as irreducible, *e.g.* alumina, silica, baryta, strontia and lime, uranium oxide, vanadium oxide and zirconia, may be reduced by carbon in the electric furnace. Many metals which are reduced with difficulty in ordinary furnaces, such as manganese, chromium, tungsten and molybdenum, may be prepared in quantity. Moreover, in the electric furnace these metals can be obtained of approximate purity in spite of their great tendency to unite with the oxygen and nitrogen of the air. It often happens that, when a metallic oxide is reduced with excess of carbon in the electric furnace, a carbide of the metal is first formed. From this the pure metal can usually be prepared by fusing the carbide with the oxide of the metal. The carbon is oxidised and an equivalent of the metal is reduced. The behaviour of such metals in dissolving carbon at high temperatures, in rejecting it on cooling, and in losing it when subjected to selective oxidation in general resembles that of iron, which is well known. One class of bodies is particularly stable at the high temperatures attainable by the electric furnace—to wit, that comprising the carbides, borides and silicides. These substances are usually of simple composition; SiC (silicon carbide), CaC_2 (calcium carbide), Mn_3C (manganese carbide), Fe_2Si (iron silicide), FeB (iron boride), CB_6 (carbon boride) will serve as examples. Some members of the group are extremely hard. Thus carbon silicide (or silicon carbide) is harder than emery, while boron carbide and titanium carbide may actually serve to cut a diamond—not merely to polish it, as does silicon carbide, but to produce definite facets. Others of the carbides have another claim to interest from an industrial as well as from a scientific standpoint. Every one knows nowadays that calcium carbide is decomposed by water and yields acetylene; but it is not always realised that the property of thus giving rise to a hydrocarbon is general for a large number of similar bodies, *e.g.* the carbides of lithium, aluminium, thorium and cerium. Lithium carbide (Li_2C_2) yields acetylene; aluminium carbide (Al_4C_3) gives methane; cerium carbide CeC_2, a mixture of the gases acetylene, ethylene and methane, and a notable proportion of liquid hydrocarbons. This brief catalogue of facts will show how large a field for industrial research exists, and how well mapped are the paths by which it may be entered.

METALS PRODUCED OR REFINED BY THE ELECTRIC FURNACE

As has been shown above, the production of aluminium has been attempted by means of the electric furnace without success. Aluminium alloys have been successfully prepared in similar manner, but this mode of preparation is now superseded. Certain other metals of industrial importance can be prepared in quantity in the electric furnace, and there is reason to believe that it is the best and sometimes the only way of preparing them. For an account of such preparations it is necessary again to refer to Moissan's work.

CHROMIUM

Chromium has scarcely been known as a metal in the reguline state until the last few years. It can be prepared in the electric furnace first as a carbide and then as the pure metal. The production of " cast chromium " corresponding with cast iron, containing about 10 per cent. of carbon, can be effected by heating a mixture of Cr_2O_3 and carbon in the electric furnace. There is evidence of the existence of two definite carbides—Cr_3C_2 (containing 13·33 per cent. of C) and Cr_4C (with 5·45 per cent. of C), but the cast metal may contain from 1–2 per cent. up to the limit set by the higher carbide. The preparation of chromium containing only a small percentage of carbon is not easy. It is true that the carbon can be removed by selective oxidation by fusing the crude cast metal with chromic oxide in a crucible lined with chromic oxide, but the resulting metal is "burnt," *i.e.* it contains a certain amount of oxygen. A better plan is to refine it by fusing it with lime. The tendency of lime to form calcium carbide causes it to remove carbon from the chromium, and by this method a metal with 1·5–1·9 per cent. C is obtained. Complete removal of C is not practicable however in this way, because at this point oxidation of the chromium itself occurs, and the metal is ultimately converted into a calcium chromite. The object to be attained can be reached by the aid of this very body. Its tendency to oxidise chromium is not so great as that of lime *per se*, and, therefore, when cast chromium containing carbon is refined in a furnace lined with this material, the oxidation and removal of the carbon take place in regulated manner. Pure chromium is obtained. It is a brilliant metal of a grey colour, rather lighter than that of iron, and though hard can be filed and polished without difficulty. The various statements as to the extreme hardness of chromium which have been current in text-books have probably arisen from the fact that the carbide Cr_3C_2 is extremely hard, scratching quartz and topaz but not corundum. Pure chromium has a specific gravity of 6·92 at 20° C. It is not attracted by a magnet. Its melting-point is higher than that of platinum, and cannot be reached by the use of the oxyhydrogen blowpipe; the carbides are less infusible. The metal keeps its polish in the air, is almost unattackable by acids, even aqua regia, and by fused alkalies.

Chromium can be produced with ease in quantity and of fair purity. A cast metal of the composition given below can be made in lots of 10 kilos at a time by the use of a current of 1,000 amperes at 70 volts, *i.e.* 94 E.H.P. The analysis of the metal gave:—

	Per cent.
Cr	97·14
C	1·69
Fe	0·60
Si	0·39
Ca	Trace
	99·82

Such a material is well suited for adding to steel to produce special alloys containing known quantities of chromium. These alloys, having for example 3–4 per cent. of Cr, are employed for making projectiles, and have been suggested for use in railway tyres, as they are both hard and tough.

There is another method of preparing chromium, which is in some respects better than the use of the electric furnace. Chromic oxide is mixed with aluminium in powder, and is fired by a fuse composed of a mixture of aluminium powder and barium peroxide, in which a strip of magnesium is embedded so that it may be kindled.

The heat of combination of aluminium with oxygen is so great that it causes not only the reduction of the Cr_2O_3, but fuses the resulting Cr into an ingot. Such metal from its mode of preparation is free from carbon, and indeed can be prepared of great purity. Even here, it is interesting to note, the method depends ultimately on an electro-metallurgical process, viz. the electrolytic reduction of aluminium (*q.v.*).

The study of the properties of pure chromium prepared by reducing chromic oxide by means of aluminium has led to remarkable results. W. Hittorf has found that although chromium is so powerfully electro-positive as to reduce zinc from its fused salts, yet in an aqueous solution of hydrochloric acid or of the chloride of an easily reducible metal it is inert. Solutions of the chlorides of zinc, cadmium, iron, nickel, gold, palladium and platinum are not affected; cupric chloride and mercuric chloride are reduced to their respective lower chlorides, but only when the solution is boiling. This greater activity in a solution at a high temperature is characteristic of the behaviour of chromium when used as an anode. At the ordinary temperature it is indeed dissolved, but not with the production of chromous chloride; it forms chromic anhydride. As an anode in solutions of metallic chlorides at their boiling-point, however, chromous chloride is produced. Chromium which has been made an anode under such conditions as to cause it to yield chromic anhydride assumes a passive state, like that known to occur in the case of iron, and is incapable of reducing metals certainly less oxidisable than itself. The whole series of phenomena exhibits many anomalies, and has not yet received full explanation. It is sufficient here to indicate that a remarkable and interesting addition to our knowledge of the chemical qualities of a fairly common element has accrued from the happy facility for the preparation of refractory metals relatively pure and in a compact state which has been afforded us by electrolytic methods.

MOLYBDENUM

This metal can be prepared in similar manner to chromium. It may be obtained free from carbon by heating a mixture of the dioxide MoO_2 with defect of carbon in the electric furnace. It is white, has a density of 9·01, is as malleable as iron, and can be filed, and, when hot, forged. It is only slightly oxidised in ordinary air. When heated in contact with carbon it absorbs a small percentage of that substance, and can then be hardened by quenching in the manner characteristic of steel. It forms a definite carbide (Mo_2C), which is hard and crystalline and has a specific gravity of 8·9. The pure metal is very infusible, the carbide somewhat less infusible.

Molybdenum is used to a small extent in making special steels. Moissan proposes to employ it instead of manganese or aluminium to deoxidise steel in the converter. The advantages of this substitution would be that the oxide which would be produced (molybdic acid, MoO_3) is volatile and would escape from the bath, and that the molybdenum which might be left in the metal would have similar properties to the iron with which it was mixed, notably in respect of its malleability and power of hardening when quenched.

TUNGSTEN

This is another metal of the same group as those already described. It is infusible save at the highest temperature of the electric furnace, in which it can be prepared by reducing tungstic acid (WO_3) by carbon. When the carbon is used in defect, and the mass is not completely fused, the pure metal results; but if an excess of carbon be employed, or if the reduced metal is fused so that it comes freely into contact with the walls of the crucible, it takes up carbon, giving a cast metal more fusible than pure tungsten. A definite carbide (W_2C, containing 3·16 per cent. of carbon) may be prepared. It has a specific gravity of 16·06 at 18° C., and is hard enough to scratch corundum. Tungsten free from carbon is soft enough to be filed; it can be forged; it absorbs carbon readily and is hardened thereby, in this respect resembling generally molybdenum and iron. It is not attracted by the magnet; its specific gravity is 18·7. Tungsten, like molybdenum, is a metal which is used to a limited extent to produce special steels. The precise properties and merits of alloys of this description are not well understood, chiefly because they have not yet been subjected to the systematic study necessary to give us the precise knowledge which (thanks largely to the researches of Hadfield) we already possess of steels containing as characteristic constituents silicon, aluminium, manganese and nickel. The easy and relatively cheap manufacture of metals almost unattainable previously in the pure state will lead to the examination of their capabilities as constituents of industrial alloys. Should such be prepared, the manufacture of metals of suitable degree of purity by the electric furnace can be begun at once on the basis of Moissan's investigations.

As in the case of chromium, there is a rival method for the manufacture of tungsten, viz. the reduction of tungstic acid by aluminium. It is perfectly possible that this method may prove preferable to reduction in the electric furnace. Titanium, although at present of no industrial importance, may be mentioned, because it has proved to be the most infusible metal which has been prepared by the electric furnace, far exceeding chromium, tungsten, and molybdenum in this respect. It also has a strong tendency to form a nitride (Ti_2N_2) and a carbide (TiC). The formation of the nitride can be prevented by using so powerful a current that the temperature in the electric furnace is higher than allows of the continued existence of the nitride; the carbide can be disposed of by re-fusing cast titanium containing carbon with excess of titanic acid (TiO_2). Thus even the most refractory of bodies may be reduced, fused, carburetted, refined and decarburetted in quantity, and with complete ease and certainty, by means of the electric furnace, which thus takes rank as a valuable instrument of research and a powerful industrial apparatus.

CARBIDES

The production of carbides by heating together certain metals or non-metals and carbon, or by reducing the oxides of these elements with excess of carbon in the electric furnace, is quite general, and has been closely studied by Moissan. He has arrived at the following conclusions:—

At the high temperature of the electric furnace certain metals, *e.g.* gold, bismuth and tin, do not dissolve carbon.

Copper will absorb only a small quantity, which suffices, however, to modify its properties considerably.

Silver at its boiling-point dissolves a small quantity of carbon, and expels it on cooling in the form of graphite; the metal containing carbon expands on solidification, just as does cast iron. Pure iron and pure silver contract on solidifying.

Aluminium dissolves carbon and ejects it as graphite; it also forms a carbide (Al_4C_3).

The platinum metals dissolve carbon, and eject it on solidifying as graphite.

Calcium, strontium and barium form carbides of the type $R''C_2$; lithium yields Li_2C_2. All these give acetylene when acted on by water.

Cerium, lanthanum and yttrium give carbides of the form CeC_2, which, however, do not yield pure acetylene, but a mixture of that gas and methane.

Manganese gives the carbide Mn_3C, which decomposes water with evolution of equal volumes of methane and hydrogen.

Uranium carbide (Ur_2C_3) gives methane, hydrogen, ethylene, and, what is most interesting, a quantity of liquid and solid hydrocarbons representing about two-thirds of its total carbon. On this and cognate facts Moissan has erected a new and ingenious theory of the mode of formation of petroleum.

Other metals form definite carbides sharply distinguished from the foregoing by their remarkable stability. Examples are Mo_2C, W_2C, Cr_4C, and Cr_3C_2. These are of metallic appearance, very hard, and fusible only at a high temperature.

The carbide of the non-metal silicon (SiC) and that of the pseudo-metal titanium (TiC) are distinguished by their hardness, which exceeds that of corundum.

Out of this long list, only two carbides are of industrial importance: the one, calcium carbide, belongs to the group of those carbides producing a gaseous hydrocarbon by the action of water; the other, silicon carbide, is an example of the carbides which are useful because of their great hardness.

CALCIUM CARBIDE

In 1862 Wohler prepared calcium carbide by heating an alloy of zinc and calcium with an excess of carbon. The body was not isolated, but the fact was recognised that it evolved acetylene on treatment with water. Travers in 1893 heated a mixture of calcium chloride, carbon, and sodium, and obtained a grey mass containing calcium carbide.

On the 12th December, 1892, Moissan published the following statement in a paper communicated to the

Académie des Sciences: "If the temperature" (in the electric furnace) "reaches 3,000°, the lime forming the furnace melts and runs like water. At this temperature carbon quickly reduces calcium oxide, and the metal is separated in quantity; it unites easily with the carbon of the electrodes to form a carbide of calcium, liquid at a red heat and easily collected." This paper was supplemented by a note to the Académie on 5th March, 1894, in which the facts were set forth that there is but a single carbide of calcium, that its formula is CaC_2, and that it yields pure acetylene when decomposed by water.

Towards the end of 1894 Willson announced that he had produced a substance giving acetylene when acted on by water, by heating lime and carbon in the electric furnace. His discovery appears to have been accidental and independent of Moissan's work, with which he seems to have been unacquainted. As soon as calcium carbide was recognised as a valuable commodity, Willson and others endeavoured to protect its production by patent. The state of knowledge at the time was, however, too well advanced to warrant the creation of a monopoly of this kind, and at the present moment it is doubtful whether any patents for the production of calcium carbide in the electric furnace, except such as relate to some particular form of furnace, are valid.

Calcium carbide prepared in the electric furnace is a dark, semi-metallic-looking solid; it can be broken easily, and its fracture is crystalline. Isolated crystals are reddish-brown in colour; their sections under the microscope are seen to be transparent and deep red in hue. Calcium carbide has a specific gravity of 2·22. It is insoluble in all ordinary organic solvents. It burns when heated in oxygen, forming calcium carbonate;

when fused it dissolves carbon, and on cooling deposits the carbon as graphite. This property is common to many carbides; those of iron and molybdenum may be cited. The most noteworthy reaction of calcium carbide is that which occurs when it is brought into contact with water. Decomposition takes place smoothly according to the equation—

$$CaC_2 + 2\,H_2O = Ca(OH)_2 + C_2H_2.$$

Given that the carbide is pure, the yield of acetylene is that required by theory, and the gas is pure. Even with the industrial material these conditions are approached. As might be expected, the carbides of barium and strontium (BaC_2 and SrC_2) can be prepared from mixtures of the respective oxides with carbon by the aid of the electric furnace. Both furnish acetylene when treated with water.

The manufacture of calcium carbide is carried out in a very simple apparatus. All that is necessary is a fire-brick box containing a charge of lime and coke, which can be fused together by the passage of a powerful current. Seeing that the production of calcium carbide is effected solely by reason of the high temperature attained in the electric furnace, and not by electrolysis, either an alternating or unidirection current may be used. The former is generally the more convenient, because it can be brought from a distance at a high voltage and transformed on the spot where it is to be used by a stationary transformer.

The simplest arrangement is that originally devised by Willson. It is shown in Fig. 32. The brickwork casing A is lined with carbon B, so as to leave a hollow which serves as the crucible. The crucible itself acts as one electrode, the other being a stout carbon rod C.

A small charge is placed in the crucible and an arc established. The electrode is gradually raised, and fresh charges are fed in. A fused mass of carbide is formed at the bottom of the crucible, and can be run off by the tapping hole E. Although it would seem that a continuous process could be worked in this manner, yet in practice it is found difficult to manage. Most of the furnaces actually at work are of intermittent type.

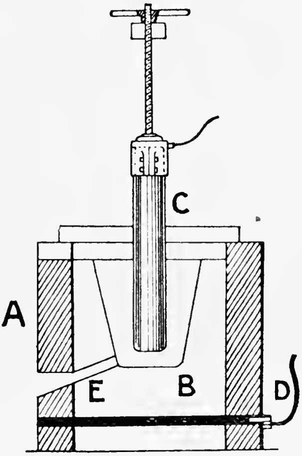

Fig. 32.

One also devised by Willson, and used by him at Spray, North Carolina, is shown in Fig. 23 which represents a pair built together. The electrode C consists of a bundle of carbon plates A, each 4 inches square and 30 inches long. They are suspended from a thick copper rod, through which electrical connection is made, and this hangs by a chain passing over pulleys and controlled by a screw and nut D. The other terminal is connected with the iron plate E, on which rests a layer of carbon F, composed of broken carbon pencils or a baked mass of coke and tar.

The upper electrode is shown at its lowest point resting on the lower electrode, but it will be understood that as the charge is fused it is raised so that a conical pile of carbide is gradually formed. The current is then cut off, and the mass of carbide, after cooling, is withdrawn, broken up, and the fully fused, nearly pure part picked out from the sintered, half-formed carbide, surplus coke, slag and similar *débris*.

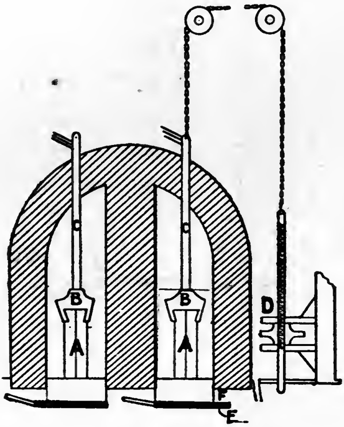

FIG. 33.

By a natural improvement on the Spray furnace, the King furnace has come into existence. It is shown in two sections in Figs. 34*a* and 34*b*.

The chief point of importance is the use of a small iron truck to contain the carbide as it is produced. The truck A, with its load of carbide, forms one electrode. It can be run into place and removed as required. It is provided with trunnions K, K, so that its contents may be tipped out. It is given a small reciprocating motion by the rod E, this being found useful in shaking down the charge and preventing the formation of channels in it, and also in slightly altering the position of the arc so that all parts of the charge are exposed to it in turn.

The other electrode consists of a bundle of carbon plates, carried by a massive rod C, consisting of a conducting band of copper strengthened with side-bars of iron. In the figure this electrode is shown resting on the floor of the truck, but it will be understood the electrode is slowly raised as the charge is fed in and fused, until it reaches the top of the truck, which is then full of carbide and can be removed and replaced by another ready for a fresh run. The raw materials are fed into the furnace through the channels G, G, which contain small rotating blades to control the descent of the charge. The air flues shown are to keep the upper part of the furnace

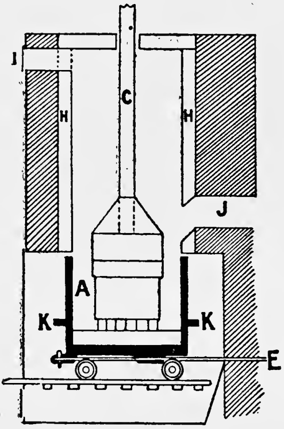

Fig. 34*a*.

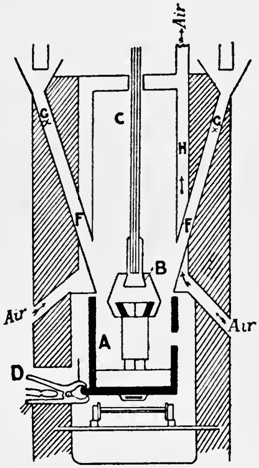

Fig. 34*b*.

fairly cool, the zone of fusion being confined to the truck. This class of furnace is semi-continuous, the only interruption to its working being that needed for removing and replacing the trucks. Many attempts have been made to construct furnaces strictly continuous in their operation, that is to say, having a continuous feeding-in of raw materials and a continuous discharge of fused carbide, but they appear to be less manageable than furnaces of the semi-continuous type.

It may be noted that the fundamental reaction $CaO + 3C = CaC_2 + CO$ expends one-third of the carbon in producing carbon monoxide. A natural suggestion is to burn this gas and use the heat for warming the charge before it descends on to the hearth of the electric furnace, but this has not yet been realised in practice. An extension of the idea is to heat the charge non-electrically to as high a temperature as can be reached by ordinary furnace methods, leaving the electric furnace to raise its temperature through the remaining 1,000° C. or 1,500° C. necessary to cause the reaction to occur. A considerable economy might be expected from this procedure, because calorie for calorie the heat generated by the electric furnace is enormously more costly than that generated direct from fuel, but up to the present no practical realisation of the idea has been attained.

Borchers has suggested the enclosing of the electric furnace with a water-jacket, which shall serve as a boiler to generate steam from heat that would otherwise escape and from the heat of the block of fused carbide, which at the end of the run has to be left in the furnace to cool. This suggestion, even if carried out, would have but a trifling effect in reducing the cost of the carbide.

Recently an attempt has been made to obtain a more even distribution of temperature in a furnace using three-phase currents. A plant of 800 H.P. has been erected at San Marcello d'Aosta, in Italy, according to the patents of Ricardo Memmo. The simplest form of discontinuous furnace for three-phase currents is shown in Fig. 35.

The carbons, although converging, cover a considerable area, and fluctuations of current taken by the furnace, due to a high resistance at any given point, are less severe than with the ordinary single electrode. The furnace has a capacity of about 70 cubic feet, and is made of brickwork, lined with refractory bricks. The bottom on which the fused carbide rests is made of magnesia bricks—magnesia being unattacked and not forming a carbide, as does lime. As shown in the figure, the carbons C, C, C (which are 5 inches in diameter) are carried by stout iron rods A, A, A. These pass through bronze collars, and can be screwed up and down by the hand wheels B, B, B. The attachment of the carbon rods to their sockets is apt to cause trouble

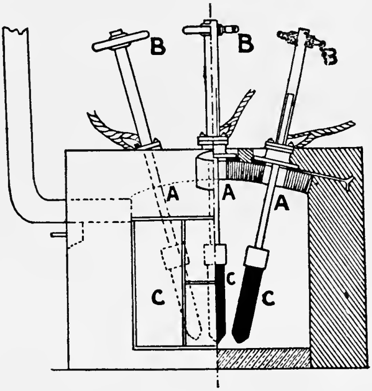

FIG. 35.

unless special precautions are taken. The carbon should be inserted when both it and the iron are as hot as they are likely to become in practice, and any crevices filled up with a graphite cement. It is well to stop the run before the carbons are quite consumed, lest an arc form between the carbide and the holder, ruining the latter.

A semi-continuous furnace for three-phase currents is shown in Fig. 36. The raw materials are fed in at the top, and fall on the cast-iron plate A, which is protected by a layer of graphite. As the fusion proceeds this plate is lowered by the screw B with its gear C. A column of carbide is thus built up, the top of the column always forming one electrode and the three carbons jointly the other electrode. These are only moved slightly to compensate

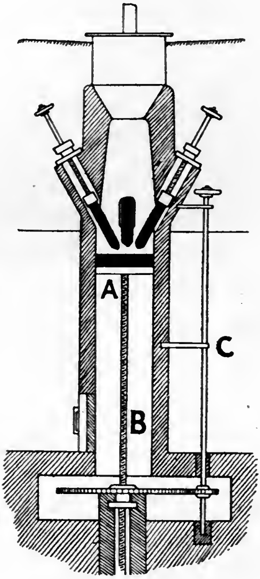

Fig. 36.

for their gradual consumption. The carbide, when it has reached the lowest part of the furnace, is sufficiently cool to enable it to be withdrawn, and the running of the furnace can be resumed.

The quality of the raw materials for the manufacture of calcium carbide is of importance. Both lime and carbon should be as nearly pure as possible. The lime should not only be free from siliceous impurities, but should also be free from magnesia. This base is unattacked by carbon at the temperature of the electric furnace; it is not reduced, nor does it yield a carbide. The most convenient form of carbon is coke; charcoal can be used and contains a smaller percentage of mineral impurities, but it is inconveniently bulky. The coke should contain as little ash as possible. Coke of good ordinary quality contains about 10 per cent. of ash; for calcium carbide manufacture the quantity should be considerably less—5 per cent., or better if procurable. The lime may, of course, be used as carbonate, but this alternative is not desirable, because the work of decomposing the carbonate is thrown on the electric furnace, the energy of which is costly. It is usually better to prepare the lime in an ordinary kiln. The comminution and mingling of the raw materials have been the subject of much study. It was at first supposed that the raw materials should be finely ground. Now, however, it is found that pieces as much as 1 inch in diameter will serve perfectly well, and the preparation of the raw materials resolves itself into a sort of cracking process instead of grinding. The machines most in vogue are of the coffee-mill type, eminently adapted to produce coarse fragments of uniform size almost free from dust.

