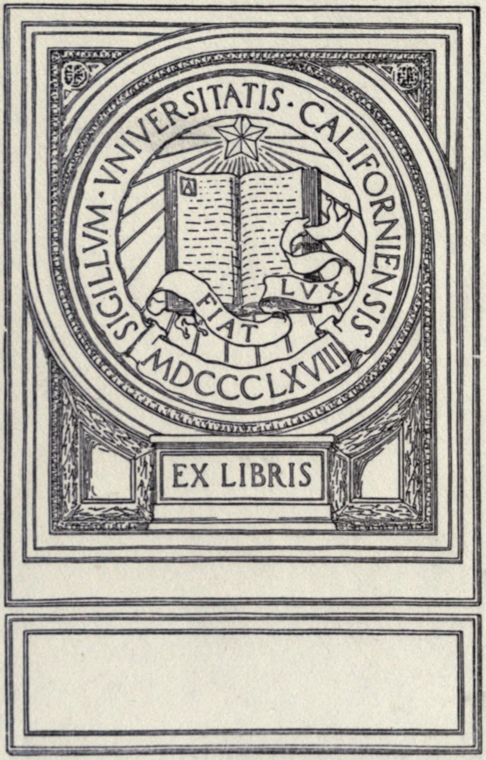

THE PRINCIPLES
OF APPLIED ELECTROCHEMISTRY

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OF
APPLIED ELECTROCHEMISTRY

BY

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TO

M. E. A.

PREFACE

In writing this volume, which is designed for both technical men and students, I have treated the subject primarily from the standpoint of the theory and principles involved, being convinced that through their thorough comprehension the best results are to be obtained in practice. At the same time I have endeavoured to describe accurately and with a certain amount of detail the methods at present technically used. Such a book (*Grundriss der technischen Elektrochemie*) was written in 1898 by my teacher Professor F. Haber, but, though reprinted, has not been brought up to date or translated into English.

The present book falls into two sections. Assuming an elementary knowledge of chemistry and electricity, Part I. is chiefly concerned with the treatment of the fundamental phenomena and theory of the electrochemistry of aqueous solutions. Particular stress is laid on irreversible effects, which though of very great importance in technical electrochemistry, seldom receive the attention they deserve. My great debt to Professor F. Foerster's *Elektrochemie wässeriger Losüngen* will here, as at certain points in Part II., be clear to all. Other chapters deal generally with the electrolysis of fused melts, electrothermics, and the discharge of electricity through gases. A chapter on *Equilibrium* is included. I have tried as far as possible to introduce no more theory than is applied at some point or other during the book, and employ frequent illustrative examples, numerical or otherwise.

Part II. treats separately of the various technical processes used, discussing *inter alia* primary and secondary cells. Here I have aimed in the first instance at an adequate description of all those methods actually worked at the present time. Other processes are only discussed if (1) they are likely to be used in the near future, (2) although obsolete, they have considerable historical value, (3) although they have never passed the experimental stage, the reasons for their failure are instructive. Throughout I have attempted to show the close connection between theory and practice, to treat the available material critically, and to exclude 'paper' processes. The diagrams are designed to emphasize the main features of the apparatus concerned, not so much its details. Many working details are omitted in the text also, as further are statistics and questions of costs. To deal with such matters would materially alter the scope of the book. The important subject of power production is however briefly discussed in Part I.

I owe to Professor F. G. Donnan, F.R.S., who proposed to me in the first instance the writing of this book, and who has criticised practically the whole of the manuscript, my warmest thanks for his many suggestions. To Mr. G. F. Horsley, of the United Alkali Co. Ltd., I am much indebted for his valuable criticism of most of Part I. He and Dr. J. T. Barker have read through the proofs, and Mr. F. D. Farrow has kindly verified the literature references.

For new data, permission to use diagrams, &c., I owe acknowledgements, amongst others, to Professor P. Askenasy; Professor W. D. Bancroft; Dr. J. Billiter; Mr. V. Engelhardt; Mr. R. Finlay; Professor F. Foerster; Professor P. A. Guye; Mr. W. E. Holland; the Reason Manufacturing Co. Ltd.; the American Electrochemical Society; the Faraday Society; the publishing firms J. A. Barth (Leipzig), L. Foss (Leipzig), W. Knapp (Halle), F. Vieweg (Braunschweig).