From the nature of the case, seeing that in the electric furnace the energy poured into it is effectively boxed in and must be transformed on the spot where it is wanted into heat of high temperature, it might be supposed that the manufacture of calcium carbide is a fairly efficient process. Enquiry shows that this is a true view. The energy strictly necessary may be computed thus. Moissan has shown that the heat of formation of calcium oxide is 145 Cal and that the reaction $CaO + C_3 = CaC_2 + CO$ takes place at 3,300° C. = 5,972° F. The specific heat of CaO may be taken as approximately 0·12; that of carbon as 0·47.[1] The energy necessary to raise 56 grammes of CaO and 36 grammes of C to this temperature is 79·5 Cal. The formation of calcium carbide from Ca and C is esteemed an endothermic reaction requiring 48 Cal. The total energy needed is, therefore, 79·5 + 145 + 48 Cal = 272·5 Cal. From this must be deducted the energy evolved by the oxidation of C to CO, *i.e.* 29 Cal. Therefore, the energy to be supplied to form 64 grammes of CaC_2 is 243·5 Cal. In this calculation the energy absorbed or evolved by the formation of CaC_2 from Ca and C_2 is a doubtful quantity. No reliable data have been arrived at. The estimate given is likely to err on the right side, the more so as no credit has been taken for possible regeneration by utilising the sensible heat of one charge for warming up the next. Thus it may be taken for practical purposes that the formation of 1 ton of CaC_2 requires 5,889 H.P. hours, or conversely for each H.P. per day of 24 hours 4·1 kilos of CaC_2 may be formed.

It must not be forgotten that this estimate includes

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[1] These values are confessedly approximate. That of carbon increases greatly with the temperature, and the figure adopted applies to temperatures not lower than 900° C. = 1,652° F.

the whole of the heat needed to raise the raw materials to the temperature of the reaction and supposes that this heat is lost. In practice at least a portion of it will be used in pre-heating the raw materials before they are exposed to the full temperature of the furnace. In like manner no credit is given for the heat which can be obtained by the combustion of the CO evolved in the production of the carbide. The output claimed by some works is as much as 5 kilos per H.P. per 24 hours, but it is probable that this is carbide containing only 90 per cent. of actual CaC_2.

The substantial correctness of these figures is proved by the data published concerning the only trial which has been fully and fairly made and published. In 1896 an American paper, *The Progressive Age*, retained Messrs. Houston, Kennelley, and Kinnicutt, electricians and chemists of repute, to make experiments at Spray, North Carolina, on the cost of production of calcium carbide. These experiments were on a manufacturing scale, and appear to have been well conceived and well executed; their results were published in full and without comment. The plant used consisted of a turbine of about 300 H.P., coupled to alternators which delivered current at 1,000 volts to transformers, whereby the pressure was reduced to 100 volts. Two furnaces were used, each with a floor area of 3 feet × 2 feet 6 inches, and having an iron base plate covered with carbon 8 inches thick. This served as the lower electrode; the upper was a built-up carbon block 3 feet × 12 inches × 8 inches. It could be raised gradually from the base plate as the mass of calcium carbide formed thereon; its consumption was $\frac{1}{16}$ inch per hour. The charge consisted of coke and lime, containing 52 per cent. of CaO and 37 per cent. of C, the balance being moisture and impurities. At the start a few shovelfuls of this mixture were placed on the lower electrode, and an arc established between this and the upper electrode. Fresh portions of the mixture were added as the reaction proceeded, until the cavity of the furnaces was filled with a pyramidal mass of crude carbide.

Two runs were made, each with a charge of 2,000 pounds; in each case an output of about 200 pounds of calcium carbide was obtained. The carbide gave 80 to 85 per cent. of its calculated yield of acetylene. In the first run 193·1 H.P. for 3 hours was used, corresponding with 579·3 H.P. hours, *i.e.* 432 kilo-watt hours. In the second run the energy consumed was equivalent to 195·3 H.P. for 2 hours 40 minutes, corresponding with 520·8 H.P. hours, or 388·5 kilo-watt hours. Taking the output of carbide as 200 pounds in each run, the first gives 3·75 kilos of 80–85 per cent. carbide per H.P. per 24 hours, and the second 4·15 kilos for the same expenditure of energy. These values are well below the 5 kilos provisionally fixed above, and have the advantage over the various figures commonly quoted of having been derived from actual experiment. The cost of the carbide prepared in these experiments may be calculated thus: The plant is one delivering 200 E.H.P., and turns out 4 kilos of 85 per cent. carbide per H.P. per 24 hours—in all, 292 tons per year of 365 days, running day and night. This may be conveniently stated as 327 short tons (of 2,000 pounds), because the remaining figures are taken from the American source cited above and refer to this unit of weight. The cost of power per H.P. year is 6 dollars.[1] The capital expenditure for the plant (other than power plant) is

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[1] This is very low; 10—20 dollars is a more ordinary figure.

12,000 dollars. Taking labour for making the carbide at 11 dollars per day; lime at 6·3 dollars per ton; coke at 4·5 dollars per ton, and carbon for the electrodes at 6 cents per pound, the cost of producing 292 tons of carbide is found to be as follows:—

	Dollars.
Power	1,200
Interest and depreciation	1,200
Labour	4,015
Lime	1,260
Coke	1,134
Carbon electrodes	450[1]
	9,259

This works out at a little more than 28 dollars per ton of 2,000 pounds, *i.e.* £6 6*s.* per ton of 2,240 pounds. In this estimate, which, though confessedly only approximate, is based on actual prices and experimental data, the chief points to be noted are that it is much below the present selling price of carbide, which is about £16 per ton of 2,240 pounds; that the cost of power is low, and that of labour and material high. All these items would vary largely according to the local conditions. Power (even water power) may well cost 20–25 dollars per year, and *per contra* the price of lime may be not more than 3 dollars per ton, and that of coke 2½ dollars per ton. Thus, though the cost of power is a large item, yet it is not of such preponderating importance as to make a calcium carbide factory necessarily a success because it can obtain the energy it requires at a low rate; the industry may be hampered beyond hope by dear and bad coke and lime. These considerations are of particular

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[1] This is so considerable an item that in well-equipped works the carbon electrodes are made on the premises, not bought from an electrode manufacturer.

importance when considering the prospect of success possessed by a given scheme for utilising water power in a manufacture of this kind.

As regards the conditions to be especially kept in view by the manufacturer, it is sufficient to say that the raw materials of each charge should be converted as nearly as possible completely into calcium carbide, to avoid the necessity of heating them over again as will be requisite if they have to be worked up with the next charge; but, however carefully the operation is conducted, there is likely to be a comparatively large part of the charge which has served as a protection and envelope to that which has been fused, and must be reworked or thrown away. Slag and similar inert products must be picked out. The quality of the carbide should be measured by the volume of acetylene which a given weight evolves when acted on by water, and the material should be bought and sold on this assay.

One kilo of pure CaC_2 evolves 348·4 litres of acetylene, the gas being measured at a pressure of 760 mm. and a temperature of 0° C. This quantity corresponds with 5·587 cubic feet for 1 pound. The commercial product rarely gives more than 300 litres per kilo, and often only 280 or even less. Even the better of these is only 86 per cent. of full strength. It is clear, therefore, that a good deal may be done to improve the quality of calcium carbide as now manufactured.

SILICON CARBIDE

The other carbide of industrial importance is silicon carbide (SiC), which can be prepared synthetically by the direct union of its elements at the temperature of the electric furnace. Commercially, the oxide of silicon, *i.e.*

silica such as quartz, is used as the source of silicon, which is reduced from silica by carbon and combined with a further quantity of carbon at a single operation, according to the equation $SiO_2 + 3 C = SiC + 2 CO$. The commercial name for silicon carbide is carborundum, a word constructed to convey the idea that the material is of the nature of corundum (crystallised alumina), but contains carbon. Of course, there is no chemical similarity of carborundum to corundum. Pure silicon carbide is colourless and crystallises in hexagonal plates. It contains 70 per cent. of silicon and 30 of carbon; its specific gravity is 3·12; it is hard enough to scratch ruby. It is extremely stable and does not oxidise even when heated in air to whiteness. It is insoluble in all acids, but is attacked by fused caustic potash. This great refractoriness is in striking contrast to the ease with which the other industrial carbide, calcium carbide, is decomposed by water. Although pure SiC is colourless, the crystals usually obtained from materials not perfectly free from iron and similar impurities are slightly coloured, and may be blue, yellow, or brown. The commercial product is dark brown or black. Its manufacture is conducted in the following manner:—

The furnace used is built of bricks put together without mortar or cement, both because of the need to allow free escape of gases and because the whole structure has to be pulled down at the end of this run. The furnaces at the works of the Carborundum Co. at Niagara, which appears to be the only manufactory in existence, are about 15 feet long, 7 feet high, and 7 feet wide. At each end is a heavy bronze casting to which the leads are connected, and which on the inner side carries a bundle of sixty 3-inch carbon rods 2 feet long. These project into the furnace cavity proper, and between them is a cylindrical mass of coarsely powdered coke making electrical connection between the carbon electrodes; this core of coke is about 9 feet long and nearly 2 feet in diameter. Thus it will be seen that the manufacture of silicon carbide, unlike that of calcium carbide, is effected by heating a resistance and not by an arc. The general arrangement of a carborundum furnace is represented diagrammatically in Fig. 37. A is the loosely-built brick box, carrying the heavy metal holders B, B, to which the cables are attached. The carbon rods C, C are set in these holders and project well into the furnace. The conductive cylinder of broken coke is shown between the ends of the carbon rods at D. The charge which is packed round this heating core and fills up the cavity of the furnace, consists of 34·2 per cent. of coke, 54·2 per cent. of sand, 9·9 per cent. of saw dust, and 1·7 per cent. of common salt;[1] it weighs about 10 tons, and the yield of carborundum from this quantity is not more than 2 tons. The calculated yield of 10 tons of silica and carbon mixed in equivalent proportions, *i.e.* 62·5 per cent. of silica and 37·5 per cent. of carbon, is $4\frac{1}{6}$ tons of silicon carbide, whence it will be seen that the output is poor. For a furnace of the size given about 1,000 H.P. is

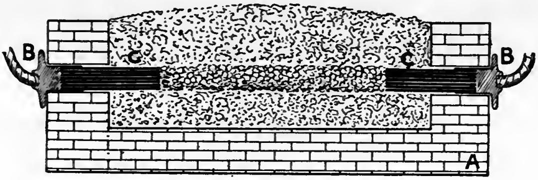

FIG. 37.

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[1] The function of the sawdust and coke is not clear.

required. When the current is switched on heating proceeds slowly until, after about 2 hours, carbon monoxide is evolved at all openings in the rough brickwork and from the upper surface of the charge, and there burns with a blue flame. When the current has been passing for some 12 hours the outside of the mass becomes red-hot; the process is continued for another 12 hours, by which time it is found that the reaction has proceeded as far as it is feasible to push it, and the current may be switched off and the furnace allowed to cool. On pulling down the walls of the furnace the charge is found to be composed of several layers; the outer consists of about 11 per cent. of salt (volatilised from the inner part of the charge), 56 per cent. of silica, and 33 per cent. of carbon, this representing the portion which has not been hot enough to form silicon carbide. Within this is a layer of harder material of a greenish colour and roughly concentric with the core; this consists of amorphous silicon carbide mixed with unaltered raw materials. It is not hard enough to be used as carborundum, and has to be worked up with the next charge. The next inner layer is crystallised silicon carbide, carborundum proper. The crystals constituting this layer are small on the outside, and increase in size towards the core. The total thickness of the useful layer may be some 16 inches. Within this again is the core of coke, which has been converted into graphite by the high temperature to which it has been subjected. The layer of properly crystallised silicon carbide is broken up, crushed in edge runners, washed with water and acid, dried, and graded by sieving. The following analyses illustrate its composition:—

	I.	II.
Si	62·70	69·10
C	36·26	30·20
$Fe_2O_3 + Al_2O_3$ . .	0·93	0·49
CaO	—	0·15
MgO	0·11	—
	100·00	99·94

Carborundum is used as an abrasive. Its extreme hardness makes it preferable even to emery for some purposes. Built-up carborundum wheels are stated to cut so much more freely than emery wheels that the article being ground is much less heated than it would be by an emery wheel. In this country the use of carborundum is very small, the only grinding apparatus made from it being the tiny wheels used by dentists. It has been proposed to use silicon carbide as a means for adding silicon to steel in regulated amount, but at its present price (about 1*s*. a pound) it is too dear. The electrical power needed for producing carborundum has been reduced from 15·5 to 8·6 kilo-watt hours per kilogramme. The output of the Niagara works for 1897 is given as about 600 tons.

BORIDES

No borides are as yet prepared on an industrial scale. A few words may, however, be added to those already set down in an earlier part of this section concerning Moissan's work on the synthesis of borides.

Boron, like silicon and carbon, combines with certain metals and non-metals to form bodies which are stable and of simple composition. Examples are the borides of iron, nickel, and cobalt—FeB, NiB, CoB—and CB_6. The first three can be prepared at ordinary furnace temperatures, but carbon boride is a typical product of the electric furnace; it is formed when the two elements are heated together at a temperature of about 3,000° C. = 5,432° F. Good crystals can be obtained when the union of the constituents is brought about in a bath of copper or silver acting as a solvent. Carbon boride (CB_6) crystallised from fused copper is a black crystalline substance of specific gravity 2·51. It ignites when heated in oxygen to 1,000° C. = 1,832° F., but burns with difficulty because the boric anhydride produced forms a protective skin. It is insoluble in all acids, but is attacked by fused alkalies. Its most noteworthy property is its extreme hardness. Silicon carbide is considerably harder than corundum, but nevertheless will only polish diamond without actually cutting it; carbon boride, however, will cut diamond, not perhaps as well as diamond itself, but still definitely enough. In the scale of hard materials diamond must still stand first, but next to it is carbon boride, then silicon carbide, and perhaps corundum as the fourth. The industrial preparation of carbon boride as an abrasive may prove useful and remunerative.

SILICIDES

Certain of the silicides are already of commercial importance. The use of ferrosilicon as an addition to steel, to raise its silicon contents and to reduce any oxide which it may contain and to cause it to pour quietly, has long been practised. It is possible to substitute silicon itself or silicon carbide (see above) for ferrosilicon, but at present prices these materials are too dear for commercial use. A definite iron silicide (Fe_2Si) can be isolated by dissolving in dilute nitric acid the siliciuretted metal obtained by fusing together iron and silicon, either in the electric furnace or at a more moderate temperature. A highly siliceous iron has a direct interest in electrolytic work in that it is not easily attacked by acids and has even proved serviceable for anodes in acid solutions. Chromium silicide (Cr_2Si) is a similar body to Fe_2Si, and is obtained in a similar way.

Silicide of copper containing 10, 15, and 30–35 per cent. of silicon is prepared as an article of commerce. The richest of these compounds corresponds approximately with the formula CuSi. Silicide of copper is employed instead of phosphide of copper as a reducing agent useful in the production of bronzes and other copper alloys, and especially for adding to copper itself to form so-called silicon-bronze, used for telephone and telegraph wire. In these materials silicon is not necessarily present in more than minute quantity; having deoxidised the metal to which it has been added, it may disappear in the slag.

SECTION V

Electro-Deposition

Electro-Deposition

THE art of winning and refining metals on a commercial scale by means of electrolysis has been practised for but a short time, and in that time has undergone a very rapid development. The electro-deposition of metals in thin films to form replicas of embossed, incised or ornamented surfaces, or to cover, protect or embellish some other metal, is of older date, and at the present moment is somewhat eclipsed by the growth and importance of its congener. But, although electro-deposition (in this limited sense) may be a smaller trade, it is absolutely large and of the greatest practical importance. Whilst it is true that such commodities as pure electrolytic copper and calcium carbide are necessaries of modern industry, it is no less true that electrotypes and electroplate are conveniences of modern life which could ill be dispensed with.

The earliest application of electrolysis to the deposition of metals in thin films, exactly clothing and reproducing the surfaces on which these films are deposited, was made in the case of copper. The art of electrotyping, as it is now called, seems to have been discovered in 1838 by at least three persons—Spencer, Jacobi and Jordan—almost simultaneously, and its obvious utility for the accurate reproduction of engraved objects was so great that its development was rapid. A year or two later an efficient solution (that of the double cyanide) for the deposition of silver was discovered, and electroplating was established as an industry.

Copper is the only metal which is used for producing electrotypes, though doubtless others could be employed if it were necessary or desirable to do so. Electrotyping differs from electroplating, nickel plating, and similar forms of electro-deposition in that the deposited metal is afterwards stripped from the surface on which it has been deposited. Forming as it does an independent object, it must needs be of fair thickness, whereas a plating proper may be (and often is) the merest film. Thus in electrotyping it is necessary that the surface to be reproduced should not be so absolutely clean as to allow the deposited metal to adhere firmly to it; the faintest imaginable film of grease or oxide will prevent such adhesion. In plating, on the other hand, perfect adhesion is essential, and the art of the plater is directed to cleansing the surface of the metal to be coated so effectually that the deposited metal is afterwards inseparable. It is failure to attain this end which often causes plating to strip and expose the metal which it is intended to embellish or protect.

ELECTROTYPING

By use this term is confined to the formation of copper replicas of articles in relief or intaglio. The principles on which the art depends are simple, and may be gathered from what has already been said on the winning and refining of copper. In their early days electrotypes were produced by making the article to be copied the cathode of a Daniell cell. A rod of zinc in a porous pot filled with dilute sulphuric acid or zinc sulphate was coupled to the mould to be covered, which was immersed in a solution of copper sulphate surrounding the porous pot. The arrangement was then equivalent to a short-circuited Daniell cell, and as the zinc dissolved an equivalent of copper was deposited on the mould. In the ordinary Daniell cell designed for the production of a current to be used outside the cell, copper is deposited on the copper plate (which may be replaced by lead, carbon, platinum and the like), and is usually fully adherent. If, however, the copper plate be not absolutely clean the copper deposited may be detached, and its surface which has been in contact with the plate will exhibit faithfully the irregularities, such as dints or file-marks, which may have existed on the original plate. Such detached deposited copper is in the fullest sense an electrotype of the surface of the cathode plate. The application of the ideas here embodied is simple. A mould of some material which can be cast on the object to be copied, so as to produce an exact copy, is made sufficiently conductive to serve as the cathode of any convenient source of current in an electrolyte consisting of sulphate of copper. The copper deposited on this mould is prevented from sticking too firmly to the mould by care in choice of the surface of the mould, which, though conductive, should not be perfectly clean, untarnished metal; otherwise the deposited metal adheres, and becomes a protective coat.

For a full description of the various technical details of electrotyping, special works must be consulted. The more important requirements of the art are set forth below.

In order to take a cast of the object to be copied, various compositions are used. Gutta-percha and mixtures of that substance with fatty materials, plaster of Paris, and fusible metal are types of the various plastic or fusible substances which may serve to take an impression. If gutta-percha is used it is softened at a temperature of about 100° C. = 212° F., and when thus made plastic is pressed on to the surface to be reproduced. After cooling the gutta-percha becomes hard, and may be detached and used as a mould, from which the original object to be copied may be reproduced with exactitude. The set gutta-percha, though hard enough to retain fine lines, is yet sufficiently elastic to allow of the removal of the cast from an object which is slightly undercut, whereas fusible metal, plaster, or sealing-wax would obviously fail under these conditions. Various prescriptions for mixtures containing gutta-percha are available. One consisting of 66 per cent. of gutta-percha, 33 per cent. of lard, and 1 per cent. of Russian tallow is approved as suitable for making a mixture so fluid that it may be poured over the engraved plate and will copy the finest lines. In such prescriptions, which pertain rather to cookery than chemistry, there is usually some ingredient chiefly valuable as an aid to faith, as, for example, the 1 per cent. of tallow in that quoted. The mould when made from gutta-percha, or from a mixture of gutta-percha and some fatty material, is non-conductive, and is usually brushed over with plumbago so as to give it a conductive coating. On this the first film of deposited metal is formed evenly, and subsequent deposition is simple. The adhesion of the metal to the film of plumbago is slight, and the electrotype can be readily detached.

Sometimes plumbago is incorporated with the gutta-percha mixture itself, but the rationale of the procedure is not obvious. It is not necessary to make the body of the cast conductive if the surface is a sufficiently good conductor to allow of the deposition of a film of metal; when this is accomplished, no further aid to conductivity is needed.

Plaster of Paris is not very well suited for making electrotype moulds. The ordinary grades are too coarsely ground to reproduce fine lines. Sharper impressions may be obtained with Keene's cement (which is calcium sulphate almost pure and completely dehydrated), but its setting is slow. But, however they may be obtained, plaster casts are porous, and are slowly soluble in water, so that their sharpness would be blurred if they were exposed directly to the electrolyte. Accordingly they are protected by soaking them in paraffin wax or some similar waterproof material; the surface is made conductive by plumbago, as in the case of gutta-percha.

Fusible metal is a suitable substance of which to make casts. One of the best of the ordinary fusible alloys is Wood's metal, composed of four parts by weight of bismuth, two of lead, one of tin and one of cadmium; it melts at 141° F. = 60·5° C. The conditions to be fulfilled by such an alloy are that it shall melt at a temperature conveniently low—low enough not to injure the object to be reproduced—and that it shall expand on solidification so as to force itself fully into contact with the object to be copied. Fusible metal evidently needs no coating to make it conductive; rather, it requires an almost imperceptible film of oil or to be slightly tarnished in order that deposited metal may not adhere to it. It is not much used because of its relatively high price; the inevitable waste in remelting and the possible deterioration of the alloy limit the use of this material in spite of certain obvious advantages.

Only one other moulding material need be mentioned. For work undercut or in high relief a flexible material is useful. This may be made from common glue, softened by soaking in cold water, and melted together with about one-quarter its weight of treacle. The composition may be made waterproof by adding to it 2 per cent. of tannin, which combines with the gelatine of the glue to form an insoluble leather-like substance, or by soaking the finished cast in a 10 per cent. solution of potassium bichromate and then exposing it to strong light. Bichromated gelatine when exposed to light becomes insoluble in water, and the cast prepared from it may be immersed in an aqueous electrolyte without much risk.

All these materials, except fusible metal aforesaid, need to be provided with a conductive film to enable the first layer of metal to be deposited. When plumbago is used it must be fine and perfectly free from grit, lest it scratch the delicate surface of the cast. Although plumbago is most commonly employed, various other substances will serve. Thus any finely-powdered metal, such as gold, silver, aluminium or bronze powder, may be painted or rubbed on to the mould. It is doubtful, however, whether any metal can be prepared by grinding its leaf or in other mechanical manner of as great fineness as that of plumbago; an equally delicate coating is hardly to be expected. Metal may be chemically deposited on the mould in several ways. Thus by Parkes's method the mould is coated with silver by dipping it in a solution of phosphorus in carbon disulphide, and then in one of a silver salt. The phosphorus reduces the silver and coats the cast. Similarly, the cast may be coated by any of the ordinary silvering mixtures, such as are used for coating glass surfaces with actual silver; such mixtures, consisting of a silver salt with a reducing agent, *e.g.* Rochelle salt, aldehyde or formic acid, are freely employed in silvering mirrors, the process displacing "silvering" with mercury and tin. A film of silver obtained in this manner may have too clean a surface to be suitable for electro-typing, because the deposited metal may adhere to it; this inconvenience may be remedied by slightly tarnishing the silver with sulphide. A metallic coating may be provided by immersing the cast in a solution of copper sulphate and sprinkling it with very fine filings of iron, these depositing copper. All these methods are, however, relatively unimportant; covering with plumbago is the simplest device, and for most purposes the best.

The mould, however it may have been prepared, is coated with copper by making it the cathode in an electrolyte prepared by dissolving 1½ pounds of crystallised copper sulphate in 1 gallon of water and adding ½ pound of sulphuric acid. A current density of 10 amperes per square foot will generally be found suitable. The concentration of the electrolyte is maintained by the use of copper anodes, which should be of pure electrolytic copper.

In short, the conditions to be observed are substantially identical with those necessary for refining copper electrolytically, save that, as the rate of deposition is usually not important and as pure materials may be used, a perfect coating may be more easily obtained. The process may be continued until an adequate thickness of metal has been deposited. Frequently this is small, as the plate can be backed with a fusible alloy. Various devices are employed to obtain a satisfactory coating on irregular objects. An indented surface will receive on its depressed portions a smaller quantity of copper than will be deposited on its more prominent parts. The difficulty may be got over by using a small movable anode, *e.g.* a thick wire, which may be approached towards the depression and thus decrease the resistance at that point, correspondingly raising the current density on the cathode at that point to its normal value. The building up of copies of objects in the round and not in the form of plates more or less indented or embossed is a difficult and delicate art too remote from the subjects of this book to be treated of here. All necessary principles for the deposition of the metal when once the mould has been prepared have been already laid down.

Copper is not commonly deposited to form a protective coating, as distinct from a thick layer which is to be stripped and to reproduce the surface on which it has been deposited. In certain cases, however, it may be used thus. It may be deposited on iron and steel either itself to serve as a protection or to act as the basis for a coating of nickel. The application of copper to protect steel has been used for plating ships, but more as an experiment than in practice. There is no metal other than iron which would benefit sufficiently by a protective coating of copper to warrant the extensive use of copper electroplating, and in the case of iron certain difficulties arise. The coating must be perfect, as otherwise corrosion of the iron will take place at the exposed spot, all the more vigorously for the presence of the copper. Deposition from the ordinary coppering solution consisting of copper sulphate dissolved in water and acid with sulphuric acid is impracticable, because iron is capable *per se* of depositing copper from such a solution and the copper is apt to come down in a non-adherent condition. It is possible to "flash" iron with copper, *i.e.* to give it an extremely thin film by rapid immersion in a solution of copper sulphate, and possibly a good coating might be built up on this film if the article were at once made the cathode in a coppering solution. The general method, however, is to deposit the copper from an alkaline bath, which will not attack iron. In electrotyping, as stated above, it is essential that the surface of a metal mould to be copied, though conductive, should not be chemically clean. In electroplating with copper, where perfect adhesion is essential, the metal to be coated must be cleaned most scrupulously. The process of cleaning is similar in most cases, whether copper or some other metal is to be deposited. The object to be coated is freed from obvious impurities by filing or scraping so as to present a smooth, bright surface. If of iron which has been machined or finished bright it may have been greased to protect it from rust. In this case the grease is wiped off as completely as possible, and the slight film remaining is removed by washing in a volatile solvent, such as benzoline or coal-tar naphtha. Seeing that the least trace of grease is objectionable in that it prevents the formation of an adherent film, it is usual to dip the goods in a hot 10 per cent. solution of caustic soda after the bulk of the grease has been removed by the volatile solvent. The cleaned surface may still be tarnished with a film of oxide: this is removed by dipping in an acid bath containing 10 per cent. of sulphuric acid or 25 per cent. of ordinary aqueous hydrochloric acid. The acid is rinsed off with clean water and the plating begun at once. If delay occurs the metal will begin to oxidise again and the acid dip must be repeated.

The perfectly clean iron goods are then coppered in an alkaline bath. That most commonly employed contains cuprous cyanide dissolved in an aqueous solution of potassium cyanide, being therefore similar to the solution of silver cyanide dissolved in potassium cyanide ordinarily used for depositing silver (see below). Another type of alkaline copper bath is prepared by adding caustic potash or soda to a solution of a copper salt containing a tartrate. The presence of this organic acid prevents the precipitation of cupric hydroxide, and allows the formation of an electrolyte which is strongly alkaline, but nevertheless contains copper in solution. The well-known capability of ammonia to dissolve copper oxide, and thus to yield an electrolyte which is alkaline and nevertheless rich in copper, does not seem to have been used in the copper-plating industry. It is possible, as Oettel has shown, to obtain adherent and coherent deposits of copper from an ammoniacal electrolyte, but it is probable that the necessary conditions must be observed somewhat too closely for convenience in an industrial process. Moreover there is always loss of ammonia going on, whereby the composition of the bath is altered and the air of the work-room made unpleasant. Such inconveniences occur to some extent with cyanide baths, but are absent from those containing an alkaline tartrate. Electrotyping, plating, and other arts depending on the deposition of metals electrolytically in thin films are now well-established trades. They have passed from the hands of the chemist and electrician to those of the works manager and foreman. Naturally, therefore, they have suffered an accretion of recipes. Save possibly in the art of tempering steel, there is no branch of metal-working so fruitful in nostrums as that now under discussion. Some of the many complex baths which have been proposed contain ingredients the use of which is intelligible; in others there are substances whose function is obscure; in some occur materials apparently chosen by lot. A bath devised by Roseleur, which is suitable for iron and can be used for other metals, is prepared by grinding up 3¼ ounces of copper acetate with a little water so as to make a smooth paste, adding to this 3¼ ounces of crystallised carbonate of soda and 1½ pints of water. Copper carbonate and sodium acetate result from this reaction. The copper is then reduced to the cuprous state by the addition of 3¼ ounces of sodium bisulphite, dissolved in 1½ pints of water. The cuprous salt is then dissolved by potassium cyanide, of which 3¼ ounces are used, dissolved in 5 pints of water. This is probably an easy way of producing a cyanide solution of cuprous cyanide, but there is no reason to suppose that an equally good result could not be obtained by starting with cupric chloride, precipitating it with sodium carbonate, reducing this with sodium bisulphite, and forming a double cyanide solution by adding excess of potassium cyanide. In like manner, one might equally well precipitate copper sulphate with caustic soda, reduce the precipitated cupric hydroxide with sulphurous acid, and add cyanide in excess. An electrolyte of the tartrate class may be prepared by dissolving 5½ ounces of copper sulphate in a gallon of water, adding 1½ pounds of Rochelle salt (double tartrate of potassium and sodium) and then 13 ounces of caustic soda. In these alkaline baths copper anodes dissolve less readily than in the ordinary acid electrolyte, and it is sometimes necessary to maintain the strength of the bath by adding a fresh supply of a copper salt. When the iron goods have received a fair coating of copper in an alkaline bath they may be transferred to the usual acid electrolyte, and the required thickness of copper obtained as in ordinary copper plating. The double operation and the need for obtaining a particularly perfect and somewhat thick covering of copper in order to protect the iron effectually make the use of copper plating on iron less common than would be expected from a consideration of its obvious advantages. It has, however, a considerable application in the coppering of rollers for printing designs on calico and other materials. Such rollers are of iron or steel, and are coated with copper thick enough to be engraved upon. The process is that already given, viz. deposition first in an alkaline and then in an acid bath, special care being taken to obtain a uniform thickness of metal. The bath may be a vertical cylinder lined with a pure copper plate serving as the anode, and having the roller placed concentrically with the cylinder and arranged so that it can be rotated. The electrolyte is circulated and the current density maintained as uniform as possible over the surface of the cathode. Alternatively the deposition may be carried out in a horizontal trough, with a large anode of pure copper plate covering the bottom and sides and with the roller rotating within this trough, the whole arrangement resembling that used in the Elmore process for making copper tubes.

Iron and steel are sometimes given a thin coating of copper in an alkaline bath as a preliminary to the deposition of nickel. Nickel can be deposited direct on iron, but it usually adheres better if the metal is first given a film of copper. The matter is further dealt with under Nickel Plating.

ELECTROPLATING

In the trade this term usually means electroplating with silver. For our purpose it may be conveniently extended to include the covering by electrolytic methods of one material with a thin and adherent layer of another. The old term for silver vessels for domestic use is "plate." Goods covered with silver by mechanical means (rolling on or soldering) are termed plated goods; when a method was devised of covering an inferior metal with silver by electrolytic means, the process was called electroplating; hence the customary restriction of the term to silver.

SILVER PLATING

This is effected by making the objects to be coated act as the cathode in an electrolyte containing silver, usually in the form of silver cyanide dissolved in potassium cyanide. Other electrolytes containing silver may be used, but this is the most generally applicable. Before an article is plated it must be carefully cleansed and made not merely mechanically but chemically clean. The process of cleaning varies to some extent according to the nature of the base metal to be plated, but is usually effected in the following stages. In the first place, all obvious impurities are removed by scouring or similar mechanical means. Next, grease may be got rid of by dipping the goods in a solvent, such as benzoline or coal-tar naphtha. This process may be supplemented or replaced by immersion in a 10 per cent. solution of caustic potash used hot. When once the removal of grease has been effected, the goods to be plated must not be touched with the fingers, lest a greasy film be again imparted to the portions touched. A rinse in water follows, and then a dip in acid, usually dilute nitric acid, to remove any film of oxide or sulphide. Finally, a second rinse in water and the goods are ready for the plating vat. All impurities have been removed from the surface and the clean metal (faintly etched and roughened by the action of the acid) is ready to receive a coating of silver. If there is delay between the final dip and immersion in the bath, oxidation and tarnishing may occur again and must be removed by dipping once more in acid. Some discretion must be exercised according to the nature of the metal composing the article to be plated. The acid liquid is highly corrosive and dipping must be done fairly quickly; the alkali also will corrode alloys containing much tin. For such reasons, as well as to avoid wasting metal and acid, the process of cleansing should not be continued longer than is strictly necessary.

For brass goods the acid dip may be replaced by one of potassium cyanide, which will dissolve any slight film of oxide, though more slowly than does the acid liquid. Iron and steel are usually dipped in dilute hydrochloric acid or sulphuric acid instead of nitric acid, the action of which is somewhat too violent.

Soft metals and alloys, *e.g.* tin, pewter, lead and Britannia metal, may be satisfactorily cleaned without an acid dip. All these small differences depend on considerations which are obvious to the chemist; in the art of electroplating they are matters of workshop knowledge and tradition. An additional means for providing a faultless metallic surface on which silver may be deposited consists in the process known as "quicking." This consists in dipping the carefully cleaned goods in a solution containing mercury, which is deposited by direct chemical action of the more electro-positive metal on the mercury salt. Mercuric nitrate in the proportion of 1–2 ounces per gallon of water is commonly used; another suitable quicking solution consists of mercuric cyanide dissolved in potassium cyanide. Momentary immersion is sufficient to give the goods a complete film of mercury, to which the silver ultimately deposited on them adheres well.

The goods thus carefully prepared are made the cathode in a bath consisting of silver cyanide dissolved in excess of potassium cyanide. A usual proportion is 10 grammes of silver cyanide, 15 grammes of potassium cyanide, and 1 litre of water, but the precise strength is not important. The bath may be prepared by precipitating silver nitrate with its equivalent of potassium cyanide, filtering and washing the silver cyanide, dissolving this in potassium cyanide solution, and diluting with water to the requisite extent. There are many variants of this prescription. Thus silver nitrate may be treated direct with excess of potassium cyanide, or silver chloride may be dissolved in the same mixture. Also a bath may be made up by dissolving silver electrolytically in potassium cyanide, but there is no especial advantage in the procedure.

Anodes of pure silver are used so that the strength of the bath in silver may be maintained. Various devices are adopted for obtaining a uniform coating of silver. If the surface is much indented, small anodes may be brought near to the concave or re-entrant portions so as to reduce the resistance at that point and thus bring the current density to an equality with that at the more prominent parts.

When the part is very difficult of access or where the article as a whole cannot be immersed so as to bring this part into contact with the electrolyte, it may be silvered by the use of the apparatus known as the "doctor," which is merely a pad of rag moistened with the electrolyte and having an anode embedded in it. This may be applied to the part in question, the article itself serving as cathode, and a deposit of silver can be, as it were, painted on to the metal wherever necessary. Seeing that most of the metals ordinarily silvered are electropositive to silver, there is always a possibility that they may by direct chemical action reduce silver from the bath and cover themselves with an imperfect and irregular film of the metal. To avoid this the use of the "striking bath," may be adopted. This is merely a separate bath, containing as a rule less silver and more cyanide than in the plating bath, *e.g.* 3 grammes of silver and 30 grammes of potassium cyanide per litre. As high a current density as possible is used in working, so as to deposit almost instantaneously a film of silver all over the object to be plated. The article can then be removed to the plating bath proper and the process of coating it with a fairly substantial layer of silver proceeded with. For this latter purpose a current density of about 4 amperes per square foot is generally suitable. Silver is deposited from the ordinary cyanide solution as a dense coherent coating, dull and lustreless. It can be brightened by any mechanical process of burnishing, and this is generally the method adopted. But for certain goods, parts of which are not easily accessible, it is convenient to deposit silver as a bright film. This can be accomplished by taking advantage of the curious fact that a cyanide bath contaminated with a small quantity of certain foreign substances will yield bright silver. The substance generally used is carbon disulphide, but other materials of the most varied nature, ranging from silver sulphide to gutta-percha, have been recommended from time to time. The carbon disulphide solution is made by shaking up a few ounces of carbon disulphide with a pint or two of plating solution and allowing the mixture to stand. There will then be obtained a saturated solution of carbon disulphide (that body being slightly soluble in aqueous liquids, although not miscible therewith), which is added to the plating bath in the proportion of 1 ounce to 10 gallons. The quantity of carbon disulphide thus introduced is not more than $\frac{1}{40000}$ of the total electrolyte, but nevertheless it suffices to cause the deposition of the silver bright instead of matt. The cause of this phenomenon is unknown. Certain precautions are necessary: the current density should be greater than that used for ordinary silvering, agitation of the liquid should be avoided, and the goods should be washed as soon as they are removed from the bath lest tarnishing occur from the formation of silver sulphide. The greatest use of electroplating is to coat spoons and forks and other domestic implements, and thus to provide them with a surface equal to that of solid silver goods; in addition, it is used for embellishing all kinds of ornaments.

GOLD PLATING

(Electro-gilding)

The covering of baser metals with gold for their protection and ornament involves the same idea as that which led to the use of silver plating. It can be effected by the old process of "water gilding," which consists in covering the object to be gilded with an amalgam of mercury and gold and driving off the mercury by heat. In modern practice, however, the gold is deposited electrolytically. The process is generally similar to silver plating but there are certain differences in detail. The goods to be gold plated must, as usual, be cleaned with scrupulous care before being placed in the electrolyte.

They are sometimes "quicked" by dipping in a mercury solution, as in silver plating. The bath may be made by adding potassium cyanide in excess to a solution of gold chloride, the proportions being about 10 parts by weight of gold and 100 of cyanide to 1,000 of water. The bath may also be formed by making a large gold plate the anode in a cyanide solution and passing a current until as much gold is deposited at the cathode as is lost at the anode in a given time. There will then be in solution a sufficient quantity of gold, and the bath can be used forthwith. These double cyanide solutions of gold are generally used hot, at about 100° F. to 150° F.; the current density is about 0·8 ampere per square foot.

There are many other prescriptions for gold plating baths, an account of which belongs rather to a collection of recipes than to the present book. It is sufficient to say that, unless pure materials are used and the anodes are pure gold, there is a probability of baser metals, *e.g.* copper and silver, being precipitated along with the gold and forming an alloy with it. To produce special effects of colour, such alloys are sometimes purposely deposited. The thickness of gold usually deposited is so small that it serves as an ornament rather than as a protection to the metal beneath. This, if silver, may tarnish from the formation of sulphide almost as readily as if the gold were not there. Rapid washing in weak cyanide solution will remove this tarnish, while not attacking the gold appreciably. Metals, such as zinc, which are apt to deposit gold from its cyanide solutions without electrolytic aid are usually protected before gilding by a coating of copper.

It is possible with gold, as with silver and copper, to deposit a second metal which shall modify the colour proper to the gold itself. Such deposition belongs to the art of the jeweller rather than to that of the electro-metallurgist, and can be but briefly dealt with here. From a mixed solution of gold and silver or gold and copper, gold may be thrown down containing a small proportion of silver which will lighten its colour or of copper which will deepen it. The proportions of the two metals can be controlled by adjusting the relation of their salts in the electrolyte and the current density at the cathode.

The process is precisely similar to the electro-deposition of brass from mixed solutions of copper and zinc, or of silver alloys from silver and copper or silver and cadmium. The use of the last-named metal was proposed a few years ago for silver plating. Plating with an alloy of silver and cadmium instead of with pure silver was said to have the advantage that the coating did not easily become tarnished by sulphureous gases in the atmosphere, and therefore kept its colour better than did pure silver. The method, however, has not been generally adopted.

NICKEL PLATING

Whereas silver is the most generally useful plating metal for domestic implements to be used in eating and drinking, nickel forms the best coating material for larger, more substantial and more exposed objects, such as the fittings of railway carriages, the bright parts of bicycles, firearms and water-taps. The process of nickel plating is wholly modern, for it is only within the last thirty years that nickel has been produced in quantity at a reasonable price. Its present price is about 1*s.* 8*d.* per pound.

Nickel, although less agreeable in colour than silver, has the advantages of being considerably cheaper and of tarnishing but little in ordinary air. It becomes somewhat dull and acquires a sort of bloom which is easily removed by gentle rubbing, but it does not become covered with a film of sulphide, such as disfigures silver after a short exposure, and moreover it is much harder than silver. It would be an ideal metal for many kinds of goods which need to be protected or embellished were it not for its tendency to flake and scale if deposited in any thickness. A good deal of the complaint which is made against nickel plating would be more reasonably made against the plater, who does not take sufficient care to obtain a perfect, continuous and adherent coating, but some of the trouble arises from inherent qualities of the metal.

When the coating is imperfect the metal beneath the nickel, if it is electro-positive to nickel, is attacked at the exposed points with greater rapidity because of the adjacent nickel, and the nickel which should protect it is peeled off by corrosion proceeding beneath the coating. Nickel plating is harder and more brittle than the metal in massive form, somewhat as electro-deposited iron (*q.v.*) is harder than pure iron in mass, but the reason for this has not been examined. Electrolytic iron is generally considered to owe its hardness to the fact that it contains hydrogen, which modifies its properties. In the chapter on the electrolytic refining of nickel will be found an account of certain experiments on the conditions necessary for depositing nickel in a coherent state, which go to show that the metal is substantially free from impurities; but no special search seems to have been made for hydrogen. It is possible that with nickel, as with iron, the presence of hydrogen may increase the hardness of the metal.

The process of nickel plating involves the preparation of the article to be plated with even more care than is requisite for silver plating. Not only must the surface be clean, but it must be smooth and indeed burnished, because a film of metal electrolytically deposited reproduces accurately the imperfections of the surface on which it is deposited, and in the case of nickel it is impracticable to smooth these out by burnishing because of the hardness of the electro-deposited nickel.

The preparation of a highly polished surface on the metal to be covered necessitates burnishing, that is the rubbing down of all projecting parts and the drawing of them over the depressed portions so as to form a continuous reflecting surface. All the small inequalities due to the actual microscopic structure of the metal of the plate disappear, and the hold available for the deposited metal is correspondingly diminished. It follows that the not infrequent failure of nickel plating to adhere may be due in some degree to the excessive smoothness of the surfaces which it is intended to cover.

But this must not be taken as the chief cause; nickel, even when deposited on a matt surface, will peel from it spontaneously and without assignable cause as soon as it becomes more than a mere film. In general the layer of nickel required for plating is so thin that this tendency is not of much practical significance.

If by any chance a stout layer is required it can be obtained by keeping the electrolyte warm, *e.g.* between 50° C. and 90° C. (see p. 122). That this method has not attracted the attention of nickel platers is no slur on their sagacity, which perceives small merit in a thick coating.

In the ordinary process of nickel plating the electrolyte used is a double sulphate of nickel and ammonium. The normal double sulphate corresponds with the formula $NiSO_4 (NH_4)_2 SO_4 6H_2O$, and as a rule a further quantity of ammonium sulphate is added. The customary proportions are about 50 parts by weight of the double sulphate and 25 parts of ammonium sulphate in 1,000 of water. The bath tends to become alkaline in working, because of the ammonium sulphate as well as the nickel sulphate being decomposed and yielding ammonia at the cathode, while its equivalent of sulphuric acid is neutralised at the anode by the nickel thence dissolved. The alkalinity is neutralised from time to time with sulphuric acid so as to maintain the bath as nearly neutral as possible; it is commonly considered that the solution should be slightly acid rather than alkaline. This is probably because a slightly alkaline bath tends to deposit basic salts, which may interfere with the coating. When a nickel solution is made strongly alkaline with ammonia so as to precipitate and to redissolve the nickel hydroxide first thrown down, there is no difficulty of this kind and good nickel deposits are obtained.

The conditions are similar to those obtaining with copper. There a perfectly neutral solution or one faintly alkaline is apt to give bad deposits from the presence of basic salts; this trouble is overcome by making the solution acid, and in the case of copper, unlike that of nickel, the amount of acid may be considerable; but good deposits may also be obtained in an alkaline solution if the alkalinity be considerable, *e.g.* the copper salt be treated with sufficient excess of ammonia to redissolve the cupric hydroxide precipitated by the addition of a small quantity of the alkali.

As is usual in electro-plating, there are many recipes for nickelling solutions, in some of which weak acids, *e.g.* boric, citric and tartaric acids, or their salts, figure largely. It does not appear that such additions give any better results than the ordinary sulphate solution worked with intelligence and care.

From a double sulphate solution nickel may be deposited on most metals. On iron and steel the deposit is sometimes not satisfactory in that it shows a tendency to strip. This is probably due to want of care in preparing the goods, which may not be perfectly clean when immersed in the electrolyte. Occasionally steel goods are coppered in an alkaline bath before being nickelled, with the view of obtaining a better and more adherent coating.

The nickel anodes used in nickel plating should be as pure as possible. It is only of late years that the commercial metal has attained a reasonable standard of purity, but it can now be procured fairly free from grosser contaminations. Electrolytic nickel or nickel prepared by the Mond process (volatilisation as nickel carbonyl and decomposition of this body by heat) is usually of fair purity, but the supply of either variety is small; metal made by older processes often leaves much to be desired.

A current density of 10–15 amperes per square foot is used for "striking," *i.e.* rapidly covering the whole surface with a film of nickel, and when this is accomplished it may be lowered to 3 amperes per square foot. This is the conventional procedure, but it is probable that much improvement might be effected if the studies in the electro-deposition of nickel detailed in the chapter on nickel winning and refining were perpended by the nickel plater. It is curious to note that, old as is the art of electro-plating, there has been scarcely any attempt to study systematically the conditions necessary to effect a satisfactory deposition. The whole art is empirical—witness the number of quaint recipes.

It is scarcely requisite to provide a separate section for cobalt plating. The metal is scarcer and dearer than nickel, and there is no great weight of evidence to show that it forms a better protective coating. It is claimed that cobalt is harder than nickel and does not tarnish so easily, but the statement rests on slender ground. Should cobalt plating be shown to be better or more permanent than nickel, it can be attained in much the same way, viz. by deposition from the solution of a double sulphate of cobalt and ammonium.

The greater rarity and cost of cobalt forbid its general employment unless it can be shown to be sensibly better than nickel as a coating.

ELECTRO-ZINCING

Zinc forms a cheap and excellent protective coating for iron and steel. It has the great advantage over tin and lead that it is electro-positive to iron, and is attacked in preference to the iron when the two metals in contact with each other are exposed to corrosion. In consequence of this property, even when the zinc coating of an iron article, *e.g.* a tank, is imperfect and a part of the metal is exposed, the iron will be to a great extent protected from corrosion while the zinc remains in sufficient quantity to make an effective couple. Evidently this protective action will not take place in the case of a plate on which is a bare spot of considerable area, so that moisture may lie thereon without reaching the surrounding zinc. The difference in the conditions, which is of some practical importance, is shown in the accompanying diagrams. A tray (Fig. 38*a*) of galvanised iron has a part of the coating stripped at c, and in the middle of this bare space is a patch of moisture d. Clearly corrosion will occur here, unaffected by the neighbourhood of the zinc. A similar tray (Fig. 38*b*) with a similar

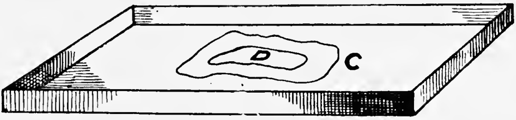

Fig. 38*a*.

bare patch E is filled with water so as to cover the bare patch entirely with the water. Both iron and zinc are in electrolytic connection with the water, and the zinc, being the positive metal, is corroded in preference to the iron. Thus it comes about that a zinc coating is generally more protection in the case of a tank than in that of a roof. In like manner one may protect an iron boiler or ship by attaching pieces of zinc to the plates where they are immersed in water, but one would hardly meet with success in attempting to protect a shed by like means. All this is obvious enough, but is nevertheless constantly overlooked, with the result that zincing is sometimes condemned because it does not perform electro-chemical impossibilities.