In conclusion I need hardly say that I shall be most grateful for any corrections on points of fact or for suggestions for improved treatment.

To those who wish to study the subject further, I recommend, besides the books of Haber and Foerster mentioned above and the numerous volumes referred to at the ends of the different chapters, the following:

Einführung in die technische Elektrochemie (edited by Askenasy).

Die elektrochemischen Verfahren der chemischen Gross-Industrie (Billiter).

Laboratory Electric Furnaces (Slade; about to be published).

Continuous Current Engineering (Hay).

Alternating Currents (Hay).

The first two books are particularly valuable for technical details; the third treats of laboratory experimental methods; the last two deal with the electrotechnical side of the subject in an elementary manner.

A. J. ALLMAND.

LIVERPOOL,
September, 1912.

CONTENTS

PAGES

List of Abbreviations xi

List of Symbols Used xii

PART I.—GENERAL AND THEORETICAL

CHAPTER I

INTRODUCTORY—POWER

Chemical and Electrochemical Methods compared—Electrical Units—Power 3–11

CHAPTER II

EQUILIBRIUM

General—Homogeneous Equilibria—Heterogeneous Equilibria—Effect of Temperature 12–25

CHAPTER III

FARADAY'S LAWS—CURRENT EFFICIENCY

Phenomena of Electrolysis—Faraday's Laws—Current Efficiency—Measurement of Quantity of Electricity—Calculation of Current Efficiencies 26–37

CHAPTER IV

OSMOTIC PRESSURE—THEORY OF SOLUTIONS

Osmotic Pressure—Solution Laws—Determination of Molecular Weight of Dissolved Substances—Anomalous Behaviour of Electrolytes . 38–48

CHAPTER V

IONIC TRANSPORT DURING ELECTROLYSIS

Mechanism of Migration of Ions—Quantitative Relations of Ionic Migration I—Determination of Transport Numbers—Quantitative Relations of Ionic Migration II—Applications of Ionic Migration Phenomena 49–57

CHAPTER VI

CONDUCTIVITY OF ELECTROLYTES—THEORY OF ELECTROLYTIC DISSOCIATION

PAGES
Specific Conductivity—Determination of Conductivity—Equivalent Conductivity—Electrolytic Dissociation Theory 58–76

CHAPTER VII

ENERGY RELATIONS

Total Energy and Maximum External Work—Reversible Processes—Irreversible Processes—Relations in Reversible Galvanic Cells—Relations during Reversible Electrolysis—Maximum Work and Affinity 77–86

CHAPTER VIII

ELECTROMOTIVE FORCE

Necessary Conditions for Electrochemical Reactions—Measurement of Electromotive Force—Electrolytic Solution Pressure—Quantitative Relations at Ionising Electrodes—Gas Electrodes—Oxidation-Reduction Electrodes—Concentration Cells—Measurement of Single Electrode Potentials 87–105

CHAPTER IX

ELECTROLYSIS AND POLARISATION—ENERGY EFFICIENCY

Polarisation—Energy Efficiency—Factors Affecting Electrolysis . . 106–116

CHAPTER X

CATHODIC AND ANODIC PROCESSES IN DETAIL

A. *Cathodic Processes.* Evolution of Hydrogen—Cathodic Metal Deposition—Electrolytic Reduction.—B. *Anodic Processes.* Discharge of Anions—Solution of Metals—Electrolytic Oxidation 117–147

CHAPTER XI

THE ELECTROLYSIS BATH

Arrangement—Voltage—Technical Electrodes and Diaphragms . . 148–157

CHAPTER XII

MOLTEN ELECTROLYTES

Phenomena of Electrolysis—Metal Fog—Anode Effect 158–166

CHAPTER XIII

GENERAL PRINCIPLES OF ELECTROTHERMICS

Electric Heating—General Principles of Electric Furnace Design—Electrical Aspects of Electric Furnace Design 167–182