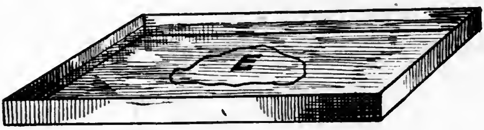

FIG. 38*b*.

For most goods zincing—or galvanising, as it is erroneously termed—is most cheaply and conveniently applied by dipping the iron or steel articles (after they have been carefully cleaned and pickled in acid), in a bath of melted zinc. The zinc alloys superficially with the iron and forms a complete and adherent coat. For certain classes of goods this method presents disadvantages. The bath must be at a temperature somewhat above the melting-point of zinc, 412° C. = 774° F. At this temperature the harder grades of steel, such as are used for wire, are annealed considerably and thus lose a part of their high tensile strength from this cause. Again, the alloy of zinc and iron formed on the surface of the article coated is of small mechanical strength compared with the iron from which it has been formed. With articles of heavy section this is not important, but with goods of relatively small section, which have to carry heavy strains, *e.g.* wires, cables, chains, bolts, hooks and the like, the diminution in strength is often of serious moment. Thus it comes about that for certain classes of work there is a demand for a coating of zinc which shall be applied cold and shall not alloy appreciably with the surface of the iron to be protected. These conditions are fulfilled perfectly by zinc electro-deposited. There are various difficulties in depositing zinc electrolytically so as to obtain a good adherent coating. These have hindered the general employment of electro-zincing, but they have now been overcome in great measure, thanks to the perseverance of one or two inventors, and the process is already fairly freely used, and its use is likely to extend.

The conditions necessary to be observed in order to obtain a good deposit of zinc electrolytically have already been described in the chapter on the winning and refining of zinc. The application of the principles there laid down will suffice to allow of the deposition of a satisfactory coating of zinc to metal to be protected.

The metal most commonly zinced or "cold galvanised" is iron (or steel); it must be cleaned before being coated by the usual pickling methods. The objects to be coated are made the cathode in a solution of zinc sulphate containing about 10 per cent. of this crystallised salt ($ZnSO_4 7 H_2O$). The electrolyte should be free from foreign metals. As it should be kept neutral or slightly acid, basic solutions tending to deposit spongy zinc (see p. 144), some difficulty will be experienced if it be attempted to maintain the strength of the bath by using zinc anodes. It is preferable to use an insoluble anode, and to add zinc oxide or metallic zinc in regulated quantity so as to neutralise the sulphuric acid set free at the anode. By this means the electrolyte can be maintained in a neutral or faintly acid condition, and, moreover, can be purified at the same time. The latter advantage is secured by reason of the fact that zinc, being a strongly electro-positive metal, is capable, whether as oxide or as metal, of precipitating less electro-positive impurities, such as iron or its oxide. The purity of the electrolyte (which is of much importance) can, therefore, be maintained by the means used to regulate its acidity. In order to obtain a good coating of zinc a fairly high current density should be employed, *e.g.* 10 to 20 amperes per square foot. Other precautions, such as circulation of the electrolyte, and maintenance of a uniform current density by specially shaped and placed anodes when objects of irregular surface are to be coated, are similar to those which must be observed in plating generally. Perfection of coating, provided the coating as a whole adheres well, is of smaller importance than in the case of less electro-positive metals. A small exposure of the underlying metal may occur without causing corrosion as long as there is abundance of surrounding zinc, at the expense of which the underlying metal may be protected.

A highly polished surface is rarely necessary for electro-zinced goods. Such articles are commonly for out-door use and a high finish is not required. It would be absurd to confer on a roof, a boat-hook, a crane chain, or a wire rope the lustre proper to an ornament. But even here æsthetic considerations have a certain force.

Hot zinced goods have a bright metallic appearance, and their coating is sometimes made to exhibit brilliant crystalline markings by adding a little tin to the zinc bath; electro-zinced goods have usually a somewhat dull and leaden appearance. Irrational though it be, a prejudice exists in favour of the former. In spite of this, the substantial advantages of a method for depositing zinc in the cold, especially for hard steel (which if heated would be softened) and objects of small section (which are weakened by hot galvanising), will cause the process of electro-zincing to come widely into use for a variety of purposes.

Cowper Coles, who has worked out a process for electro-zincing which has been put successfully into use, has given an estimate of the cost of the operation. He reckons that to cover steel plates of an average thickness of $\frac{5}{16}$ inch with zinc at the rate of 1 ounce per square foot (a sufficient coating) will cost £2 8*s.* 6*d.* per ton of plate coated. This is probably somewhat greater than the cost of hot galvanising, but the extra cost is more than compensated for by the advantages which have been set forth above. Further, a tank of fused zinc for big objects such as large plates or for things which are galvanised after they have been riveted up, *e.g.* tanks, is troublesome to heat evenly, and contains a good many tons of zinc, which represent so much capital locked up. The quantity of zinc in an electrolytic bath capable of coating objects of the same size is relatively insignificant. The iron tank is also somewhat perishable, in that it is attacked by the melted zinc and eventually eaten through. The alloy of zinc and iron resulting from this attack not only represents destruction of the tank, but useless consumption of zinc, which would otherwise go to coat the goods to be galvanised.

ELECTRO-DEPOSITION OF IRON

(*Aciertype*)

Iron is not used as an ornamental plating material, and (naturally) not as a coating to protect the metal beneath from corrosion. But the hardness and toughness of the metal make it suitable as a protective coating against abrasion or attrition. Thus it comes about that the use of iron as a plating substance is confined to facing electrotypes in copper or similar soft metal which have to be exposed to considerable mechanical wear. The only case in which iron is used for its chemical, as distinct from its mechanical, properties is that in which it is employed to face electrotypes which come into contact with vermilion or other pigments containing mercury. Copper electrotypes would reduce mercury from such pigments and be destroyed by the layer of amalgam which would be produced thereby; with iron no such action occurs.

Apart from this minor use, the main merit of a coating of electro-deposited iron arises from its hardness, which is much greater than that of pure iron prepared by other means. Hence the term "aciertype," implying that the plating is not iron, but steel. The cause of the hardness of electro-deposited iron is generally asserted to be the presence of hydrogen, which is co-deposited with the metal and influences its condition much as does a small percentage of carbon. It is known that electro-deposited iron contains hydrogen, but whether this fact and the hardness of the metal are connected causally cannot be definitely asserted. The quantity of hydrogen present in electro-deposited iron may be considerable, *e.g.* 240 times the volume of the metal. This hydrogen is driven off when the metal is heated to redness, and the characteristic hardness of electro-deposited iron disappears at the same time. Nickel, like iron, is deposited from an electrolytic bath in an extremely hard state; it is not known whether this is due to the presence of hydrogen. The hardness of electro-deposited nickel is sufficient to enable it to be used in the same way as iron for facing electro-types. Its greater resistance to corrosion makes it preferable to iron; therefore, the replacement of aciertype by plating with nickel appears probable. At the present time, however, there is sufficient use of electrolytic iron to warrant a description of the means by which it may be deposited.

It is a mistake to suppose that electrolytic iron is necessarily pure. Not only is hydrogen deposited along with the metal, but several other impurities may appear. In the first place, it is clear on general principles that as iron is a highly electro-positive metal its deposition will require the use of a current of relatively high voltage; this will tend to deposit all metals present in the electrolyte as impurities which are electro-negative to iron. Further, iron deposited from solutions containing organic salts, *e.g.* oxalates, tartrates and citrates, usually contains carbon; as much as 0·08 per cent. may be present—a quantity capable of modifying the properties of the metal materially. From solutions containing sulphates iron is thrown down contaminated with a small amount of sulphur. In fact, the preparation of pure Fe electrolytically is as difficult as it is by purely chemical means, and this, as every chemist knows, is one of the most exacting tasks which he can set himself.

But to obtain a coating of iron which is satisfactory physically and mechanically, although, or rather because, it is impure, is perfectly practicable. The usual electrolyte is a solution of ferrous ammonium sulphate ($FeSO_4(NH_4)_2\,SO_4\,6\,H_2O$) in the proportion of 150 grammes per litre. A double chloride of (ferrous) iron and ammonium is also suitable. The bath should be nearly neutral, and the whole of the iron in the ferrous state. Pure wrought iron anodes should be used, so that the supply of ferrous ions may be maintained; otherwise oxidation will occur at the anode and the electrolyte will become partly ferric. This ferric salt will have to be reduced at the cathode before it will again yield its iron.

THE ELECTRO-DEPOSITION OF ALLOYS

When a single metal is to be deposited in a state as nearly pure as possible from a solution containing a second metal, the heat of formation of whose salts is greater than that of its own, the object can be attained by working with a voltage below the critical voltage of the second metal. Conversely, when an alloy of the two metals is desired the voltage used must be above this critical point. The two metals will be simultaneously deposited, their proportions varying with the proportions of their salts in the electrolyte. The formation of alloys in this manner is more curious than important, having a somewhat limited field of application. The alloy most commonly deposited is brass. It can be obtained by electrolysing a solution of zinc cyanide and copper cyanide dissolved in potassium cyanide, the proportions being about 15 grammes of copper cyanide and 8 grammes of zinc cyanide to 100 grammes of potassium cyanide in a litre of water. The number of prescriptions which have been published is very large, and many of the recipes are frankly obscurantist. Acetates, chlorides and sulphates of the metals may be employed; ammonia and its salts are freely used, and such unlooked-for ingredients as bisulphites and arsenious acid are not unknown. The double cyanide solution is used hot with brass anodes. The reason why cyanide solutions are commonly employed is probably because electro-brassing is generally applied to zinc or iron, and these metals would spontaneously deposit copper from most of its other salts. Should it be desired to deposit brass on any less electro-positive metal than copper there is no reason why it should not be effected from a mixed solution of the sulphates of copper and zinc, approximately neutral and mixed in such proportions as would ensure a sufficiency of zinc ions being always present at the cathode.

In similar manner alloys of copper and tin (bronzes) may be deposited from mixed solutions of salts of the two metals. Silver may be deposited alloyed with tin or cadmium, the advantage claimed being that plating of this description is not only cheaper than silver, but also better resists the discolouring action of air containing sulphureous gases.

Most other metals (save those, like aluminium, which are too highly electro-positive) may be deposited in thin films by electrolytic means. Their applications are, however, too limited to warrant separate mention. For details, special works on the electroplater's art must be consulted.

SECTION VI

Alkali, Chlorine and their Products

Alkali, Chlorine and their Products

MANY attempts, extending over a number of years, have been made to manufacture alkali and chlorine by the electrolysis of salt. The fundamental reaction $NaCl + H_2O = NaOH + H + Cl$ is simple, and is easily realised experimentally. Its accomplishment on a large scale at a remunerative rate is, however, more difficult. By much costly experiment and experience, bought by many disastrous failures, it has been found that the following conditions are essential for success: (1) the cost of power must be very low, certainly not more than £10 per E.H.P. year; (2) the process should be continuous; (3) the electrodes should be as nearly permanent as possible; (4) the products of electrolysis should be removed from the electrolyte continuously as the process proceeds; (5) the units of plant should be as large as is practicable; (6) the output per unit of plant should be great, as otherwise the process is burdened by an unduly heavy charge for interest on the necessary capital. It is only lately that a few processes have succeeded in fulfilling most of these conditions.

GENERAL CHEMICAL CONSIDERATIONS

It is convenient to regard the electrolytic decomposition of sodium chloride as being primarily represented by the equation $NaCl = Na + Cl$. This can actually be realised when fused salt is electrolysed. The number of calories required for the decomposition of 1 gramme equivalent (58·5 grammes) of salt is 97·7 Cal, and the critical voltage corresponding with this heat of combination is 4·22 volts.[1] Various processes to obtain caustic soda (by the action of the liberated sodium on water) and chlorine in this manner have been devised. They will be described in due course. The great obstacle to their use is the corrosive action of fused salt on most materials that can be used for making the vessels in which the electrolysis can be conducted. Apart from this the process is attractive, because both chlorine and sodium can be removed continuously from the electrolyte, the resistance of the electrolyte is low, no diaphragm is required, and a large output can be obtained from a small apparatus. Nevertheless, at the present time, those processes which have attained a fair measure of success are methods for the electrolysis of aqueous solutions of common salt. When the electrolysis is conducted in the presence of excess of water, it may, for the sake of simplicity, be supposed that the reaction takes place in two stages, thus:—

$$(1)\quad NaCl = Na + Cl;$$
$$(2)\quad H_2O + Na = NaOH + H.$$

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[1] This is the critical pressure corresponding with the heat of formation of salt at the ordinary temperature; but as salt is solid at the ordinary temperature and is not an electrolyte, this critical voltage is of only theoretical interest. The critical voltage of salt at its fusing-point (772° C. = 1,422° F.) is approximately 3·81 volts.

In computing the energy required it is unnecessary to consider the stages of the reaction; the original materials, salt and water, and the end products, viz. chlorine, hydrogen, and a solution of caustic soda, may alone be regarded. The number of calories required for the decomposition of 1 gramme equivalent (*i.e.* 58·5 grammes) of sodium chloride according to the pair of equations given above is 53 Cal, and the critical voltage is 2·29 volts. Caustic soda and hydrogen, instead of metallic sodium produced by the electrolysis of fused salt, being the end products, the energy and critical voltage required are naturally lower than those requisite for fused salt. But against this must be set the higher resistance of the electrolyte, the need (usually) of a diaphragm, and the difficulty (overcome in the best processes) of continuously separating the products of electrolysis from the electrolyte. As a standard by which the various processes about to be described may be judged, the calculated output for a process of theoretical efficiency may usefully be computed. The decomposition of 58·5 grammes of NaCl into caustic soda, hydrogen and chlorine requires 53 Cal. Therefore the quantity of salt decomposed by 1 E.H.P. year (= 5,646,205 Cal) is 6·13 tons. Taking the cost of an E.H.P. year at £9 16*s.* for steam power and at £2 10*s.* for water power, the cost of electrical power for decomposing 1 ton of salt is £1 12*s.* with steam power and 8*s.* with water power. These figures correspond with £2 6*s.* 8*d.* and 11*s.* 8*d.* for a yield of 1 ton of pure caustic soda, *i.e.* a little better than the trade grade known as 77 per cent. (which is calculated on the percentage of Na_2O and on an erroneous atomic weight for sodium), together with 2½ tons of chloride of lime containing 35 per cent. of chlorine available for bleaching purposes. This last figure is slightly inexact, because commercial chloride of lime contains a certain small percentage of chlorine which is not available for bleaching purposes, and this represents so much of the total chlorine won by electrolysis wasted. Nevertheless, the approximation is sufficient for practical purposes, and enables one to see that, having regard to the present selling price of caustic soda and bleaching powder per ton, the cost of the power required for electrolysis is not excessive. Even when allowance is made for the facts that the current efficiency of the best processes does not exceed 90 per cent. and the pressure efficiency does not exceed 50 per cent., making an energy efficiency of 45 per cent., it remains clear that the cost of electrical energy is moderate enough.

That large profits have not been realised hitherto in the electrolytic manufacture of alkali and bleach arises from the heavy cost of the plant (including, in many cases, interest on large sums sunk in experiments or expended in the purchase of patent rights) and costly up-keep, management and supervision charges.

PROCESSES USING A FUSED ELECTROLYTE

A large number of these have been devised, patented, tried and abandoned. Only one, the Hulin process, is at present being exploited on a considerable scale. The chief obstacles which inventors have encountered may be understood by a consideration of the defects of the simplest possible apparatus for the electrolysis of fused salt.

A fireclay crucible A (Fig. 39) is set in a furnace and filled with salt, which is thus kept fused. A rod of iron serves as a cathode C, and one of carbon functions as the anode D. When a current is passed between these electrodes, sodium is liberated at the cathode and chlorine at the anode. But the sodium, which is liquid at a temperature far below the fusing-point of salt, is also lighter than liquid salt, and rises to the surface and there takes fire and burns. The first difficulty is here encountered, and it is clear that in a workable process means must be taken to protect the sodium from the action of the air, and to draw it off without giving it a chance to inflame. Next it is found that the carbon anode D suffers severely from the action of the fused salt, and possibly from that of the chlorine. An anode thus used gradually disintegrates, and its fragments float in the electrolyte, contaminating it and causing many inconveniences. Lastly the fused salt creeps over the edge of the crucible, runs down outside, and soaks into the ware. The bulk of the salt acts similarly on the inside of the crucible. Both from within and without the crucible is saturated with fused salt, which at the temperature prevailing may act chemically on the ware,

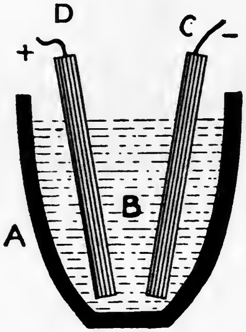

Fig. 39.

and in any case causes mechanical disintegration. The destructive effects produced by fused salt on the most refractory materials are very remarkable; they are due to a variety of causes, chemical and mechanical, and for our present purpose it is sufficient to accept their existence as a fact.

It is not altogether convenient to obtain metallic sodium as the cathode product. The substance to be prepared is caustic soda, and when sodium is obtained instead it has to be oxidised and hydrated to caustic soda, thus involving a violent reaction with water. Not only is this reaction superfluous and objectionable, but it also connotes a considerable waste of energy, because more than the amount of energy necessary to prepare caustic soda from salt has been expended in the production of sodium, and then this surplus has to be run to waste as heat in the aforesaid violent reaction with water. These drawbacks, as well as that caused by the sodium being considerably lighter than the fused salt, are avoided to some extent in the following way:—

THE VAUTIN PROCESS

Instead of a cathode of solid metal one of fused lead is used, as shown in Fig. 40, which represents a form of apparatus devised by Vautin. A, lead cathode; B, decomposing vessel in which the lead-sodium alloy is acted on by steam; C, carbon anode; E, pipe for escape of chlorine; D, pipe for admission of steam; F, pipe for escape of hydrogen.

The sodium, as it is liberated, dissolves in the lead and is transferred to the vessel at the side of the electrolytic cell, where the lead-sodium alloy comes into contact with water or steam and reacts, the sodium yielding caustic soda and the lead being fit for use again in the cell. As lead and sodium unite with considerable energy to form an alloy, the total expenditure of energy necessary to produce a lead-sodium alloy by the electrolysis of sodium chloride with a cathode of fused lead is smaller than would be requisite were sodium itself prepared. In like manner the energy liberated by the action of water on the lead-sodium alloy is also smaller, and the reaction is thus more moderate. Unfortunately a comparatively small proportion of sodium makes an alloy with lead which is not very mobile, and the sodium thus fails to diffuse freely to the steam space. In consequence of this the surface of the lead becomes crusted with sodium, which eventually floats up through the fused salt and is reoxidised at the anode. If oxygen as well as chlorine be present in the space above the level of the electrolyte, this sodium will form oxide and enhance the attack of the materials of which the cell is constructed. Such difficulties led eventually to the abandonment of the Vautin process.[1]

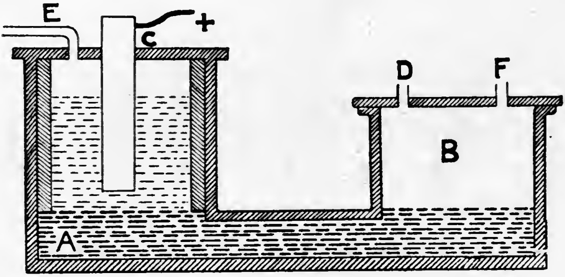

Fig. 40.

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[1] There was also considerable difficulty in lining the anode compartment so as to resist the action of the fused salt.

THE HULIN PROCESS

This process has been adopted by the Société des Soudières Electrolytiques, which has erected works at Clavaux Isère, where energy is obtained from the water of the river Romanche. A steel pipe, 900 metres long and 2·5 metres in diameter, brings the water to the turbine house, where a head of 42 metres is available. The power obtainable is 5,000 H.P. The turbines are coupled direct to the dynamos, which yield 375 kilowatts apiece. The works have been designed for an output of 4 tons of caustic soda and its equivalent (about 10 tons) of bleaching powder.

The principle of the Hulin process is identical with that of the Vautin process described above, save that the electrolyte consists of a mixture of lead chloride and sodium chloride instead of sodium chloride alone. By this alteration the cathode product is a mixture of lead and sodium, and the continual supply of a proportion of lead together with the sodium prevents the crusting over of the surface of the lead with sodium, which, as mentioned above, is apt to occur when a cathode of fused lead alone is used. In order to maintain a proper proportion of lead chloride in the electrolyte, part of the current is sent through lead anodes instead of carbon anodes, and these, being attacked by the chlorine liberated at their surface, dissolve in regulated degree. No authentic description of the plant used by Hulin has been published, but it may be represented diagrammatically by Fig. 41.

A vessel A contains the fused salt mixed with lead chloride, and at the bottom a layer of lead-sodium alloy B. The carbon anode C dips into a suspended vessel D, containing melted lead. This is thus made an anode and is attacked, producing lead chloride. In practice it is probable that separate lead anodes would be used, so that the current passing through them may be more easily regulated and the proportion of lead chloride in the electrolyte readily controlled. It is evident that, as lead is dissolved and reprecipitated, no consumption of energy is theoretically necessary for its transference from the lead anode to the lead-sodium cathode. But, as in practice a considerable current has to be caused to pass between these electrodes through an electrolyte of considerable resistance, it is evident that there will be a noteworthy expenditure of energy. (The principles governing such an operation are fully expounded in the section on Copper Refining, p. 35.) All this must be reckoned as a disadvantage of the process, but in practice may be more than compensated for by the convenience of obtaining continuously an alloy of regular and suitable composition.

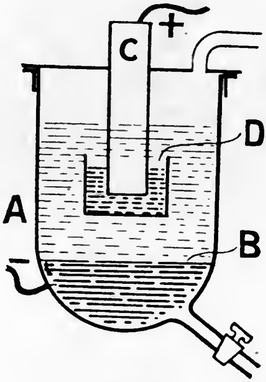

Fig. 41.

Certain figures have been published giving the results of a trial of the Hulin process on a small manufacturing scale. They may usefully be transcribed here. The power available was about 120 H.P.; a current of 2,000 amperes at 32 volts was obtained therefrom and sent through four electrolytic cells of the type described above, arranged in series. Each cell when working normally required a voltage of 7 volts and had a current density of 700 amperes per square foot at the cathode. This current density is enormously greater than the highest current density hitherto found practicable with electrolytic cells using solutions of salt; in these 10 to 20 amperes per square foot is a common current density. The large output thus made possible for a given cell will go far to compensate for the low energy efficiency of the process, of which more anon.

The lead-sodium alloy is drawn off periodically and the sodium is converted into caustic soda in one of two ways. If water be allowed to act on the alloy in its cold solid state, the reaction proceeds quietly and is not dangerous. A solution of pure caustic soda is obtained, which may be made fairly strong by using the same liquid to act repeatedly on fresh portions of the alloy. The liquor thus obtained, having a specific gravity of 1·54 and containing 750 to 800 grammes of NaOH per litre, may be boiled down to solid caustic soda with a moderate expenditure for fuel. If steam could be used to act directly on the fused alloy, a stronger solution of caustic soda could be obtained, and moreover the lead, freed from sodium and still liquid, could be returned at once to the electrolytic cell. It is stated, however, that the action of steam on fused lead-sodium alloy is dangerously violent, and the method is, therefore, not employed. When the solidified alloy is acted on with water, spongy lead is left, which may be used for the plates of storage cells. The alternative method is to roast the lead-sodium alloy in air. Sodium oxide or peroxide, and lead oxide are obtained, the latter apt to oxidise to peroxide and combine with the soda, forming sodium plumbate. This salt would be decomposed on treatment with water, yielding a solution containing caustic soda (and probably some sodium peroxide) and leaving a residue of lead peroxide, useful, like the spongy lead, for the plates of storage cells. The solution containing caustic soda and sodium peroxide would be boiled down for solid caustic soda, and in the process the sodium peroxide would be decomposed, producing an equivalent of caustic soda. Thus, save for the possible presence of traces of lead, the solution of caustic soda ultimately obtained should be pure.