CHAPTER XIV

ELECTRICAL DISCHARGES IN GASES

PAGES
Gas Ions—Different Types of Discharge—Chemical Effects . . . 183–192

PART II.—SPECIAL AND TECHNICAL

CHAPTER XV

PRIMARY CELLS

General Considerations—Primary Cells in General Use—Fuel Cells . 195–219

CHAPTER XVI

SECONDARY CELLS

General Considerations—Lead Accumulator—Iron Accumulator . . 220–244

CHAPTER XVII

COPPER—SILVER—GOLD

Copper Refining, Theory—Copper Refining, Practice—Copper Extraction —Silver Refining—Gold Refining—Gold Extraction . . . 245–280

CHAPTER XVIII

ZINC—TIN—NICKEL—IRON—LEAD—VARIOUS

Electrometallurgy of Zinc—Electrometallurgy of Tin—Electrometallurgy of Nickel—Electrolytic Refining of Iron—Electrometallurgy of Lead—Bismuth and Antimony 281–307

CHAPTER XIX

ELECTROPLATING AND ELECTROTYPING 308–317

CHAPTER XX

HYPOCHLORITES AND CHLORATES

General Theory—Hypochlorites, Theory—Hypochlorites, Technical—Chlorates, Theory—Chlorates, Technical 318–341

CHAPTER XXI

ALKALI-CHLORINE CELLS

General Theory—Mercury Cells—Diaphragm Cells with Stationary Electrolyte—Cells with Moving Electrolyte—Comparative . . . 342–385

CHAPTER XXII

OTHER ELECTROLYTIC PROCESSES

PAGES
Hydrogen and Oxygen—Regeneration of Chromic Acid—Potassium Permanganate—Perchlorates, etc. 386–406

CHAPTER XXIII

METALS FROM FUSED ELECTROLYTES—CAUSTIC SODA AND CHLORINE FROM FUSED SALT

Sodium—Magnesium—Calcium—Zinc—Aluminium—Acker Process . 407–433

CHAPTER XXIV

ELECTROTHERMICS IN THE IRON AND STEEL INDUSTRY

Pig-Iron Production—Electric Steel, General—Arc Furnaces—Induction Furnaces—Comparative—Ferro-Alloys 434–468

CHAPTER XXV

CALCIUM CARBIDE AND CALCIUM CYANAMIDE

Carbide, General and Theory—Carbide, Technical—The Nitrogen Problem—Cyanamide, General and Theory—Cyanamide, Technical . . 469–485

CHAPTER XXVI

OTHER ELECTROTHERMAL PRODUCTS

Carborundum and Allied Products—Graphite—Alundum, Silica—Distillation Products, Carbon Bisulphide, Phosphorus, Zinc 486–504

CHAPTER XXVII

THE OXIDATION OF ATMOSPHERIC NITROGEN

Theoretical—Early Attempts at Technical Apparatus—Birkeland-Eyde Process—Pauling Process—Schönherr-Hessberger Process—Working up of Furnace Gases 505–521

CHAPTER XXVIII

OZONE 522–527

APPENDICES

I. Transport Number of Anion for Different Aqueous Salt Solutions at 18° 528
II. Current Densities Used in Technical Practice 528
III. Yields and Energy Expenditure in Technical Practice . . . 530
IV. Theoretical Quantities of Electrolytic Products resulting from the passage of 1 ampere-hour of Electricity 531