The following tabular statement indicates the degree of efficiency of the Hulin process, both as regards current and energy :—

	Hulin process.	Theory.
Voltage required . . .	7 volts	4·2 volts.[1]
Cl per ampere hour . . .	0·907 gramme	1·322 grammes.
NaOH per ampere hour . .	1·052 grammes	1·490 grammes.
Cl per H.P. hour . . .	97 grammes	235 grammes.
NaOH per H.P. hour . . .	112 grammes	265 grammes.
Current efficiency . . .	68·6 per cent.	100 per cent.
Pressure efficiency . . .	60 per cent.	100 per cent.
Energy efficiency . . .	41·1 per cent.	100 per cent.

THE BORCHERS PROCESS

Borchers has designed an apparatus for the production of alloys of sodium and lead or other fusible metals,

[1] This value is calculated from the heat of combination of Na and Cl at the ordinary temperature. At the temperature of fusing salt the critical pressure is probably lower, viz. 3·81 volts (see p. 286). In this case the efficiency of the Hulin process is even smaller than appears from the figures given above.

and incidentally for the preparation of chlorine. This apparatus, like many of those devised by experimenter, presents several apparent merits and is worth description. Like most of the same inventor's designs, it appears not to have been put to practical use.

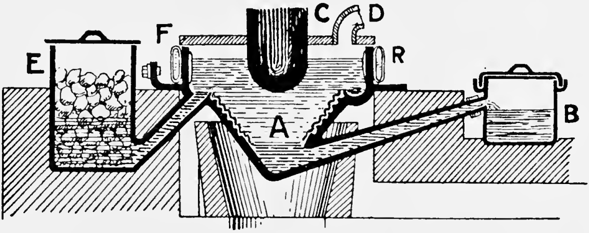

Fig. 42.

A is a conical vessel of iron which serves to contain the electrolyte (fused salt). It is set in a furnace so that its contents may be kept fused. The lower part of the vessel is grooved on the inside, the grooves serving to contain molten lead, a supply of which is delivered from the vessel E at the side of the electrolytic cell. This lead is made the cathode by connection with a dynamo through the terminal at F. The anode C is a carbon rod, while D is a pipe to carry off the chlorine. The lower part of the electrolytic cell is protected from the action of the electrolyte by the lead contained in the stepped grooves shown in the figure; the upper part is protected by congealed salt, which is caused to solidify and form a crust on the inside of the vessel by the cooling action of a water-ring R.

This plan of protecting a vessel serving as an electrolytic cell by a crust of the solidified electrolyte is undoubtedly based on a sound principle. In the manufacture of aluminium (*q.v.*) it is easily adopted, because the heat necessary to maintain the electrolyte in a fused condition is obtained from the current itself, and is therefore internal; thus it is simple to keep the walls of the containing vessel at a temperature below the fusing-point of the electrolyte. The local solidification of the electrolyte by water-jackets and similar devices is less easy of accomplishment, but is practicable in certain cases, of which the present appears to be one. The lead charged with sodium flows away into the collecting pot B, whence it can be removed for the extraction of its sodium; the recovered lead is returned to the vessel E and passes again through the apparatus. Borchers states, " A plant of this kind, twenty times the actual size of the foregoing illustration, is adapted to a current of 300 amperes, which corresponds to a current density of about 5,000 amperes per square metre [3·2 amperes per square inch of cathode surface]. The electromotive force required may be only 6 or 8 volts, which is considerably less than that needed for the reduction of sodium in the unalloyed condition." The high current density would tend to keep the electrolyte fused independently of external heating; any such internal heating by means of the current secures convenience of working and prolongation of the life of the plant at the cost of an extra consumption of energy in a somewhat expensive form. The statement of the pressure required is misleading, in that it implies that the critical pressure necessary to produce a lead-sodium alloy is 6 to 8 volts. As shown above, it is not higher than 3·8 volts. The extra pressure is needed for forcing through a current of a density as high as that employed in this case. As has been already stated, *ceteris paribus*, the voltage which will suffice for the production of a lead-sodium alloy is lower than that which is necessary for the production of metallic sodium, and therefore, given a certain current density, the "6 to 8 volts" is lower than the pressure which would be needed for making sodium unalloyed; nevertheless the method of stating this fact adopted by Borchers is elliptical and consequently obscure and likely to cause error.

PROCESSES USING DISSOLVED SALT AS AN ELECTROLYTE

A great number of these might be described if this were a history of electro-chemical invention. All but a very few have, however, proved failures and may be dismissed at once. Of the remainder which will be dealt with it may be said that their use has been seriously attempted on a large scale. It must not be thought from this that they are all commercial successes. It must also be remembered that there are probably in existence other processes which are working remuneratively and are kept as secrets. This is the natural and inevitable condition of things in a novel and difficult industry, and the consequent lack of completeness of information in a book treating of the industry cannot well be avoided.

THE ELECTRO-CHEMICAL COMPANY'S PROCESS

This process, known in its original form as the Holland & Richardson process, has been employed on a large scale by the Electro-chemical Company of St. Helen's, Lancashire. The generating plant consists of three vertical compound engines of the marine type, each driving two dynamos giving jointly 2,500 amperes at a pressure of 180 volts. The electrolytic cells are of the type shown in the figures.

In Fig. 43*a*, A is a rectangular slate tank in which dips an inverted stoneware trough B, containing the anode C, composed of blocks of retort carbon cast into a lead cap D. E is iron wire netting, serving as the cathode. The shape of this netting may be gathered from the section, plan, and perspective sketch given (Figs. 43*a*, 43*c*, and 43*b*), and from the diagram (Fig. 43*d*),

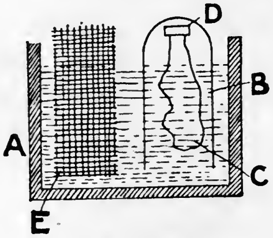

FIG 43*a*.

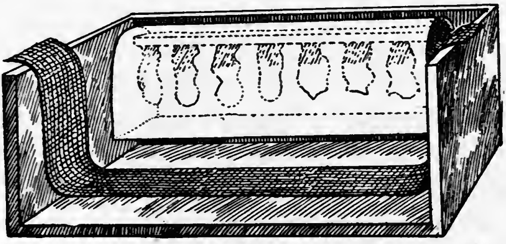

FIG. 43*b*.

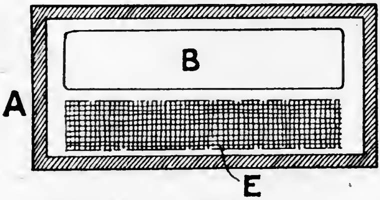

FIG. 43*c*.

where A is a longitudinal section of the cell and E is the profile of the piece of netting. In like manner a section of the "bell" or inverted stoneware trough is shown in Fig. 43*e*. Here the lead cap D has cast into it numerous rough lumps of retort carbon, forming a cheap and effective anode, connection with which is made by lugs passing through the stoneware "bell." The ends of the wire netting serving as cathode project above the surface of the electrolyte and allow of electrical connection being made. The apparatus is, therefore, cheap and simple.

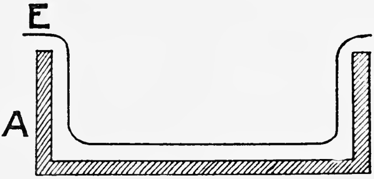

FIG. 43*d*.

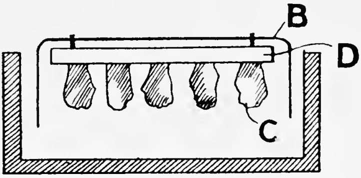

FIG. 43*e*.

The method of working is as follows: Brine (nearly saturated) is fed into the anode compartment through a trapped pipe to prevent escape of chlorine. At the same time chlorine is drawn off through tubes from the top of the stoneware troughs by a rotatory exhauster. The slight suction (less than 1 inch) maintained in the anode compartment helps to remove the chlorine as fast as it is generated, and tends to prevent it from diffusing into the cathode division. In like manner the influx of brine into the anode compartment tends to keep the liquid therein fairly free from caustic soda, which would otherwise be gradually transferred from the cathode compartment. The process of electrolysis is continued until the cathode liquid contains about 8 per cent. of caustic soda. It is then drawn off and boiled down, the salt being fished out and used to make a fresh batch of brine.

The voltage required is stated to be 5 volts for each tank, and the current efficiency when the cells are working normally, 66 per cent. The energy efficiency is, therefore, 30 per cent. The current density at the cathode is 10 amperes per square foot, and at the anode 14 to 15 per square foot. On account of the necessity for drawing off the chlorine under slight suction, a certain amount of air is inevitably drawn in through the numerous joints needed to connect the large number of single cells with the main chlorine trunks. Thus the gas (about 30 per cent. Cl) is used in Deacon chambers[1] for making chloride of lime, and is still more conveniently employed in the manufacture of chlorate.

Undoubtedly one of the merits of the process is the simplicity of the plant and the absence of a porous partition. This latter feature has, however, a certain

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[1] In the Deacon process (a purely chemical method) for making chlorine, a somewhat dilute chlorine is prepared by the action of air on hydrochloric acid in the presence of an active material composed of burnt clay saturated with a solution of cupric chloride. The chlorine always contains a large excess of air, and is not adapted by conversion into chloride of lime in the ordinary bleaching powder chambers. Larger chambers worked systematically are, therefore, necessary to obtain a satisfactory absorption.

disadvantage. In spite of the efforts, described above, to keep the anode and cathode products apart, a good deal of mingling is apt to occur, lowering the current efficiency and contaminating the caustic liquor drawn off to be boiled down for solid caustic soda. Moreover, in drawing off the contents of the cell no means exists of allowing only the cathode liquor to be taken and retaining the anode liquor. Thus the whole contents of the cell have to be boiled down in order to obtain the caustic soda in the cathode compartment. In spite of these drawbacks the plant has been lately increased.

THE HARGREAVES-BIRD PROCESS

This process is one of those in which the cathode product is removed as fast as it is formed, this being one of the objects set down on p. 285 as desirable of attainment. The alkali is obtained as sodium carbonate, instead of caustic soda, and in this respect the process is inferior to those methods which prepare caustic soda at a single operation. An experimental plant has been set up at Farnworth, in Lancashire; its description will suffice to indicate the chief features of the process.

A gas engine of 20 H.P. nominal drives a dynamo delivering 2,100 amperes at 4·3 volts. The leads in this experimental plant are somewhat too small in section, and thus it happens that the pressure drops on its way to the electrolytic cell, and at the terminals thereof has a value of 3·3 volts. Thus the single cell absorbs 9·3 H.P. The electrolytic cell is a cast-iron box, 10 feet long, 5 feet high, and 2 feet wide. Its general appearance is shown in Fig. 44*a*. It is lined with firebrick set in Portland cement. The internal arrangement is shown in

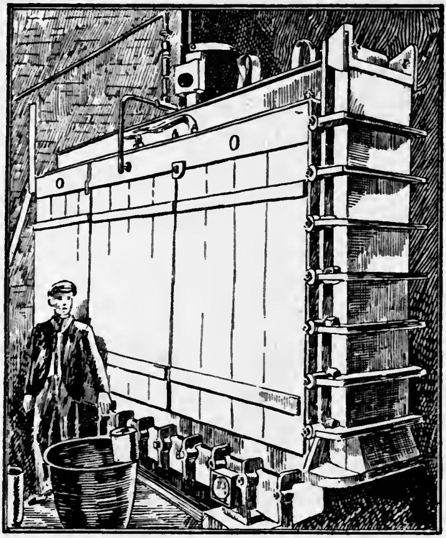

FIG. 44*a*.

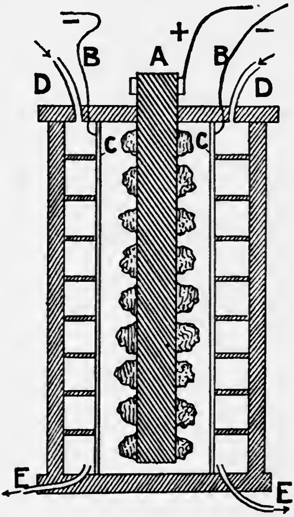

FIG. 44*b*.

the vertical section (Fig. 44*b*). A is the anode, consisting of a leaden rod passing through holes drilled in a number of blocks of gas carbon. The rod itself is protected by a special cement.[1] The cathodes are sheets of copper gauze, which with their leads are shown at B, B in the diagram. They support the diaphragms C, C, and are themselves supported by distance pieces, which keep them from contact with the walls of the cell, so that a clear space is left on the outer side of the cathode diaphragm. Brine is circulated through the anode compartment, passing in its course a box where the chlorine is trapped and led off, and where salt is added so as to compensate for that consumed. A stoneware pump forces the brine back to the anode compartment.

This arrangement will be understood from Fig. 45. A is a box with a hopper B, through which salt can be introduced. The salt enters a compartment cut off by the curtain C, which does not quite reach to the bottom. Into the other compartment the brine + chlorine from the

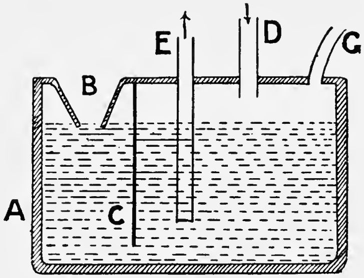

FIG. 45.

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[1] According to a recent patent, connection between the carbon blocks and the metallic conductor on which they are strung is made in a hollow vessel filled with oil, the object of which is to prevent the electrotype soaking into and attacking the carbon blocks and their connections.

anode division of the electrolytic cell enters by the pipe D; the chlorine is trapped and delivered by the pipe G, while the brine is pumped out through the pipe E and is returned to the anode compartment.

The space between the cathode and the outer wall of the cell is not filled with salt solution. Into it steam and carbon dioxide are blown through the pipes D, D, and a solution of sodium carbonate trickles away through the pipes E, E (Fig. 44*b*). The practicability of this procedure depends on the character of the diaphragm. It is claimed that the diaphragm is not pervious to ordinary solutions, but nevertheless allows electrolysis to proceed through it. Thus the liquid in the anode cell cannot ooze through *en masse*, but the cathode products of its electrolysis can pass through the diaphragm and make their appearance at the exterior surface of the cathode. According to the inventor's views sodium is first liberated at the cathode, and there acts on water and carbon dioxide, yielding hydrogen and sodium carbonate.

It is evident from this that the diaphragm is a highly important part of the apparatus. It is made by spreading a mixture of asbestos, silicate of soda and Portland cement on a paper-making sieve, which is stretched over a chamber that can be evacuated. The asbestos mixture is thus sucked together to form a compact felt. The sheet is dried, and then soaked for some days in a hot bath of silicate of soda. The finished diaphragm is about ¼ inch thick, and is of good mechanical strength. At the time of the author's visit to the works the diaphragm then in use had been running day and night for thirty-four days, and seemed to be still working well. The CO_2 necessary for the carbonation of the soda is (in the experimental plant) obtained from the exhaust of the gas-engine, first scrubbed free from sulphur dioxide. The chlorine is obtained of full strength, the joints of the apparatus being few considering its output, and serious leakage of air being thus avoided. At Farnworth the chlorine is being used for making both bleaching powder and sodium chlorate. With regard to the working of the apparatus, it is stated that the current efficiency is 97 per cent. and that the pressure required is 3·3 volts. The energy efficiency will be discussed in a succeeding paragraph. The current density used is about 20 amperes per square foot of cathode surface, and rather less on the anode, the exposed area of which is somewhat greater than that of the cathode on account of its irregularity. The results obtained by the experimental apparatus have been so good that a large installation is about to be started to work the process on an industrial scale.

The Hargreaves-Bird process presents several features of merit and interest which may be usefully discussed. In the first place, as stated on p. 302, the process is designed to produce chlorine and sodium carbonate, and does not attempt to manufacture caustic soda. The end products being sodium carbonate, hydrogen and chlorine, instead of caustic soda, hydrogen and chlorine, the amount of energy which has to be supplied to bring about the decomposition of the salt is smaller than that necessary when caustic soda is produced, being indeed 42·96 Cal, instead of 53·06 Cal. This corresponds with a critical voltage of 1·85 volts instead of 2·29. Now the Hargreaves-Bird process is stated to have a current efficiency of 97 per cent., and to require a working voltage of 3·3 volts. Therefore its energy efficiency is $97 \times \frac{1{\cdot}85}{3{\cdot}3}$ per cent., i.e. 54·4 per cent. This is appreciably better than that of most processes making caustic soda instead of sodium carbonate. It must be noted, however, that this calculated energy efficiency is somewhat higher than the truth, because a certain amount of heat energy is supplied to the apparatus by the steam which is blown in together with the CO_2. Making all reasonable allowance for this, the result remains satisfactory, though it is instructive to observe how large a waste of energy occurs even in a well-devised process, distinguished from its rivals by its economy of working.

The next point of interest in the Hargreaves-Bird process is the comparatively large size of the apparatus. The single ten-foot cell which has been run continuously for considerably more than a month is capable of producing 1 ton of bleaching powder per week of seven days of twenty-four hours each, and ·53 ton of sodium carbonate. These figures correspond with 13·3 pounds of bleach and 7·1 pounds of sodium carbonate per hour for a single cell. Most other processes which have been tried can only be worked with cells which are comparatively small, e.g. giving one-fiftieth of this output per cell. The multiplication of parts thus needed is a serious disadvantage, and therefore the large cell with large output must be reckoned as a substantial merit of the Hargreaves-Bird process. The next point is the nature of the diaphragm. A good deal of mystery attaches to this part of the apparatus. Whether the inventor is right in stating that a diaphragm made as described above is impervious to water, but will allow electrolysis to proceed through its pores, is a question difficult to answer. The fact remains that the diaphragm is efficient for its purpose, which is to keep the salt solution in the anode compartment, and to allow the cations of sodium to make their way to the copper gauze cathode, and there in the presence of CO_2 and steam yield the cathode products hydrogen and sodium carbonate. These continuously escape from the cathode, and thus the sodium carbonate is not liable to be in its turn electrolysed, as is the caustic soda produced in a cell of the ordinary type, in which the cathode product accumulates in the neighbourhood of the cathode until it reaches a sufficient concentration to warrant its removal and recovery by boiling down the cathode liquor. It is by no means clear why the Hargreaves-Bird process should not be used for the manufacture of caustic soda, by blowing steam without carbon dioxide into the cathode compartment. No doubt the plan has been tried; some working difficulty may have prevented its adoption. Precise information on the subject is lacking. The fact that caustic soda is not made is a drawback of the Hargreaves-Bird process, the price of sodium carbonate being considerably lower than that of a chemically equivalent amount of caustic soda. A process producing sodium carbonate can, however, always turn out caustic by adding to the process proper the simple chemical operation of causticising the soda ash by means of lime. Thus caustic soda or soda ash (sodium carbonate) can be made and sold according to the state of the market. An ideal electrolytic process would turn out either at need, by a slight alteration in mode of working, but the time for this is not yet.

The remaining point of interest in the Hargreaves-Bird process is that it makes chlorine of full strength. This is chiefly due to the large size of the apparatus and the absence of those innumerable tubes, all with joints, most of them leaky, which are necessary in a process having numerous small units of plant. Thus bleaching powder is made as readily as by any purely chemical process, and no special apparatus or process for utilising chlorine largely diluted with air is necessary. Taking all these things into consideration, it is clear that the Hargreaves-Bird process presents much that is worth study, and has as good a prospect of attaining commercial success as it is possible for any process to possess which has not been actually worked on a manufacturing scale.

THE CASTNER-KELLNER PROCESS

This is the only process which is being worked in this country on a large scale and in a profitable manner. The principles on which the process depends are well known. The precise mode of working is kept scrupulously secret. In consequence of this only a diagrammatic sketch (Fig. 46) of the apparatus can be given.

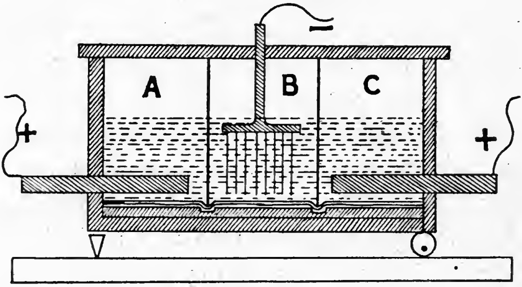

Fig. 46.

The cell shown in the figure is divided into three compartments A, B, C, by two vertical partitions reaching almost to the bottom of the cell, but not making a water-tight joint therewith. Each partition reaches down into a shallow groove, so that when the bottom of the cell is covered with liquid each compartment is completely trapped. The liquid used to cover the bottom of the cell is mercury, a layer of which is indicated by the shaded portion in the figure. On this mercury a layer of salt solution rests in the two compartments A and C, and a layer of water in the compartment B. In A and C are carbon anodes and in B is an iron grid acting as the cathode. The cell is supported on a knife edge at one end and on an eccentric at the other. On rotating the latter the cell is given a slight vertical motion at that end and rocks on its knife edge at the other. The layer of mercury at the bottom of the cell is thus gently oscillated. The cell is completely closed and there are pipes (not shown in the figure) for leading off chlorine from the anode compartments and hydrogen from the cathode compartment. Means are also provided for supplying fresh salt solution to the anode compartments and for drawing off the solution of caustic soda which forms in the cathode compartment.

The action of the cell is as follows:—

The mercury acts as an intermediate electrode between the anodes and the cathode. At the anodes chlorine is evolved and sodium is produced at the surface of the mercury facing each anode. The sodium dissolves in the mercury, and, on account of the oscillating movement of that liquid, passes into the cathode compartment. Arrived there the mercury acts as anode towards the iron cathode. The sodium which it contains reacts with water, and caustic soda and hydrogen appear at the iron cathode. The mercury, therefore, acting as a true intermediate electrode, functions first as a cathode towards the anode of the cell, and then as an anode towards the cathode of the cell. But besides this it serves effectively as a diaphragm to keep the aqueous liquids in the anode and cathode compartments separate. It also serves as a solvent for the sodium and a means of transferring it from the anode to the cathode compartment. It is, therefore, at once an anode, a cathode, a diaphragm, a carrier and a liquid seal.

The critical voltage necessary for the electrolytical decomposition of salt by the Castner-Kellner process is precisely that necessary for any other process having chlorine, caustic soda, and hydrogen as its end products. Although sodium is liberated at the cathode surface of the mercury facing the anode of the cell, yet it is oxidised in due course at the anode surface of the mercury facing the cathode of the cell. Thus the extra energy needed for the liberation of sodium instead of caustic soda in compartments A and C is precisely balanced by the energy provided by the oxidation and hydration of the same amount of sodium in compartment B. Looking at it in another way, one may say that the critical voltage between the anode and the cathode of the cell is the algebraical sum of the voltage between the anode and the mercury and between the mercury and the cathode. The case may be argued step by step thus:—

(1) An aqueous solution of sodium chloride decomposed so as to yield sodium and chlorine requires the expenditure of 96·51 Cal per gramme equivalent.

(2) The combination of sodium and mercury to form sodium amalgam liberates 21·60 Cal per gramme equivalent.

Therefore on the anode side the energy required is $96{\cdot}51 - 21{\cdot}60 = 74{\cdot}91$ Cal, *i.e.* 312,125 joules, corresponding with a critical voltage of 3·23 volts.

But on the cathode side we have :—

(1) Sodium amalgam being decomposed and requiring for its decomposition 21·60 Cal per gramme equivalent.

(2) The reaction of sodium with water, displacing hydrogen and forming caustic soda with an evolution of 43·31 Cal.

Therefore on the cathode side we have a source of energy amounting to 43·31 – 21·60 Cal = 21·71 Cal, *i.e.* 90,458 Cal, corresponding with a maximum available voltage of 0·94 volt.

This voltage is in a direction opposed to that previously calculated for the anode compartment, wherefore the actual critical voltage of the cell is their algebraic sum, viz. 3·23 – 0·94 = 2·29 volts, which is the value previously calculated as the critical voltage of a cell electrolysing a solution of sodium chloride without the use of mercury as an intermediary.