INDEX OF AUTHORS AND FIRMS 532

SUBJECT INDEX 537

LIST OF ABBREVIATIONS

Abhand. Bunsen Ges.	Abhandlungen der Deutschen Bunsen Gesellschaft.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Amer. Chem. Jour.	American Chemical Journal.
Ber.	Berichte der Deutschen Chemischen Gesellschaft.
Berg-und Hütten. Zeit.	Berg-und Hüttenmännische Zeitung.
Bull. Soc. Chim.	Bulletin de la Societé Chimique de Paris.
Chem. Ind.	Chemische Industrie.
Chem. Zeit.	Chemiker Zeitung.
Compt. Rend.	Comptes Rendus des Séances de l'Académie des Sciences.
Ding. Poly. Jour.	Dinglers Polytechnisches Journal.
Drud. Ann.	Annalen der Physik (Fourth Series).
Electr.	Electrician.
Electrochem. Ind.	Electrochemical and Metallurgical Industry.
Electrochem. and Metall.	Electrochemist and Metallurgist.
Elektrochem. Zeitsch.	Elektrochemische Zeitschrift.
Elektrotech. Zeitsch.	Elektrotechnische Zeitschrift.
Engin.	Engineering.
Jahrb. der Rad.	Jahrbuch der Radioaktivität und Elektronik.
Jour. Amer. Chem. Soc.	Journal of the American Chemical Society.
Jour. Chim. Phys.	Journal de Chimie Physique.
Jour. Four Élect.	Journal de la Four Électrique.
Jour. Phys. Chem.	Journal of Physical Chemistry.
Jour. Prakt. Chem.	Journal für Praktische Chemie.
Jour. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Lieb. Ann.	Annalen der Chemie.
Metall.	Metallurgie.
Metall. Chem. Engin.	Metallurgical and Chemical Engineering.
Manch. Mem.	Memoirs of the Manchester Literary and Philosophical Society.
Philos. Mag.	Philosophical Magazine.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Chem. Soc.	Transactions of the Chemical Society.
Trans. Farad. Soc.	Transactions of the Faraday Society.
Wied. Ann.	Annalen der Physik (Third Series).
Zeitsch. Angew. Chem.	Zeitschrift für Angewandte Chemie.
Zeitsch. Anorg. Chem.	Zeitschrift für Anorganische Chemie.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Phys. Chem.	Zeitschrift für Physikalische Chemie.

LIST OF SYMBOLS USED

A	'Free energy' decrease.
C	Concentration in $\frac{\text{grams}}{\text{litre}}$.
$[\mathrm{C}]$	Concentration in $\frac{\text{gram-molecules}}{\text{litre}}$.
$[\mathrm{C}]_{Eq}$	Concentration in $\frac{\text{gram-equivalents}}{\text{litre}}$.
C_p, C_v	Molecular specific heats at constant pressure and volume.
Cal.	Large (kilo-) calorie.
E	Potential, voltage.
E.M.F.	Electromotive force.
F	Valence charge (96540 coulombs).
I	Current.
K	Constant; particularly equilibrium constant.
L	Latent heat of change of state.
L	Coefficient of self-induction.
M	Molecular weight.
Mol.	Gram molecule.
P	Osmotic pressure.
Q	Quantity of heat.
R	Resistance.
R	Gas-constant.
S.G.	Specific gravity.
T	Absolute temperature.
U	'Total energy' decrease.
$\mathrm{U_A}$, $\mathrm{U_C}$	Ionic mobility $\left(\text{velocity under gradient } 1\ \frac{\text{volt}}{\text{c.m.}}\right)$.
V	Velocity.
a	Area.
c	Specific heat.
cal	Small (gram-) calorie.
k	Constant; velocity constant.
l	Length.
l_C, l_A	Ionic conductivity.
m	Mass.
n	Transport number.
n	Periodicity (alternating current).
p	Pressure.
q	Heat effect in reversible process.
r	Specific resistance.
t	Time.
u_C, u_A	Ionic velocity (actual, under experimental conditions).
v	Volume.
α	Degree of dissociation.
δ	Specific gravity.
ϵ	Single electrode potential.
κ	Specific conductivity.
Λ	Equivalent conductivity.
η	Concentration in $\frac{\text{gram-equivalents}}{\text{c.m.}^3}$.
θ	Temperature in degrees C.
$\cos\theta$	Power factor.

(*a*) One ton is taken as 1000 kilos.
(*b*) A H.P. year is taken as 8760 H.P.H.

PART I

GENERAL AND THEORETICAL

CHAPTER I

INTRODUCTORY—POWER

1. Chemical and Electrochemical Methods Compared

CHEMICAL reactions can be divided into two classes—those which give out energy (usually in the form of heat), and those which absorb energy, whilst they are taking place. Examples of the former class are the combustion of fuels, the Goldschmidt Thermite processes, the slaking of lime. To the latter class belong the reduction of metals from their ores, and the formation from their elements of oxides of nitrogen or metallic carbides.

Electrochemical reactions can be similarly divided. Those which proceed with liberation of energy are not so important practically as those of the second kind, and will occupy little space in this book. The reaction being electrochemical, the liberated energy appears as electrical energy, and the systems in which the reaction takes place are known as **primary cells.** The Daniell cell is an example. The corresponding reaction is

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

and, when allowed to take place chemically, liberates its energy as heat.