It is clear from this that the use of mercury as an intermediate electrode does not give rise to any increased consumption of energy in the cell. Such advantages as it presents are, therefore, free from a drawback which might be feared on casual inspection. These advantages are sensible enough. There is a complete separation of anode and cathode products. Formation of such substances as sodium hypochlorite and sodium chlorate by interaction of caustic soda and chlorine is impossible under normal conditions of working. From the cathode compartment sodium chloride is completely absent and the caustic soda obtained is pure. The ordinary porous diaphragm, which has usually either a high resistance or a short life (and frequently both), is abolished altogether. Against these advantages must be set the large quantity of mercury required, which represents a considerable amount of capital locked up. The loss of mercury, given careful handling, is in no way serious. Neither does there appear to be any ground for the outcry against the process made in its early days on the ground that sufficient mercury vapour escapes to endanger the health of the workpeople.

The current efficiency of the process is said to be high (90 per cent.). The voltage usually required is 4 volts, wherefore the energy efficiency is $\frac{2{\cdot}29}{4} \times 90$ per cent. = 51·5 per cent., a value similar to that calculated for the Hargreaves-Bird process (p. 302), viz. 54·4 per cent. But it must be remembered that the Hargreaves-Bird process yields sodium carbonate; the Castner-Kellner gives caustic soda. The smaller efficiency is more than compensated for by the greater value of the product.

Few details of the practical working of the Castner-Kellner process have been allowed to become public. The only point of special interest which is generally known is that it is advisable to purify the brine from calcium and magnesium salts by precipitating these impurities with carbonate of soda.

The process is at work in England, at Weston Point, in Lancashire, where a plant of about 1,000 H.P. is in use; a second plant of equal size is now being put down. Another plant of 2,000 H.P. (also about to be doubled) belonging to the Mathieson Alkali Company is running at Niagara, using current supplied by the Niagara Falls Power Company, and of this, too, a few details may be given. The output is stated to be 10 tons of caustic soda and 24 tons of bleaching powder per day of 24 hours; the current efficiency 85 to 90 per cent.;

the pressure required 3·5 volts, *i.e.* the energy efficiency is 55·6 to 58·9 per cent. These statements are found to be concordant if we assume that the joint efficiency of the transformers and dynamos is 80 per cent.

This is not an unreasonable loss, inasmuch as the current has not only to be let down in voltage, but has to be transformed from an alternating to a direct current. The current comes from the power house at a pressure of 2,200 volts; it is transformed down in stationary transformers to a pressure of 120 volts. At this pressure the current (which is, of course, still alternating) passes to motor-transformers, which transform it to a direct current delivered at a pressure of 200 volts, this being a convenient voltage for working a group of electrolytic cells.

The anodes used are ordinary "squirted" carbons; they are subjected to a "special treatment," designed to render them more refractory, and are said to last a year. Connection is made with them by means of a lead cap cast on one end. The caustic soda solution obtained is fairly concentrated, *e.g.* about 20 per cent. strength. Much is sent in liquid form in tank-waggons to soapmakers in Buffalo, which is about twenty miles from Niagara. Some is boiled down and sold in the solid state to the Electro-chemical Company, whose works are close to those of the Mathieson Alkali Company. This company (not to be confused with the English company of the same name) uses it for making sodium by the Castner process (*q.v.*). The Solvay process uses an intermediate electrode of mercury, which is arranged so as to flow continuously over a weir, its surface containing sodium going to the cathode compartment, and a new surface being thus exposed in the anode compartment. In this process, the salt solution standing immediately over the mercury is kept of a higher sp. gr. than that surrounding the anode, whereby access of chlorine to the mercury-sodium surface is hindered. The Rhodin process is one having a mercury electrode. Its general principles are so similar to those of the Castner-Kellner apparatus that prolonged litigation has taken place between the companies owning the respective patents. The Le Sueur apparatus, as first devised, resembled that of Holland & Richardson in respect of the fact that the anodes were blocks of carbon contained in a stoneware bell dipping in a trough of salt solution. The process, which is at work at Rumford Falls, Maine, has lately been modified and very thin sheets of platino-iridium are now used instead of carbon as anodes. These, though high in first cost, are permanent, and their use is found to be economical. At the bottom of the anode bell is an asbestos diaphragm; on this is stretched a sheet of wire gauze, serving as the cathode. Each cell is 9 feet × 5 × 1½ feet, therefore the units of plant are conveniently large. A pressure of 4 volts is needed; the current efficiency is stated to be 70 per cent. These figures correspond with an energy efficiency of 40 per cent. The liquid in the anode cell is kept slightly acid with hydrochloric acid. By this means any sodium hypochlorite which may be momentarily formed by the incursion of caustic soda from the cathode side of the diaphragm is at once decomposed, and caused to yield its equivalent of chlorine instead of oxygen. A good many other processes are at work in different parts of the world, but the details of their working have not been disclosed. The following table (taken, with a few alterations, from *The Electrician*) gives a summarised statement of such information as is available:—

Names of Companies.	Locality of plant.	Power.		Products.	Process used.	Date manu-f'ture comm.
		Kind.	Am'nt.			
Germany.			H.P.			
Allgemeine Elektricitäts Act. Gesellschaft	Bitterfeld . .	S.	1,500	Caustic alkali and bleach .	?	1896
" Elektron " A. Gesellschaft	,, . .	S.	?	,, ,, .	?	1894[1]
,, ,, ,, ...	Frankfort . .	S.	400	Caustic potash, bleach, and liquid chlorine	?	1890[2]
Elektrochemische A. Gesellschaft . . .	Berlin . . .	S.	?	Caustic potash	?	?
Solvay Ammonia Soda Company . . .	Osternienburg	?	?	Caustic alkali and bleach. .	?	1895
,, ,, ,, ,, . . .	?	?	?	,, ,, .	C'stn'r-Kelln'r	1897
Vereinigte Chemische Fabrike	Leopoldschall.	?	?	Potassium carb. and chlorine	Spilk'r & Löwe	1892
England.						
Castner-Kellner Alkali Company . . .	Weston Point.	S.	2,000	Caustic alkali and bleach .	C'stn'r-Kelln'r	1897
The Electro-chemical Company	St. Helen's. .	S.	1,100	,, ,, .	Richardson and Holland	1895
General Electrolytic (Parent) Company .	Farnworth. .	S.	?	Carb. soda and bleach. . .	Hargreaves-Bird	?
United States, America.						
Electro-chemical Company	Niagara. . .	W.	800	Caustic alkali and bleach. .	C'stn'r-Kelln'r	1896
Electro-chemical Company of U.S.A. . .	Rumford Falls	W.	1,100	Alkali and bleach	Le Sueur . .	1892
Mathieson Alkali Company	Saltville . .	?	?	Caustic alkali and bleach. .	C'stn'r-Kelln'r	1895
,, ,, ,, ...	Niagara. . .	W.	4,000	,, ,,	,,	1897
Walton-Ferguson Electro-chemical Co. .	,, . . .	W.	1,000	,, ,,	?	1896
Austria.						
Cons'rtium f. Elektro-chemische Industrien	Golling . . .	W.	2,500	Caustic alkali and chlorine .	Kellner . . .	1896
Kellner-Partington Paper Pulp Company.	Hallein . . .	W.	2,500	Bleached wood pulp . . .	,,	1895
Sweden and Norway.						
Electro-chemical Company	Stjernfors, S. .	W.	75	Bleached pulp	Hermite . .	1892
Kellner-Partington Paper Pulp Company.	Sarpsborg, N.	W.	5,000?	,, ,, ...	Kellner . . .	1895

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[1] Doubled in size in 1895.

[2] Doubled in size in 1892.

ALKALI, CHLORINE, AND THEIR PRODUCTS

PRODUCTS OTHER THAN CAUSTIC SODA AND CHLORINE

Cognate with the industries dealt with above are those concerned with the manufacture of caustic potash, chlorates and hypochlorites. Substituting potassium chloride for sodium chloride in a practicable apparatus such as the Castner-Kellner, one would obtain chlorine and caustic potash instead of caustic soda. The trade in caustic potash, although smaller than that in caustic soda, is nevertheless very considerable. For certain purposes, *e.g.* in making soft soap and in preparing oxalic acid from saw-dust, caustic soda cannot be used in place of caustic potash. The dearer alkali must be employed, and the demand for it is not likely to decrease. The raw material, potassium chloride, is much dearer than sodium chloride, and thus it is of more importance to economise raw material than to decrease to its utmost limit the cost of manufacture. Therefore an electrolytic process, even if as costly as, or somewhat more costly than, one which is purely chemical, has a greater chance of success when working on potassium chloride than on sodium chloride by reason of its economy of raw material. The cost of raw materials, of power, and the selling price of products when a potassium salt is used may be compared with similar figures for a sodium salt in the following table. The calculation is made for a consumption of energy of 1 H.P. (at the terminals of the electrolytic cell) acting for a year. The cell is assumed to work with an energy efficiency of 57 per cent.

POTASSIUM CHLORIDE

Weight of electrolyte decomposed.	Products.		Value of raw materials.	Value of products.
	Caustic potash.	Chloride of lime.		
4·4 tons	3·3 tons	5·2 tons	£33 8*s.*	£121

SODIUM CHLORIDE

Weight of electrolyte decomposed.	Products.		Value of raw materials.	Value of products.
	Caustic soda.	Chloride of lime.		
3·5 tons	2·4 tons	5·2 tons	£5 3*s.*	£54

It is assumed that steam power is used in each case, and that a H.P. year costs £9. Comparison of this with the value of the raw materials dealt with by that power, viz. £33 8*s.* for potassium chloride and £5 3*s.* for sodium chloride, shows at a glance the much smaller proportion which the cost of the energy bears to the cost of the raw materials in the manufacture of caustic potash than that which it does in the manufacture of caustic soda. The difference is still more marked when the selling price of the products is used as the basis of comparison. It is easy to see that the electrolytic manufacture of caustic potash by a process not wasteful of raw materials and turning out a product of high grade should be remunerative, even if the cost of energy be somewhat larger than that given. There is not, as far as present information goes, any electrolytic process specially devised for the production of caustic potash as distinct from caustic soda.

ELECTROLYTIC MANUFACTURE OF CHLORATES

If the products of the electrolysis of sodium chloride (hydrogen, caustic soda, and chlorine) are brought together and caused to combine, they reproduce the common salt and water from which they have been derived. If one of these products, viz. hydrogen, be eliminated, the caustic soda and chlorine interacting will produce either a mixture of sodium hypochlorite and chloride or one of sodium chlorate and chloride, according to the temperature at which the reaction is caused to occur. Thus:—

(*a*) $2\,NaOH + 2\,Cl = NaCl + NaOCl + H_2O$; or

(*b*) $6\,NaOH + 6\,Cl = 5\,NaCl + NaClO_3 + 3\,H_2O$.

It must not be supposed, because a portion of the sodium chloride used in preparing the caustic soda and chlorine is regenerated, and thus chlorine appears to be uselessly consumed, that there is any waste of the oxidising or chlorinating power of the chlorine. For 1 molecule of sodium hypochloride (NaOCl) is equivalent in oxidising power to 2 atoms of chlorine, and similarly, 1 molecule of sodium chlorate is equivalent to 6 atoms of chlorine. It may, therefore, be accepted that the oxidising and bleaching products formed when the anode and cathode products (excluding H) of the electrolysis of sodium chloride are brought together are precisely equivalent in oxidising or bleaching value to the chlorine normally evolved in the anode compartment. It might be assumed from this that the simplest manner in which a bleaching solution could be prepared would be by electrolysing a solution of common salt or other suitable chloride in a cell without a diaphragm. But such electrolysis could be conducted only up to a certain point. The hypochlorite (or chlorate) formed by the union of the caustic soda from the anode and the chlorine from the cathode would not be confined to the neighbourhood of the anode. It would be free to diffuse to the cathode, and would there be reduced to chloride. Thus the energy impressed on the electrolyte would be consumed in oxidising chloride to hypochlorite (or chlorate) and subsequently reducing it again to chloride. The net result is merely the conversion of electrical energy into heat—an outcome unintended, costly and useless. Therefore the simple plan whereby sodium chloride can be directly oxidised to hypochlorite (or chlorate) in an undivided electrolytic cell can be utilised only under particular conditions; in general a more complex arrangement is necessary. The methods which promise greatest prospect of success may be usefully discussed.

PRODUCTION OF HYPOCHLORITES

Sodium hypochlorite may be made by the electrolysis of a solution of sodium chloride, using carbon electrodes, employing no diaphragm, and mixing the anode and cathode products by agitation. The temperature of the electrolyte should be kept low, *e.g.* below 60° F. = 15° C. The concentration of the sodium chloride solution may be high, but that of the hypochlorite should be low, *e.g.* 8 grammes per litre. It is impracticable to convert more than a small fraction of the sodium chloride into hypochlorite, because, as the concentration of the latter rises, it is itself acted on and reduced at the cathode. Therefore the commercial production of a hypochlorite in this manner is confined to cases where the electrolysed liquor can be used for bleaching purposes and returned to be again oxidised and made again effective as a bleaching agent. Should the use of the bleaching liquor contaminate it seriously (as in the bleaching of paper), it may not be feasible to return it to the electrolysing cell. In this case the process described can only be used when the raw material, *e.g.* sodium chloride, is so cheap and abundant that it can be used wastefully. Similar bleaching liquids suitable for circulation through a bleaching process and return to the electrolytic cell can be prepared from calcium chloride and magnesium chloride. In the case of the latter, the liquid is particularly active, because magnesium hypochlorite is an unstable salt, and is readily hydrolysed, yielding free hypochlorous acid. It is this property which has led to extravagant statements concerning the remarkable bleaching and oxidising effects of an electrolysed solution of magnesium chloride; these are due to the presence of free hypochlorous acid. Where it is desirable to obtain a particularly active bleaching agent, a solution of hypochlorous acid formed by treating a solution of common bleaching powder with carbonic acid can be adopted. Choice between such a solution and one prepared by electrolysis is governed wholly by their cost.

A method for electrolysing sea-water, known as the Hermite process, and intended for the production of an oxidising, deodorising and bleaching liquor, chiefly for the treatment of sewage, has been tried in this country at various seaside places without achieving any great success. It merits no detailed description, being merely an arrangement for producing a weak solution of hypochlorites by the electrolysis of the chlorides naturally present in the sea-water. In cost it compares unfavourably with that of bleaching powder and similar chlorinating agents.

Should a demand arise for pure hypochlorites, *i.e.* for solutions free from the large excess of chlorides inevitably present in any chlorinating solution produced by the direct electrolysis of a chloride without separating cathode and anode products, it can be met by any successful process for the manufacture of alkali and bleach, *e.g.* the Castner-Kellner process. It will then be worked as an adjunct to the main manufacture of caustic soda and bleaching powder; the cost of such a bleaching liquor will depend primarily on that of the chlorine produced electrolytically, and if that is smaller than the price of chlorine made by chemical processes, there will be a corresponding saving in the cost of production of the bleaching liquor.

PRODUCTION OF CHLORATES

What has been said with regard to hypochlorites applies generally, *mutatis mutandis*, to chlorates. The obvious method of preparation is to manufacture caustic soda and chlorine in any good electrolytic apparatus, and to use the chlorine for the production of chlorates precisely as it is used when its mode of preparation is purely chemical. Seeing that the chlorine may happen to be diluted with air, drawn in through the many joints usually requisite in an electrolytic chlorine plant, its utilisation for making chlorate is, on the whole, preferable to its employment for the production of bleaching powder, which is best made with chlorine of full strength. This view has commended itself to the Electro-chemical Co. (whose process is described on p. 298), who consume a good portion of their output of chlorine for making chlorate. Granting that chlorate is to be made with electrolytic chlorine, it becomes sufficient to indicate the usual chemical process for chlorate manufacture.

Potassium chlorate is that which is manufactured in the largest quantity. It is not made directly by the action of chlorine on caustic potash according to the equation—

$$6\ KOH + 6\ Cl = 5\ KCl + KClO_3 + 3\ H_2O,$$[1]

because five-sixths of the necessary caustic potash would be converted into potassium chloride, a comparatively low-price salt. The plan used to get over this difficulty is first to prepare calcium chlorate thus:—

$$6\ Ca(OH)_2 + 12\ Cl = 5\ CaCl_2 + Ca(ClO_3)_2 + 6\ H_2O,$$

and then to act on this with potassium chloride thus:—

$$Ca(ClO_3)_2 + 2\ KCl = 2\ KClO_3 + CaCl_2,$$

giving potassium chlorate and calcium chloride. There is, therefore, no waste of any potassium salt, and the use of caustic potash, which is comparatively costly, is dispensed with. The manufacturing operation consists in passing the chlorine into hot milk of lime, contained in a series of cylindrical vessels. The contents of the vessels are kept agitated and the absorption of the chlorine is conducted systematically, *i.e.* the chlorine as it enters is passed into a vessel already nearly saturated, and as it leaves passes out through a vessel containing fresh milk of lime. The liquor containing calcium chlorate is run into settling tanks and is there treated with potassium chloride. The solution, which may be regarded as containing, potentially at least, potassium chlorate and calcium

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[1] The action of chlorine on a caustic alkali gives a hypochlorite as the main product when the solution is cold, and a chlorate when the solution is hot. The two reactions are shown on page 319.

chloride, is evaporated until it attains a specific gravity of 1·35, when potassium chlorate crystallises out. The calcium chloride liquor, retaining a portion of potassium chlorate, is run off and cooled strongly to induce a further fraction of the potassium chlorate to crystallise. The crude potassium chlorate is recrystallised to free it from adhering calcium chloride, and is then pure enough for ordinary commercial purposes.

When, however, chlorate is made by some special process of electrolysis, distinct from those designed for the manufacture of alkali and bleach, certain difficulties arise. The direct method of electrolysing a hot solution (*e.g.* one at a temperature approaching that of the boiling-point of water) of potassium chloride in a vessel without a diaphragm, and causing free mixture of the caustic potash and chlorine produced, is feasible only up to a small concentration. The recovery of the chlorate from a solution rich in chloride by means of any process of crystallising out the chlorate is somewhat expensive. Thus some means must be sought to permit the production of a more concentrated solution. Where no diaphragm or other means of separation exists, the anode or oxidised product (the chlorate) will reach the cathode and be there reduced. At the same time the caustic alkali formed at the cathode may itself serve to convey the current and yield as ultimate products oxygen and hydrogen. In either case electrical energy is expended uselessly, in the first instance appearing as heat in the solution, and in the second being represented by the chemical energy of products which are not required and are useless to the chlorate manufacturer. Several suggestions have been made to remedy these disadvantages. Thus Kellner proposes to add to the solution of potassium chloride a sm quantity of a sparingly soluble hydroxide, such as slaked lime or magnesia. He takes a saturated solution of potassium chloride and adds to it about 3 per cent. of slaked lime; a portion of this dissolves, but the greater part remains in suspension. The electrolyte may, therefore, be regarded as saturated with calcium hydroxide, and containing a store of undissolved calcium hydroxide ready to dissolve should that already in solution be used up from any cause. In order to provide a supply of lime to all parts of the electrolyte, the liquid is agitated so as to prevent the slaked lime from settling out. On electrolysing this solution, electrolysis is confined practically to the potassium chloride; the quantity of calcium hydroxide in solution is so small that no appreciable proportion of the current is conveyed thereby. The chlorine evolved at the anode comes in contact with the dissolved calcium hydroxide, and at the temperature proper to the reaction forms calcium chlorate and calcium chloride. The former reacts with the potassium chloride, yielding calcium chloride and potassium chlorate. The latter, together with the calcium chloride produced by the reaction of the calcium chlorate with the potassium chloride, is decomposed by the caustic potash liberated at the cathode, giving calcium hydroxide and potassium chloride. Thus all the materials return to the *status quo ante*, except a portion of the potassium chloride which has been converted into potassium chlorate. The function of the calcium hydroxide is merely to provide a medium for the absorption and utilisation of the chlorine, which is then passed on to the caustic potash at the cathode. It may be said that the same effect could be produced by adding caustic potash to the electrolyte. This is true, but the plan has the disadvantage that on account of the solubility of caustic potash the whole of that added would be in solution, and not chiefly undissolved and in suspension as a reserve to be drawn upon as occasion required. To have the whole of the caustic alkali in solution would lead to the inconvenience (dealt with above) of a part of the electrolysis proceeding with the caustic potash as an electrolyte instead of the potassium chloride exclusively acting thus. It would therefore be necessary to add the caustic potash little by little as it was required, whereas the slaked lime, on account of its sparing solubility, regulates the supply of alkaline hydroxide automatically.

This idea of Kellner is ingenious and appears sound in principle. No information, however, is forthcoming as to its having been used on a manufacturing scale. This lack of specific information is characteristic of the chlorate manufacture, which is being quietly pursued by various firms who guard their particular methods with much care. Nevertheless, it may be taken that all essential principles have been treated of in the foregoing paragraphs, and that novelties and secrets of manufacture relate rather to the form of apparatus and small details of working than to any great or fundamental difference from what is generally accepted and understood.

The idea underlying the method of Kellner, which is described above, receives fresh illustration from the researches of Bischoff and Förster on the electrolysis of a solution of calcium chloride. When calcium chloride is used instead of potassium chloride, the calcium hydroxide liberated at the cathode forms a coating thereon, which confines the reducing action of the hydrogen simultaneously formed to very narrow limits, acting, in fact, as a sort of diaphragm, preventing access of the chlorate (or hypochlorite) to the cathode. It is evident also that the solution of calcium chloride must contain calcium hydroxide in solution, and indeed in suspension, as portions of the film on the cathode become detached. Thus the electrolyte is in much the same condition as Kellner's, in which there is an automatically regulated supply of alkaline hydroxide capable of absorbing and utilising the chlorine evolved at the cathode. The resistance at the cathode is considerably increased by the film of calcium hydroxide adhering there, and in this respect the arrangement is inferior to Kellner's. Another difference is the greater solubility of calcium hydroxide in calcium chloride solution than in water (or a solution of potassium chloride). This is of doubtful advantage, inasmuch as the presence of any considerable quantity of alkaline hydroxide in solution and acting as an electrolyte will tend to waste current by allowing the formation of oxygen and hydrogen as end products instead of the chlorate, which is the object of manufacture.

It may be noted, in closing this section, that a still higher state of oxidation than that represented by the chlorates may be attained electrolytically. When a solution of potassium chlorate is electrolysed with platinum electrodes, and with the observation of certain conditions about to be described, potassium perchlorate ($KClO_4$) is formed. In order to get a good yield, *e.g.* 70 to 90 per cent. of the total oxygen in the form of perchlorate, the electrolyte should be kept cool, certainly not above 10° C.; the current density at the anode should be high, *e.g.* 4 to 12 amperes per square decimetre; and the electrolyte should be a saturated solution of the chlorate, preferably the sodium salt, because of its solubility being greater than that of the potassium salt. It is noteworthy that a good deal of ozone is given off during the electrolysis, and it has even been suggested to utilise this fact for the manufacture of that gas. At present, however, there is no great commercial demand for either ozone or perchlorate.

SECTION VII

The Electrolytic Manufacture of Organic Compounds and Fine Chemicals

The Electrolytic Manufacture of Organic Compounds and Fine Chemicals

SEEING that by means of electrolysis a reducing action can be exerted on an electrolyte at the cathode and an oxidising action at the anode simply by the impress of energy without the introduction of any foreign matter, it is evident that electrolytic methods for the preparation of many chemical substances have a *prima facie* advantage over purely chemical methods, which, from the nature of the case, frequently involve the use of some substance which ultimately, having done its work, forms no part of the product which it is sought to obtain, but is rather an encumbrance and impurity to be eliminated. To take a simple case: If copper is to be precipitated as metal from its sulphate, the work can be done by metallic zinc; it can also be done by passing a suitable current (using an insoluble anode). In the one case the solution at the end of the operation is encumbered by zinc sulphate; in the other there remains no foreign substance, but there are present simply the products of resolution—copper and sulphuric acid. Silver may be precipitated from its solution by a variety of reducing agents, *e.g.* tartrates, formaldehyde and milk sugar; the products of their oxidation remain in solution. It may be precipitated electrolytically without the addition of any foreign material. A solution of cupric chloride may be reduced to cuprous chloride by means of sulphurous acid, but the resulting solution is contaminated with sulphuric acid; it may be reduced electrolytically and remain free from such contamination. A lead salt may be oxidised so as to yield lead peroxide by the action of caustic potash and chlorine; it may be obtained pure and directly by electrolysis. Nitrobenzene may be reduced to aniline by iron and hydrochloric acid; at the cathode the same product may be obtained *per se.* Examples might be multiplied. It must not be concluded that an electrolytic method of preparing a given substance is necessarily preferable to a strictly chemical method. Considerations of cost, convenience, speed of output, obtainment of a high yield or of useful by-products, must all be taken into account, and these sometimes turn the balance of advantage against the electrolytic method.