On the other hand, electrochemical processes of the second kind—those which take place with absorption of electrical energy—have achieved very considerable technical significance, frequently supplanting a purely chemical process, and in some cases furnishing new products which could hardly be obtained in any other way. Thus copper is now chiefly refined electrochemically; the bulk of the world's chlorate production is made electrochemically; the electrochemical production of caustic alkali and bleach becomes continually more important; whilst the manufacture of aluminium, of CaC_2 (and hence acetylene), and of nitrates from the air could not have reached their present proportions without the introduction of electrochemical methods.

In chemical processes, the necessary supply of energy is usually introduced as heat. This often results in considerable wear and tear of plant, and in products rendered impure by the fuel used. Further, it often happens that the simplest and most direct (on paper) of purely chemical methods for reaching a certain result cannot be used, owing to great reaction resistances, or to the impossibility of converting heat energy into chemical energy under the given conditions. And consequently several successive reactions have to replace a single direct one. Thus, to obtain aluminium from alumina, the old chemical process consisted in preparing $AlCl_3$ by passing chlorine gas over a mixture of the alumina with carbon, forming a double salt of $AlCl_3$ with NaCl, and reducing this double salt by heating with metallic sodium.

Electrochemical processes differ in the following respects :—

(*a*) the energy needed is usually introduced as electrical energy, not as heat ;

(*b*) when introduced as heat, the heat is produced from electrical energy just where it is needed, not by means of furnaces or flue gases ;

(*c*) the processes are generally simpler and more direct than the corresponding chemical processes ;

(*d*) in consequence of (*a*) and (*b*) the products are usually purer ;

(*e*) the wear and tear of plant is generally less.

On the question of the relative costs of chemical and electrochemical processes, it is impossible to generalise. Sometimes one is the cheaper, sometimes the other. It is a matter decided by numerous factors which vary with each separate case, such as the local power charges, their cost compared with that of raw material, the relative charges for labour and maintenance of plant, the purity of product required, etc. Sometimes the electrochemical method is more expensive, but gives a purer product and is therefore preferably used.

Electrochemical processes should always be of as simple a nature as possible. This statement of course holds good of any kind of technical chemical operation, but particularly of electrochemical ones. They cannot 'stand such hard knocks' as chemical processes can, and generally only work satisfactorily when run under constant conditions. Simplicity is therefore of importance. The raw materials used should also be as pure as possible. When once impurities begin to accumulate, the efficiency of an electrochemical process usually decreases very rapidly. The most successful electrochemical processes are those in which a constant supply of a raw material of high purity and constant composition is assured. If impure, it will usually pay to subject it to a preliminary chemical purification.

2. Electrical Units

Electrical energy, like all other kinds of energy, can be divided into two factors, the *quantity factor* and the *intensity factor*. The possibility of a change taking place in the energy content of a system is determined by the intensity factor only, the extent of the change by both factors. Whether or not a quantity of water can move spontaneously from one level to another is determined in the first instance by the relative heights of the two levels. If movement does take place, the change of potential energy is expressed by the product of the weight of water which has flowed down into the difference in height between the two positions. Here difference in height is the intensity factor, weight of water the quantity factor. A possible transference of heat energy from one part of a system to another is decided by the difference in temperature between the two regions—the intensity factor of the heat energy. Excluding the effect of passive resistances, it is the affinity of a chemical reaction which decides whether it will set in or not; whilst the amount of chemical energy transferred in such a reaction is given by the product of the affinity of the reaction and the quantity of matter which has been transformed.

Similarly, electrical energy has its intensity factor, **potential difference** (E), and its quantity factor, **quantity of electricity.** The former determines the direction of transference of electrical energy, the product of the two quantities determines the magnitude of the change.

From these fundamental conceptions we can directly pass on to others. When the energy content of a system is increasing or decreasing (*i.e.* when work is being done on or by the system), the change of energy per unit time (the rate of consumption or production of work) is termed the **power.** In the same way, when a transference of electricity takes place across a certain point, the quantity which passes per unit of time is termed the **current**[1] (I). Finally, the rate at which electricity can pass between two points at different electrical potentials is directly proportional to the magnitude of this potential difference, and also depends on the nature of the path along which the current travels.

The relation may be expressed in the form

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

where R is called the **resistance** of the conductor (Ohm's Law). If the resistance be great, the current passing for a given difference of potential will be small, and *vice versâ.*

In deciding on the units[2] to serve for the measurement of these

---

[1] The current flowing across any point, divided by the area of the conductor at that point at right angles to the direction of the current, is called the **current density.**

[2] The units here defined were specified by the International Conference on Electrical Units and Standards, 1908. They are known as the *international* units. Ohms and volts of slightly lesser magnitude were used some years back, but need no further mention here.

magnitudes, it has been found most convenient to define first the units of resistance and current, and to deduce from these the units of potential, energy, power and quantity of electricity. The first primary unit is that of resistance, the **ohm,** which is defined as the resistance offered to an unvarying electric current by a column of mercury at the temperature of melting ice, the column to be 14·4521 grams in weight, of a constant cross-sectional area, and of a length of 106·300 cm. The second primary unit is that of current, the **ampere.** As we shall see later,[1] when electricity is passed through a solution of a metallic salt in water, the salt is decomposed, and in many cases the metal is deposited in the free state. It has been found that the phenomenon is a quantitative one, and the ampere is defined as the unvarying electric current, which, when passed through a solution of $AgNO_3$ in water, deposits silver at the rate of 0·00111800 gram per second. It is specified[2] that the $AgNO_3$ solution shall contain 15–20 grams salt to 100 grams distilled water. The solution must only be used once, not less than 100 c.c. at a time, and not more than 30 per cent. of the metal must be deposited. The current density must not exceed 0·02 amp./$cm.^2$ at the cathode,[3] and 0·2 amp./$cm.^2$ at the anode.[3]

From this follows directly the definition of the unit quantity of electricity—the **coulomb**—as that quantity of electricity which, when passed through a solution of silver nitrate, will deposit 0·00111800 gram of silver.

The unit of potential difference or electrical pressure is the **volt,** defined as that potential difference or voltage which, when steadily applied to a conductor whose resistance is one ohm, will produce a current of one ampere.[4]

The unit of power is the **watt,** and is defined as the rate at which energy is expended by an unvarying electric current of one ampere, flowing under an electric pressure of one volt. Finally, the unit of electrical energy, the watt-second or **joule,** is defined as the energy expended in one second by an unvarying electric current of one ampere flowing under an electric pressure of one volt. For technical uses, the power and energy units are inconveniently small, and others have been introduced. Of power units we have the **kilowatt** (K.W.), which is 1,000 watts, and the **horse-power** (H.P.), which is 746 watts.[5] Corresponding to these are the energy units, **kilowatt-hour**[6] (K.W.H.) and

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[1] P. 26. [2] Cf. also p. 32. [3] *Loc. cit.*

[4] For purposes of voltage comparison, certain *standard cells*, furnishing accurately known and constant potential differences, can be conveniently employed. The best known is the Weston normal element with a potential of 1·0184 volts at 20°. (See p. 91.) The potential difference given at the terminals of a primary cell (such as the Weston element) is known as the **electro-motive force** (E.M.F.) of the cell.

[5] The horse-power in use in Germany is 736 watts.

[6] The Board of Trade unit (B.T.U.).

horse-power-hour (H.P.H.), which represent the energy consumption per hour of systems absorbing energy at the respective rates of one kilowatt and one horse-power.

In the course of this book we shall have to consider the quantitative relations existing between electrical energy on the one hand and heat energy on the other. These relations are expressed by the equations :—

1 joule = 0·23865 gram-calorie (units of heat energy, written *cal.*).

1 kilo-joule (K.W.~~H~~S.) = 0·23865 kilogram-calorie (written *Cal.*),

and inversely :—

1 cal. = 4·189 joules.
1 Cal. = 4·189 K.W.~~H~~S. = kilowatt seconds

A few simple calculations are here appended.