The manufacture of organic compounds, such as dyestuffs, and of fine chemicals, is an industry relatively insignificant, although absolutely considerable. The processes used are simply laboratory processes writ large, and their practice and control are in the hands of a few highly trained chemists. It follows that the methods employed are in essence laboratory methods, and that any advance which may be made, being in few hands, is carefully guarded from public scrutiny. Such published processes as are rational and promising are here recorded.

The typical electrolysis of common organic substances recorded in the text-books is that of sodium acetate. It may be supposed to take place in two stages:—

$$(1)\ 2\,(CH_3CO(ONa)) = C_2H_6 + 2\,CO_2 + 2\,Na;$$
$$(2)\ 2\,Na + H_2O = 2\,NaOH + 2\,H.$$

The salt is resolved, yielding ethane and carbonic anhydride at the anode and caustic soda and hydrogen at the cathode.

The reaction is general, though not necessarily quantitative, with alkali metal salts of the acetic series. The acids themselves should split up thus:—

$$2\,(CH_3CO(OH)) = C_2H_6 + 2\,CO_2 + 2\,H,$$

but in dilute solution act simply as aids to the electrolysis of water, much as does sulphuric acid. This decomposition of the salts of organic acids may be correlated with that of certain of the salts of inorganic acids, where the salt is resolved primarily into the metal and the acid radicle, both undergoing consequent changes. Thus the resolution of sodium sulphate in the presence of water may be represented by the equations:—

$$\begin{aligned} &(1)\ Na_2SO_4 &&= 2\,Na + SO_4; \\ &(2)\ 2\,Na + 2\,H_2O &&= 2\,NaOH + 2\,H; \\ &(3)\ SO_4 + H_2O &&= H_2SO_4 + O; \end{aligned}$$

the final products being caustic soda and sulphuric acid. Similarly the resolution of sodium benzoate may be regarded as passing through corresponding steps, and its ultimate result may be represented thus:—

$$C_6H_5CO(ONa) + H_2O = \underset{\text{Benzoic acid.}}{C_6H_5CO(OH)} + NaOH,$$

and of the sodium salt of phthalic acid:—

$$C_6H_4(COONa)_2 + 2\,H_2O = \underset{\text{Phthalic acid.}}{C_6H_4(COOH)_2} + 2\,NaOH.$$

This is the simplest case.[1] If sodium acetate were decomposed in this manner it would yield CH_3COOH and NaOH. It is the splitting up of the acid radicle which gives the products set forth above. The salts of certain acids, such as hydroxy acids like lactic and tartaric acids, give products which suffer a further oxidation, which may extend to the complete destruction of the radicle and the production of so typical a product of limited oxidation as CO. The large number of possible changes, which are controlled not only by the materials electrolysed, but by the conditions of electrolysis, make prediction of the course of a given reaction dubious and compel constant experiment. This is in process of being carried out by several investigators.

The very obvious idea of reducing nitro-compounds by exposing them to the action of the current at the cathode appears to have been patented by Die Farbewerke vormals Friedrich Bayer in 1893. According to this patent, the nitro-compound is dissolved in sulphuric acid either concentrated or only slightly diluted and placed in a cell surrounding the cathode; the anode is immersed in sulphuric acid of 70 to 90 per cent. strength. Examples of this method of reduction are furnished. Thus nitrobenzene, $C_6H_5(NO_2)$, is dissolved in sulphuric acid in the proportion of 20 kilos in 150 kilos of sulphuric acid and electrolysed. The product is para-amido-phenol sulphonic acid, $C_6H_4(NH_2)(OH)$; the reaction is supposed to take place in two stages,

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[1] Although this reaction proceeds smoothly in acid or neutral solution, yet in alkaline solution decomposition goes farther, the anode products being carbon dioxide, carbon monoxide and sometimes acetylene; a smell of oil of bitter almonds is frequently observed.

with the intermediate formation of phenylhydroxylamine, thus:—

$$C_6H_5(NO_2) + 2\,H_2 = \underset{\text{Phenylhydroxylamine.}}{C_6H_5(NH)(OH)} + H_2O;$$

$$C_6H_5(NH)OH \qquad = \underset{\text{Amido-phenol.}}{C_6H_4(NH_2)(OH)}.$$

The ultimate product, para-amido-phenol sulphonic acid, separates in crystals from the electrolyte and can be filtered off through asbestos. In like manner, from ortho-nitrotoluene can be obtained ortho-amido-meta-cresol, and from meta-nitrotoluene, meta-amido-mortho-cresol. Corresponding amido derivatives can be prepared from dinitrobenzene and dinitrotoluene. Such transformations are the alphabet of industrial organic chemistry, and the only interest or importance attaching to their execution by electrolysis turns on questions of cost and yield. On these points no information is available.

The flexibility of electrolytic processes for effecting organic reactions is shown by the fact that two other products (distinct from amido-phenol) may be prepared by the reduction of nitrobenzene:—

(1) In dilute acid solution aniline is formed—

$$C_6H_5(NO_2) + H_6 = C_6H_5(NH_2) + 2\,H_2O.$$

(2) In alkaline solution azobenzene may be obtained—

$$2\,C_6H_5(NO_2) + H_8 = C_6H_5NNC_6H_5 + 4\,H_2O.$$

A large number of similar processes, many of which have been patented, deal with the reduction of nitro-compounds to the corresponding hydroxylamine and amido derivatives—reactions which are accomplished without difficulty by purely chemical methods. Any advantage which may lie with the electrolytic process will rest rather on the greater control of the course of the reaction which an electrolytic process may give, or on the avoidance of waste products and consequent increase of yield, than on any novelty in the reaction itself. In certain cases, however, electrolytic reduction of organic substances takes a characteristic course. Thus certain nitraldehydes of the aromatic series yield, not amido compounds, as might be expected, but hydroxylamine derivatives. The following examples may be given:—

10 kilos of meta-nitrobenzaldehyde ($C_6H_4(NO_2)COH$) are dissolved in 150 kilos of sulphuric acid, and electrolysed with a current having a pressure of 4 to 6 volts and a density at the cathode of 6 to 7 amperes per square decimetre. When the reduction is complete the electrolyte is diluted with water; a colourless substance is precipitated. This is an anhydro-derivative of meta-aldehydephenylhydroxylamine, $C_6H_4NH(OH)COH$. In like manner para-nitrobenzaldehyde yields a product which is an hydroxylamine derivative, though not in this case an anhydro-derivative. Such products are utilised in the manufacture of colouring matters and synthetic drugs; their production is simply a step in a long chain of reactions which is conveniently and economically accomplished electrolytically instead of chemically. An example may be given of the direct production of a dye-stuff by electrolytic means. Naphthazarine (alizarin black) is dihydroxyanthraquinone, $C_{10}H_4(OH)_2O_2$; it may be prepared by reducing alpha-dinitronaphthalene by means of zinc in the presence of strong sulphuric acid. Equally it may be made by electrolysing a solution of dinitronaphthalene in strong sulphuric acid. This solution is placed in the cathode compartment of the cell and electrolysed with a current having a density of 15 amperes per square decimetre.

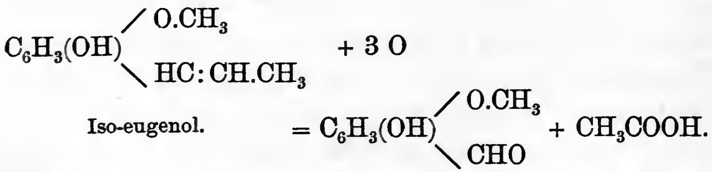
Elbs has studied the conditions of reduction of nitrobenzene with intent to obtain a high yield of aniline. When sulphuric acid is used as a solvent for the nitrobenzene to be electrolysed it may be regarded as serving a three-fold use: (1) as a solvent, (2) as aiding conduction, (3) as bringing about the transformation of phenylhydroxylamine, which may be regarded as the first product of reduction, into para-amidophenol, $C_6H_4(OH)NH_2$. Seeing that aniline, $C_6H_5(NH_2)$, is obtained as well as para-amidophenol, it seemed possible by a modification of the conditions of electrolysis to obtain this substance as the main resultant and not merely as a by-product. When acetic acid is substituted for sulphuric acid as a solvent the yield of aniline is considerably increased; an increase occurs also when a lead cathode is substituted for one of platinum; under these conditions the quantity of para-amidophenol is correspondingly reduced. It appears from direct experiment that para-amidophenol is not reduced to aniline, whence it follows that the use of a lead cathode must aid in determining the course of the reduction of nitro-benzene to aniline instead of to para-amido-phenol; it is suggested that lead itself may effect this reduction, much as iron does in the ordinary chemical process of making aniline from nitrobenzene. The lead oxidised and transformed into a salt (sulphate or acetate) by the action of the nitrobenzene is promptly reduced by the current and deposited as lead sponge, which again acts as a reducing agent. Thus the formation of aniline may be truly said to be effected by the action of the lead, in spite of the fact that no appreciable quantity of lead is permanently oxidised and dissolved. A zinc cathode will act in a similar way, doubtless for the same reason. Such results may be compared with the various products of reduction of nitric acid when treated with different metals—nitrous oxide with zinc, nitric oxide with copper, nitrous anhydride with silver, and nitrogen peroxide with tin. The current may be looked upon merely as a convenient method of bringing into play reactions proper to the several metals which are alternately oxidised and reduced.

A direct instance of this is afforded by the patented process of Castner for the reduction of nitro-compounds in the cathode compartment of the Castner-Kellner cell (see page 309). Here the substance to be reduced is exposed to the action of sodium amalgam formed and continually renewed electrolytically. A large number of investigations have been made to determine the course of reaction in similar processes of reduction or oxidation of organic compounds by electrolytic means, but the discussion of these pertains to the domain of a particular branch of organic chemistry and is not cognate with the subject of this book.

Sometimes, however, it occurs that a reaction can be brought about electrolytically which cannot be directly accomplished chemically. Thus in the normal course of oxidation of para-nitrotoluene, $C_6H_4CH_3(NO_2)$, para-nitrobenzoic acid, $C_6H_4(NO_2)COOH$, is produced; by electrolysis, however, it is possible to obtain para-nitrobenzyl alcohol, $C_6H_4(NO_2)CH_2OH$. An illustration of the use of electrolysis in the preparation of synthetic dye-stuffs is afforded by the oxidation of certain hydroxy acids of the benzene series. The Badische Anilin und Soda Fabrik has patented alternative processes for the manufacture of a yellow dye-stuff from meta-dihydroxy-benzoic acid, $C_6H_3(OH)_2COOH$. According to the chemical method 10 kilos of this substance are dissolved in 200 kilos of strong sulphuric acid and treated with 15 kilos of ammonium persulphate, the temperature being kept below 50° C. = 122° F. The reaction is allowed to proceed for 12 hours and the mixture is thrown into 1,000 litres of cold water. The colouring matter separates in yellow flocks and can be filtered off and washed.

The corresponding electrolytic operation is conducted as follows: 10 parts of meta-dihydroxybenzoic acid are suspended in 40 parts of sulphuric acid of 50° B. (specific gravity 1·53); the mixture is placed in the anode compartment and subjected to the action of a current of 20 amperes at a pressure of 8 volts. The current density is 20 amperes per square decimetre. The product is identical with that produced chemically. It is a fast yellow colour applicable to both cotton and wool. Other hydroxy acids—*e.g.* gallic acid $C_6H_2(OH)_3COOH$, cresotic acid $C_6H_3(OH)CH_3COOH$, and hydroxy-benzoic acid ($C_6H_4(OH)COOH$)—may be similarly treated so as to yield analogous dye-stuffs.

Another instance of the electrolytic preparation of organic compounds is afforded by the oxidation of iso-eugenol to vanillin. Eugenol is converted into iso-eugenol by treatment with alkalies; its alkaline solution is then exposed to oxidation at the anode, a current density of 13 amperes per square decimetre and a temperature of 60° C. = 140° F. being used. The reaction may be expressed thus:—



$$C_6H_3(OH)\begin{cases} O.CH_3 \\ HC:CH.CH_3 \end{cases} + 3\,O = C_6H_3(OH)\begin{cases} O.CH_3 \\ CHO \end{cases} + CH_3COOH.$$

Iso-eugenol. Vanillin. Acetic acid.

Vanillin is the odoriferous principle of vanilla, and has a high price. It can be prepared from coniferine ($C_{16}H_{22}O_8$) by purely chemical methods. The success of its electrolytic manufacture from eugenol is obviously a question of cost and yield by the two processes. It must be remembered also that a synthetic product is not always as marketable as the natural material. There may be a real difference due to the presence of an impurity in one or the other, or the difference may be imaginary—for imagination plays a great part in trade—but, however this may be, the artificial body has usually to win an uphill fight before it is accepted as on a par with the native substance.

The electrolytic manufacture of iodoform has occupied inventors. The ordinary chemical method for preparing this body is by heating alcohol or acetone with caustic potash and iodine, thus:—

$$\underset{\text{Alcohol.}}{C_2H_5OH} + 10\,I + 9\,KOH = CHI_3 + K_2CO_3 + 7\,KI + 7\,H_2O;$$

$$\underset{\text{Acetone.}}{(CH_3)_2CO} + 12\,I + 8\,KOH = 2\,CHI_3 + K_2CO_3 + 6\,H_2O + 6\,KI.$$

The same changes can evidently be brought about by electrolysing a warm solution of potassium iodide in the presence of alcohol or acetone and water. Potassium iodide electrolysed in the presence of water may be regarded as potentially iodine and caustic potash, thus:—

$$2\,KI + H_2O = KOH + H + I.$$

Seeing that alkali is necessary for the reaction which results in the production of iodoform, and that it is formed at the cathode, together with an equivalent of hydrogen which would tend to reduce the iodoform or to combine with the iodine to form HI, it is desirable to work with a diaphragm and to provide a supply of alkali from without. Of course the alkali formed in the cathode compartment can be withdrawn and transferred to the anode compartment, the process being thus made self-supporting. In an experiment made by Elbs a platinum anode was immersed in a solution consisting of 15 grammes of Na_2CO_3 and 10 grammes of KI in 100 c.c. of water and 20 c.c. of alcohol; this was contained in a porous cell and was thus separated from the cathode compartment, which contained caustic soda solution and a nickel cathode. The temperature was 70° C. = 158° F. and the current density 1 ampere per square decimetre at the anode. After a three hours run a yield of 70 per cent. of the calculated quantity of iodoform was obtained. The chief by-product was sodium iodate. Bromoform and chloroform can be prepared in a similar manner.

For the manufacture of chloroform an apparatus has been devised consisting of a leaden still, which can be heated by steam and contains an agitator armed with carbon plates to serve as anode in a 20 per cent. solution of common salt. The still itself acts as the cathode. Acetone is admitted at the bottom of the still and is converted by the joint action of chlorine and caustic soda into chloroform. The reaction may be regarded as occurring in two stages:—

$$(1)\ (CH_3)_2CO + 3\,Cl_2 = \underset{\text{Chloracetone.}}{CH_3COCCl_3} + 3\,HCl;$$

$$(2)\ CH_3COCCl_3 + NaOH = \underset{\text{Sodium acetate.}}{CH_3COONa} + \underset{\text{Chloroform.}}{CHCl_3}.$$

The chloroform is distilled off and collected in the usual manner. It is stated that from 100 parts by weight of acetone 180 parts of chloroform are obtained, as against a theoretical yield of 206 parts. Assuming the substantial correctness of this claim, it will be noted that only one of the two methyl groups in the acetone is utilised for the production of chloroform.

The preparation of an indigo vat for dyeing can be accomplished by reducing indigo to indigo-white by means of zinc in alkaline solution. Experiments on the electrolytic reduction of indigo have shown that it takes place much more readily when a solution of zinc oxide in caustic soda is used as the liquid at the cathode than when caustic soda alone is used. In fact, it appears to be necessary to use the zinc as an oxygen carrier, and thus ensure the reduction proceeding to the desired point; otherwise either the indigo is not fully reduced or the reduction is carried a step farther than indigo-white and the vat is spoiled.

The case is parallel to that already cited on page 337 viz. the reduction of nitrobenzene to aniline by the aid of a lead cathode.

There has been much systematic study of the course of electrolysis and of the products obtained in the case of definite classes of organic substances, such as the alcohols, the salts of acids of the fatty series, salts of acids of the aromatic series, nitro-compounds and the like, which will doubtless form a starting-point for many industrial processes in due time. At present such work is of purely academic interest, and special manuals such as Dr. W. Löb's *Elektrolyse und Elektrosynthese organischer Verbindungen* must be consulted for a knowledge of its details.

Sharply distinguished from this systematic enquiry are certain processes which are almost wholly empirical, but have nevertheless attained a sufficient measure of success to justify a description.

In the purification of crude sugar juice, lime is commonly used to neutralise organic acids and to precipitate albuminous substances and colouring matter. It has been proposed to accomplish this defecation by electrolysing the juice between electrodes of zinc or aluminium. The anode is attacked, giving a zinc or aluminium salt, and alkali is produced from the alkaline salts naturally present in the juice; the products of the two electrodes intermingle, giving rise to a precipitate of hydrated zinc oxide or alumina, which acts as a defecating agent. It is stated that a few minutes' treatment is effective.

Assuming that the defecation is better accomplished thus than with lime, there appears to be no reason why the use of hydroxides produced electrolytically should present any advantage over the same substances prepared chemically. A similar process has been proposed in which lead anodes are used, and the same remark applies.

Somewhat elaborate experiments by Baudry (*Jahrbuch für Elektrochemie*, 1897, 323) have shown that, when raw juice from beets is defecated with a small quantity of lime and then electrolysed with zinc anodes, a greater purification is effected than with lime alone. A large consumption of zinc and a considerable expenditure of electrical energy, however, make the process unduly expensive. It does not appear that a comparison has been made between the use of zinc hydroxide made chemically as a defecating agent and that of the same substance prepared electrolytically. Failing such data it is impossible to decide how much of the advantage claimed arises from employing a defecating agent other than lime and how much is due to the use of electrolysis. Endeavours have been made to aid the purification of crude sugar juice by treatment with ozone alone or aided by electrolysis. The degree of purification attained is not high, and the process offers little prospect of practical employment.

The process of tanning, which consists essentially in treating hides with an aqueous solution of tannin derived from various barks, berries and other vegetable products, is one of the slowest operations industrially carried out, being comparable in this respect with the seasoning of timber or the manufacture of white lead by the old Dutch or English corrosion process.

This slowness is largely due to the difficulty with which the tannin penetrates into the hide. As the penetration progresses, the outer part of the hide becomes converted into leather and is thereby made impervious, consequently the rate of penetration decreases. Months of soaking in the tan pit are, therefore, necessary for thick hides. Many attempts have been made to hasten this absorption of tannin by hide. The methods used include circulating the tan liquor so that fresh portions are continually presented to the hide, forcing the liquor through the hide by pressure, and using strong aqueous extracts of tanning materials. It has been sought to attain the same object by passing a current of electricity through the vat in which the hides are suspended. One such process (Groth's) has been found to shorten the time of tanning to a quarter of that necessary when no current is used, and the leather is said to be unexceptionable. The apparatus devised by Groth is designed to hasten tanning by circulation of the tan liquor as well as by the use of electricity. The tan liquor is contained in a tank in which is a frame carrying hides and capable of being moved to and fro or rotated so as to bring the hides continuously into contact with fresh liquor. Copper electrodes are placed at the side of the tank. For a vat holding 1,500 gallons a current of not more than 4 amperes is used.

The current density is not more than 0·1 ampere per square foot of transverse section of the vat. With this mild stimulus it was found that the rate of tanning was sixteen times as fast as when the hides were simply immersed in the tan liquor and allowed to be stationary, and four times as fast as when the hides were moved and no current passed. Considering the well-authenticated tests which have been made, it is noteworthy that tanners at large will have nothing to say to electric tanning. In the Worms and Bale process (which was the forerunner of Groth's) the apparatus used is a barrel of about 12,000 litres capacity and taking a charge of 700 kilos of hide and 5,000 litres of oak-bark extract. The electrodes attached to the inside of the drum are of copper. A current of 11·5 amperes at a pressure of 74 volts is used. Tanning is said to be complete in 48–144 hours, but the process is somewhat violent, the leather suffering from the mechanical pounding which it receives.

Another process, consisting essentially in passing a current of 12 amperes at 60 volts between electrodes of nickel-plated copper through a bath in which tanning liquor was continually circulated by a pump, proved to be capable of tanning heavy leather in about six days, the product being not inferior to that prepared by the old process in twelve months.

SECTION VIII

Power

Power

IN certain electro-chemical industries, such as the electrolytic recovery of gold from cyanide solutions used to extract its ores, in plating, and in refining as distinct from winning metals, the quantity of energy required is not large.

The fact that in a large copper refinery some hundreds of H.P. (or even a few thousands) may be utilised is a contradiction to this statement, not real, but only apparent. The huge size of modern copper refineries obscures the fact that the energy needed per ton of copper handled is by no means large. Thus on page 40 it is shown that, with a liberal allowance for waste, a plant of 1,000 H.P., working day and night for a year of 365 days, will give an output of 15,000 tons of copper—an enormous amount of what is a relatively costly metal.

In other electro-chemical industries, however, such as the manufacture of caustic soda and chlorine, of sodium, of aluminium, and of calcium carbide, the expenditure of energy is extremely great. So large is it that a source of cheap power is indispensable for these industries.

At present the cheapest form of power is that afforded by moving water. A large steam plant deriving its energy from cheap coal comes next. Water power is usually obtainable only in mountainous regions difficult of access, remote from supplies of raw materials and labour. Thus it comes about that frequently when both raw materials and labour are required in quantity it may be more remunerative to use somewhat dear steam power at a spot where both are abundant than to seek cheaper power from water in an industrial desert. This holds good to-day, when the quantity of energy obtainable from coal by means of a boiler and steam engine is not greater than 10 per cent.; it will apply with greater force when it is possible to extract from coal something approaching a fair fraction of its energy—say 50 per cent. The problem of obtaining from carbonaceous fuel a large fraction of its total energy is the greatest of those set before the modern technical investigator. By present methods the loss is almost wholly in the steam engine, which is a device depending for its efficiency on the drop of temperature from the cylinder to the condenser. The boiler gives a fair return of the heat put into it—say 70 per cent. The dynamo gives a good return of the energy put into it—say 95 per cent. The combined efficiency of the two is 66·5 per cent. The rest of the loss, which brings the efficiency of the combination down to something less than 10 per cent., is due to the steam engine. Now when suitable material, such as zinc, is oxidised in a battery, the fraction of its energy which returns as electrical energy is high, *e.g.* 90 per cent. But zinc is too costly a fuel to be used for any but highly special purposes, where cost is a secondary consideration. Therefore it has long been a matter of endeavour to convert the energy of carbon or carbonaceous fuel directly into electrical energy. There have been many attempts to reach this goal—some ill-considered and doomed to failure, others rational but unsuccessful. The task is still unaccomplished and the problem unsolved.

The fundamental difficulty in the way of constructing a primary cell which shall yield electrical energy by the oxidation of carbon instead of zinc depends on the fact that carbon will not dissolve in any electrolyte by simple displacement of the positive ion of that electrolyte. The sort of reaction which must be sought if carbon is to be utilised as the positive element in a primary cell may be stated as follows. Suppose a carbon electrode immersed in fused silica, and opposed to a platinum electrode immersed in fused lead oxide. One may conceive the carbon being oxidised at one end of this chain and lead being liberated at the other, the balance of energy represented by the difference between the heats of combination of oxygen with carbon and lead appearing as electrical energy. If the carbon were immersed in fused lead oxide and opposed to a platinum electrode it may be assumed that the combination would be less effective, because of the oxidation of the carbon being chemical and local instead of electrolytic. Such a condition is comparable with a cell consisting of zinc and platinum immersed in strong nitric acid. No doubt a portion of the energy of the dissolving zinc would appear as electrical energy, but the greater part would appear as heat. Separate the zinc from the oxidant, as in a Grove's cell, and the combination becomes efficient. If a successful carbon cell is to be constructed on the lines of ordinary primary cells using zinc, it must have the carbon dissolving in a non-oxidising electrolyte and it or its equivalent being oxidised at the other electrode by an oxidising electrolyte. The difficulty of devising such a cell, is enhanced by the fact that the only practicable oxidant, air, is a gas, and the products of the oxidation of carbon, carbon monoxide and carbon dioxide, are gases. These and like considerations make the task of devising a rational carbon cell so difficult that one may well believe that the solution of the problem of converting the energy of carbonaceous fuel direct into electrical energy will be on lines totally different from those furnished by the analogy of the zinc primary cell.

The difficulty of using carbon as the attackable electrode in a primary cell is not unique. It occurs with most non-metals. Thus it is not easy to scheme a cell in which sulphur shall furnish energy smoothly and completely by virtue of its heat of combination with oxygen; the same holds for phosphorus. It is true that both these elements, and indeed carbon itself, will dissolve when made the attackable electrode in an electrolyte consisting of hot concentrated sulphuric acid, but the reaction in all cases is more or less local and confined and does not yield a favourable return of electrical energy.

Becquerel in 1855 seems to have been the first to observe that when a rod of carbon was immersed in fused nitre at such a temperature as to cause its oxidation a current was produced if an unattackable electrode was present, *e.g.* the platinum vessel containing the nitre. This observation was repeated by Jablochkoff in 1877, who constructed a cell consisting of a cast-iron pot serving as the unattacked electrode and containing fused nitre, in which hung a basket of iron wire containing coke. The coke was oxidised at the expense of the nitre and a current was produced; the combination is said to have given a pressure of 2–3 volts—a somewhat doubtful statement. This apparatus had the considerable defect that the inevitable and wasteful local chemical oxidation of the carbon was enhanced by local electrolytic attack, due to the iron basket used to contain the coke. It was, however, better than some inventions of later date, in that it attempted to use coke instead of plates of artificial carbon of impracticable cost.

Before proceeding to a further discussion of the carbon cell a calculation of its possible output may be usefully made. Carbon in being oxidised to CO_2 gives 96·96 Cal, *i.e.* 24·24 Cal per gramme equivalent. This corresponds with 96,540 coulombs at a pressure of 1·04 volts. Therefore a cell in which carbon is oxidised by air cannot have a higher E.M.F. than 1·04 volts. Zinc similarly oxidised will give current at a pressure of 1·86 volts. In this respect the carbon cell is inferior to one burning zinc, because it is generally convenient to obtain current at a high pressure to avoid the necessity of multiplying units, *i.e.* cells. But when the total electrical energy, as distinct from the pressure at which it is delivered, is considered, the superiority of a carbon cell becomes manifest. One kilo of carbon gives 8,080 Cal as against 1,329 Cal for 1 kilo of zinc, *i.e.* a given weight of carbon will give more than six times as much energy as an equal weight of zinc. Zinc is at least twenty times as dear as carbon in the form of coal, wherefore a given quantity of energy could be produced from carbon in a primary cell for $\frac{1}{120}$ of the cost of the same quantity of energy from zinc, assuming identical efficiency. The disadvantage of a slightly lower voltage is insignificant compared with this great economy.

In all the early experiments—and there are many—on the production of electrical energy by the oxidation of carbon and other non-metals there is a sad lack of quantitative records. The voltage of a given cell is generally stated, but the output of current for a given consumption of electrode almost never. It is, therefore, impossible to say how far the experiments approached towards a practicable cell; it is certain that they never came within reasonable distance, as otherwise that cell would be in use now.

Other oxidants than nitre have been used in the carbon cell. Barium peroxide will serve, and has the advantage of being capable of regeneration by air from the barium monoxide to which it is reduced. Copper or lead oxide would not act in this manner apparently, because the metals which are produced by their reduction establish direct metallic conduction between the electrodes and prevent the progress of the electrolysis. When, however, the carbon is not directly in contact with the oxide, but is covered with a layer of fused salt, *e.g.* potassium carbonate, the conditions necessary for electrolytic dissolution are re-established.

One of the latest attempts to devise a practicable carbon cell has been made by W. W. Jacques. The chief features of the cell proposed are shown in Fig. 47. A is a carbon electrode, immersed in fused caustic soda contained in an iron pot B, set in a furnace (not shown) so that the alkali may be kept liquid. The pot serves as the unattacked electrode. Oxygen is supplied in the form of air blown in through the pipe C, ending in the perforated ring D. Surplus air and the gaseous products of oxidation escape by the vent E in the cover F, which is of insulating material, *e.g.* fire-clay.

The carbon is said to be oxidised to carbon dioxide by the finely divided air issuing from the ring and to yield its energy as current. It is claimed that from a battery of 100 cells a current of 16 amperes at a pressure of 90 volts was obtained for 18¾ hours with a consumption of 8 pounds of carbon. This corresponds with an efficiency of 79 per cent., reckoned on the amount of carbon consumed. Even accepting these figures the true efficiency of the cell cannot be stated thus, because a large quantity of heat is required to keep the electrolyte fused and a good deal of energy is needed to drive air through the molten mass. But the fact of the matter is that the cell is a chimera. Various elaborate calculations and experiments have been published tending to attack it in detail; they are unnecessary, because the device is wrong in principle. There is no evidence that the current is due to oxidation of carbon; such evidence as there is goes to show that it is due to a thermo-electric action and occurs as well with a non-consumable electrode. Next, if it be supposed that the energy is produced by the oxidation of carbon it may be rightly concluded that the product of oxidation, CO_2, will be absorbed by the electrolyte, caustic soda, which will be speedily spoiled. Thirdly, the carbon proposed to be

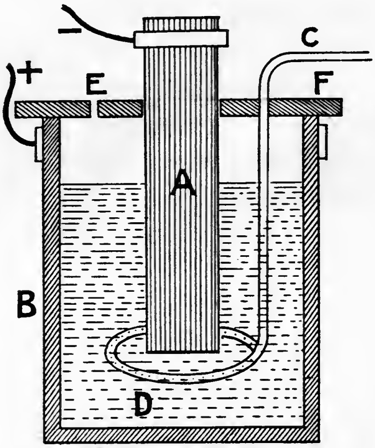


Fig. 47.

used is battery carbon, *i.e.* carbon in the form of expensive manufactured electrodes. These, even if consumed economically, would be a costly form of energy. The best proof of the correctness of these strictures is found in the fact that the Jacques cell, although much extolled at the time of its invention by the lay and the less intelligent part of the technical press, is extinct.

The only other cell which attempted with any plausibility to convert the chemical energy of carbon directly into electrical energy is that devised by Borchers. This was the outcome of a luminous and exact dissertation by Ostwald, and was in its inception an honest attempt to follow the principles laid down by that great chemist. Ostwald's pronouncement is sufficiently fundamental to demand reproduction here. He indicated with clarity and precision that direct chemical action is not adapted for the production of electrical energy; that if the reaction on which the production of energy ultimately depends is caused to occur on the spot where is the source of energy, *e.g.* the dissolving electrode, the energy evolved will be as heat and not as electricity. An experiment illustrates this point fully. Two vessels are filled with a solution of potassium sulphate and are put into electrolytic connection by means of a syphon. In one vessel is placed a rod of zinc and in the other a rod of platinum. On connecting these electrodes through a galvanometer a current passes momentarily and then ceases because the zinc cannot continuously dissolve in such a medium and give up its energy. In order to make the current continue it is necessary to provide an acid which will dissolve the zinc. Now comes the question: into which of the two vessels shall the acid (*e.g.* sulphuric acid) be poured? Obviously (and erroneously) into that containing the zinc; correctly (and evidently when the evidence is weighed) into that containing the platinum. The zinc dissolving from the zinc electrode traverses the electrolyte and appears in the form of its equivalent of hydrogen at the platinum electrode. The zinc may be regarded as becoming ionised, each of its ions bearing a positive charge, and transferring this charge through the electrolyte from ion to ion, ultimately neutralising the charge of a hydrogen ion negative to its own, deionising the hydrogen, and causing it to appear in the ordinary molecular state as a gas at the platinum electrode. The fact that the connection between the electrodes consists of an electrolyte containing ions neither of zinc nor of hydrogen is immaterial; the fate of the zinc at one end, and the ultimate product (hydrogen) at the other, alone need to be regarded for the purpose of the present case. It will be observed that when, as in this experiment, the acid is in the compartment remote from the zinc, dissolution of the zinc is dependent on the passage or production of a current, and is not local and wasted in the liberation of heat.

The broad fact that the action on the attacked electrode should be, as it were, at a distance, leads to the conclusion that cells of the Jablochkoff type, consisting of carbon, opposed to an unattackable electrode in a strongly oxidising electrode, such as nitre, are wrong in principle. The carbon should dissolve in a non-oxidising electrolyte, and it, or its product, should be oxidised by an oxidising electrolyte at the other electrode. To return to our old illustration: it is no doubt possible to obtain a current from a couple of zinc and platinum in strong nitric acid, but the combination is absurd. The nitric acid has to perform two functions: (1) that of a simple solvent at the surface of the zinc, and (2) that of an oxidant of the zinc or its equivalent (a depolariser in the old phraseology) at the surface of the platinum. Incidentally there is tumultuous and wasteful local chemical action of the nitric acid as an oxidant on the zinc. For the proper understanding of such questions nothing is needed but a sound chemical instinct; this is, unfortunately, rare, and its absence accounts for many errors. Ostwald has gone beyond his negative criticism of the carbon cell as it is, and has indicated the lines on which its construction should be attempted. "The carbon cell of the future," he says, "should have the oxidising agent in the place where the carbon is not"; this oxidising agent must be either the oxygen of the air or some carrier thereof. Such a cell will work precisely like an ordinary furnace. On one side coal will be thrown in, and on the other air will be introduced, energy and CO_2 being the products. Between the coal and the oxygen must be an electrolyte which will suffer no permanent change, and can be used continuously to bring about electrolytically the oxidation of the carbon. Fired by these beautiful and exact ideas, Borchers attempted to devise a cell for obtaining electrical energy direct from carbon, or at least carbon partially oxidised. Carbon monoxide, in being oxidised to CO_2, yields about two-thirds of the total quantity of energy obtained by the complete oxidation of carbon to CO_2. CO is soluble in cuprous chloride, forming therewith a loose compound (Cu_2Cl_2CO). Oxygen in the presence of an acid, *e.g.* HCl, is capable of oxidising cuprous chloride to cupric chloride. Here, then, were all the elements of success. A cell consisting of two carbon electrodes immersed in an acid solution of cuprous chloride and supplied, the one with CO and the other with O (or air), might be expected to yield a current at the expense of the CO and O, and with no permanent change of the electrolyte. A cell constructed on these lines gave a feeble current, which was slightly increased by increasing the surface of contact between gas and liquid by surrounding the electrodes with coke. When copper electrodes were substituted for electrodes of carbon, a somewhat better result was obtained, but the results put forward tend to show that the current was produced by the dissolution of the copper electrodes rather than by the oxidation of CO. Borchers brings forward almost no quantitative evidence, especially concerning the consumption of CO and production of CO_2. He claims an efficiency of 27 per cent., but this claim appears to be based on an observed maximum voltage of 0·4 volt, as compared with 1·47 volts, the calculated maximum for the equation $CO + O = CO_2$. Seeing that no data are given respecting the consumption of CO necessary to produce the feeble current (0·008 ampere) which could be maintained at this pressure, it is evident that the claim for a 27 per cent. efficiency is groundless. Throughout the investigation the evidence adduced is weak and inconclusive from the chemical and quantitative side. There is, for example, no attempt to measure the consumption of CO, to prove that it is actually oxidised to CO_2, or to show that the source of current is not merely the oxidation of Cu_2Cl_2 by air. Later attempts, by the use of copper electrodes and the like, to attain a better result are still more indecisive, because they import questions (such as the dissolution of the copper) other than the plain issue, "Do CO and O unite electrolytically with the production of current when supplied to two unattackable electrodes immersed in a solution of cuprous chloride? if so, what is the efficiency of the combination?" Direct experiments by R. Mond with two carbon electrodes immersed in a solution of cuprous chloride and supplied, the one with CO and the other with air, showed that the voltage of the combination was only 0·0015 volt. This most destructive observation has never been explained or refuted by Borchers, and until it is his cell must be considered as based on an illusion. This is the present situation of the only earnest attempt to follow a course of enquiry consonant with Ostwald's dicta.

It is clear that, if it is attempted to obtain electrical energy direct from carbon by methods analogous to those used for obtaining electrical energy direct from zinc in a primary cell, some plan must be found whereby carbon can be dissolved in an electrolyte in such a way as to form ions. The balance of evidence goes to show that carbon has not been thus dissolved to form ions but, nevertheless, some ground exists for maintaining a contrary opinion. Dr. Coehn has called attention to the work of Bartoli and Papasogli, and has extended the line of enquiry there indicated. Bartoli and Papasogli observed that when a current is passed between carbon electrodes in dilute sulphuric acid the anode is not quite unattacked, but takes part in the process of electrolysis, as is witnessed by the fact that CO and CO_2, as well as O, appear as anode products. By varying the concentration and temperature of the acid and the density of the current, Coehn succeeded in obtaining conditions in which the carbon was consumed, with the production at the anode, no longer of oxygen, but of a mixture containing 70 per cent. CO_2, about 30 per cent. CO, and not more than 1 per cent. O. During the electrolysis the acid became red-brown in colour, and evidently contained carbonaceous matter in solution; the gradual destruction of the anode is due, not to mere disintegration, but to actual dissolution of the carbon. When electrolysis is continued, using in such a solution a carbon anode and a platinum cathode, a black deposit appears on the cathode. Coehn has succeeded in collecting a small quantity of this, and finds that it consists of carbon, with hydrogen and oxygen in proportion to form water. He is disposed to regard it as an hydrated form of carbon, and to consider that he has succeeded in effecting the electro-deposition of carbon; hence that carbon ions are formed under the conditions of his experiment. These interesting observations may be recorded, but the deductions drawn from them must be received with some reserve. Even if the deposit is an hydrated form of carbon, it by no means follows inevitably that carbon ions are present in the electrolyte and are deprived of their charges and deposited in the usual way as elementary carbon. It is quite as likely that the dissolution of the carbon anode forms complex organic substances, which by reduction at the cathode yield highly condensed carbohydrates of the general form $C_mH_{2n}O_n$, such as the body $C_{12}H_6O_3$, said to be left in the carbonaceous residue from the dissolution of highly carburetted iron (*e.g.* white cast iron) in cupric chloride solution. It will be observed that there are here two distinct questions. The first is whether carbon will dissolve in sulphuric acid to form ions; it is indifferent for the purpose of this enquiry whether the ions are formed by the spontaneous dissolution of the carbon with the production of current, or by the enforced dissolution of the carbon by the impression on it of a current from without. This question must be considered undecided; the balance of evidence is on the negative side. The second question is whether carbon under these conditions dissolving in sulphuric acid can (whether it forms simple ions or not) act as a positive plate and produce electrical energy. Direct experiment by Coehn goes to show that this is possible. When a plate of carbon is opposed to one of lead peroxide in sulphuric acid it gives a constant current until the lead peroxide is reduced or the carbon consumed. No data are available as to the output of this combination per equivalent of carbon consumed. The efficiency is probably not high, and in any case the combination is not a practicable means of consuming carbon for the production of electrical energy on a large scale. There have been many other attempts to devise cells which shall dissolve carbon and render its energy electrically. With none of them has any real success been attained. In the greater number there has not been even an attempt to show success; all inventors have shrunk from recording the two factors needed to judge of the efficiency of the cell, viz. the consumption of the carbon per unit of current and the pressure at which the current is delivered. Many investigators seem to think that, if they show their cell to have a voltage of 0·7 on open circuit, or through a high resistance when the calculated voltage is approximately 1, the cell has an efficiency of 70 per cent., the current per unit of material consumed being ignored. The fallacy is the converse of that frequent in the description of electrolytic processes, in which it is common to find the efficiency stated in terms referring solely to the output per unit of current, irrespective of the pressure at which that current is delivered. In either case the error is sufficiently obvious and gross.

Gas cells of the type of Grove's gas cell have also been tried. In the Grove gas cell, hydrogen and oxygen are fed to platinum electrodes, which are platinised and partly immersed in acidulated water. By reason of the power of platinum, especially when finely divided, to condense gases in its pores, the two gases are brought into such intimate contact at once with the electrode and the electrolyte that they unite electrolytically and produce a current. The possibilities of the cell are great, and an attempt has been made to realise them by Mond and Langer, who have striven to improve the cell mechanically so as to economise platinum and to use purified water-gas as a source of hydrogen. It was found possible to construct a cell, having 700 square centimetres of active surface and containing only 0·35 gramme of sheet platinum and 1 gramme of platinum black, which yielded a current of 2 to 2·5 amperes at a pressure of 0·73 volt, and gave an energy efficiency of 50 per cent. Although ingenuity and perseverance have been lavished on it, the Mond-Langer cell has failed to achieve any practical success.

The roundabout conversion into electrical energy of the chemical energy of carbon is represented by all ordinary primary cells using zinc, which metal has been reduced from its oxide by coal. The energy efficiency is very low, say 2½ per cent., and the money efficiency greatly lower, *e.g.* less than 1 per cent. Now it may be possible to utilise in some circuitous way the energy of carbon more efficiently than can be done with zinc as an intermediary, and Reed has sketched such a method, which may be summarised thus. A current is obtained from cells supplied by a solution of sulphur dioxide (SO_2) opposed to one of sulphuretted hydrogen (H_2S); the electrodes are of inert material, *e.g.* platinum (or carbon). The combination of SO_2 and H_2S gives as its chief products sulphur and water, thus:—

$$SO_2 + 2\,H_2S = 2\,H_2O + S_3,$$

the energy evolved being obtainable as electrical energy. A constant supply of SO_2 and H_2S can theoretically be obtained by a cycle of reactions, needing for its realisation nothing but a limited stock of sulphur and water, on which is impressed at intervals the energy represented by the oxidation of carbon. The requirements of the cycle are that sulphur shall be burned in air, the SO_2 sent to the electrolytic cell, and the heat used to induce the formation of CS_2 from C and S, and H_2S from CS_2 and H_2O, the carbon being thereby oxidised to CO_2. The H_2S is then sent to the electrolytic cell, where, reacting with the SO_2, it regenerates sulphur; this is collected and again burned at the first stage of the cycle. For the details of the idea, the reader is referred to Reed's paper, "The Transformation of the Energy of Carbon into other Available Forms," appearing in *The Electrical World*, xxxviii., 1896, page 44. The various steps mentioned above lead ultimately to the formation of CO_2 as the end product of the circuitous oxidation of carbon, with the calculated production of 61 per cent. of the total energy thus liberated as electrical energy. The sulphur and water are perpetually oxidised and decomposed, and are merely intermediaries. The CS_2, H_2S, and SO_2 are still more ephemeral intermediaries. The whole scheme is sound and philosophical, but hardly to be realised in practice.

It will be seen from this brief sketch that the present position of the problem of converting the energy of carbon into electrical energy by means other than the boiler engine and dynamo is one of attempt, not of achievement. Much has been done to prepare the way for final success; of practical success at present there is absolutely none. The enormous importance of the solution of this problem must be my excuse for the space which I have given to its consideration.

Returning from the possibilities of the future to the accomplished facts of the present, let us examine the question of the cost of electrical energy under different local conditions.

WATER POWER

A large waterfall is the cheapest source of power. An artificial fall of water, such as may be obtained by impounding the head waters of a river and conveying the collected water to a lower point in a closed channel, such as a steel pipe, comes next in order of merit. The power station at Niagara is a type of the first. Here a canal is cut from the river, above the falls, to the power house. In this canal are the intakes of large steel pipes which descend to the bottom of the turbine pit, which has a depth somewhat less than the height of the falls. The water passes from these pipes through the turbines to the tail race, which is carried out at a point below the falls. Thus the whole head of water represented by the height of the falls is utilised without the employment of any great length of steel main. A typical example of the other mode of construction is afforded by the power station at Brieg, on the Swiss side of the Simplon tunnel. Some miles above Brieg is the glacier from which the Rhône issues. The river flows torrentially down the valley, but there is no definite waterfall. A portion of the river is impounded at the glacier end, and is conveyed in steel pipes along the course of the river and delivered to turbines at the power house. The head is of course represented by the difference in level of the upper and lower end of the pipe. The turbines are used to drive dynamos which supply electrical energy representing a large fraction of the total calculated energy of the falling water. Thus, if the efficiency of the turbine is taken at 70 per cent., and that of the dynamo at 90 per cent., the joint efficiency of the plant will be 63 per cent. at the terminals of the dynamo. It is often found necessary to transmit current to some distance, and for this purpose that supplied by the dynamo may be sent into a step-up transformer, transmitted at a high pressure, and reconverted into current at a low or moderate pressure suitable for the work in hand by means of a step-down transformer. The expenditure for capital sunk in the transformers, together with that represented by their joint losses, is smaller than that needed to cover the interest on the capital sunk in a copper conductor of large section—at least when the distance of transmission is considerable. Thus it comes about that the process of converting low-pressure current into its equivalent of high-pressure current, transmitting the current at high pressure, and retransforming it to low-pressure current, complicated as it sounds, may be rational and economical.

The cost of water power naturally varies according to local circumstances. Where the engineering difficulties in impounding the water and utilising it are small, the cost per H.P. year, allowing for interest on and depreciation of plant, may be as low as £2 to £3. It must not be concluded that power to be acquired at the rate of £2 per H.P. year is necessarily twice as cheap as power at £4 per H.P. year. The value of the power clearly depends on its prospect of being commercially utilised, and since the ordinary object of these large water-power plants is to manufacture some chemical product, it is evident that the value of a given plant depends not only on its inherent cheapness, but on its accessibility. Raw materials must be brought to the spot, and finished goods must be taken away; local labour must be obtained. Generally speaking, the cost of all means of doing the same thing becomes ultimately identical. Power from a waterfall is at present cheaper in money than power derived from coal—first, because its inherent value is less understood; secondly, because its utilisation involves a heavy expenditure of capital, a return on which is dependent on the establishment of novel industries, and thirdly, because it has to offer some attraction to the user of power to induce him to leave a known manufacturing centre for a wilderness, access to which for his goods is difficult and expensive. An estimate based on actual expenditure is afforded by the calculated cost of power from the Lachine Rapids on the St. Lawrence River, near Montreal. The power house is designed for the production of about 20,000 H.P. The total capital cost is taken at £222,653, *i.e.* £11 3*s.* per H.P. Interest and depreciation on this at 10 per cent. will equal £1 2*s.*, and to this must be added a sum for operating expenses of 9*s.*, making for the H.P. year £1 11*s.* This estimate rests on the assumption that the whole of the 20,000 H.P. will be needed day and night for 365 days per year, a condition of things obtaining in electro-chemical manufacture. For intermittent supply, such as that required for lighting and traction, the cost would be greater, because interest and other permanent charges run on while no return takes place.

With steam the cost per H.P. year is higher. A modern plant of not less than 1,000 H.P., using coal of fair quality costing 8*s*. per ton, may succeed in producing power at about £5 per H.P. year (reckoned at the engine-shaft), corresponding with about £7 per H.P. year of electrical energy at the terminals of the dynamo. A plant to work at this low cost must be exceptionally well placed; under less favourable conditions the cost of an electrical H.P. year will approach £10. In all these cases the cost is inclusive, due allowance having been made for interest, depreciation, and the like. Broadly it may be taken that with water power a normal figure is £4 per H.P. year; a good figure may be taken as £2 10*s*. per H.P. year, and an unusually good figure as £1 10*s*. per H.P. year. In all cases it is assumed that the plant will be driven day and night for seven days a week, and for as nearly 365 days a year as need for cleaning and repairs will admit. Under modern conditions the comfortable, old-fashioned plan of periodical pauses is as obsolete as the ancient military method of going into winter quarters. It is possible that, for large installations a power plant consisting of gas engines driven by producer, gas might be even more economical than a good steam plant. In this case a portion of the nitrogen of the coal used in the producers is recovered as ammonium sulphate, and this turns the balance of advantage on the side of the gas engine. Failing such by-product, the advantage is dubious.

INDEX

INDEX

INDEX

INDEX

INDEX

INDEX

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