1. A current is kept flowing along a wire of 160 ohms resistance by means of a constant potential difference of 20 volts. The whole of the electrical energy consumed is turned into heat by the wire. What is the power used, and how many gram-calories are produced per hour?

$$I = \frac{E}{R} = \frac{20}{160} = 0{\cdot}125 \text{ amp.}$$

$$\begin{aligned}
\text{Power used} &= 0{\cdot}125 \times 20 \text{ watts} \\
&= 2{\cdot}5 \text{ watts.} \\
\text{Joules used} &= 2{\cdot}5 \text{ per second} \\
&= 2{\cdot}5 \times 3{,}600 \text{ per hour.} \\
\text{Calories produced per hour} &= \frac{2{\cdot}5 \times 3{,}600}{4{\cdot}189} = 2{,}148 \text{ cals.}
\end{aligned}$$

2. A small alkali-chlorine plant is driven by means of three dissimilar dynamos. The first—400 H.P.—gives 4,000 amperes at full load, the smaller ones give 15 K.W. at 15 volts and 80 H.P. at 60 volts respectively. The alkali-chlorine cells number thirty. Each takes 2,500 amperes at 5 volts, including all leads and connections. How must dynamos and cells be arranged?

Assuming 1 H.P. = 750 watts, which is accurate enough for the present purpose, we calculate that the dynamos give respectively :—

$$\begin{aligned}
(a)\quad 400 \times 750 &= 300{,}000 \text{ watts} \\
&= 4{,}000 \text{ amperes at 75 volts.} \\
(b)\quad 15 \times 1{,}000 &= 15{,}000 \text{ watts} \\
&= 1{,}000 \text{ amperes at 15 volts.} \\
(c)\quad 80 \times 750 &= 60{,}000 \text{ watts} \\
&= 1{,}000 \text{ amperes at 60 volts.}
\end{aligned}$$

If (*b*) and (*c*) are run in series, they will yield 1,000 amperes at 75 volts. But this is the voltage of (*a*), and hence the combination of (*b*) and (*c*) can be run in parallel with (*a*), the whole yielding 4,000 + 1,000 = 5,000 amperes at 75 volts. If the cells were all run in series, they would need 2,500 amperes at 5 × 30 = 150 volts. To adjust them to the dynamo conditions, they must be run in two parallel series of fifteen cells. Each branch then requires 2,500 amperes at 75 volts, or altogether 5,000 amperes at 75 volts, which is what the dynamos can supply.

3. An electric-steel induction furnace consumes 170 K.W. and produces 4·7 tons of steel per day by melting up together a mixture of scrap wrought-iron and washed pig-iron. The heat content of the melted product is 350 Cals. per kilo.

What is the electrical energy required per ton of steel produced? What is the thermal efficiency of the furnace? If one-third of the material used were added molten, already containing 275 Cals. per kilo., what would be the production per day, and the power required per ton of product?[1]

(*a*) Energy used per ton of steel

$$= \frac{170 \times 24}{4{\cdot}7} = 870 \text{ K.W.H.}$$

(*b*) Heat equivalent of electrical energy consumed in furnace per ton of product

$$= 0{\cdot}239 \times 60 \times 60 \times 870 \text{ Cals.}$$

Heat content per ton of product

$$= 1{,}000 \times 350 \text{ Cals.}$$

Thermal efficiency of furnace

$$= \frac{1{,}000 \times 350}{0{\cdot}239 \times 60 \times 60 \times 870}$$

$$= 47 \text{ per cent.}$$

(*c*) Heat supplied with starting material

$$= 275 \times \frac{1}{3} \text{ Cals. per kilo.}$$

$$= 92 \text{ Cals. per kilo.}$$

The current must therefore supply

$$350 - 92 = 258 \text{ Cals. per kilo.}$$

Production per day under these conditions:

$$= \frac{350}{258} \times 4{\cdot}7 = 6{\cdot}4 \text{ tons.}$$

Electrical energy required per ton

$$= \frac{170 \times 24}{6{\cdot}4} = 640 \text{ K.W.H.}$$

3. Power

General.—The question of power costs bulks largely in all technical electrochemical processes with few exceptions. Such, is for example, the electrochemical refining of the noble metals, where interest charges on the silver or gold under treatment are of more importance. To a lesser extent, this also applies to the refining of copper, where a very large quantity of a valuable product is obtained with a low energy expenditure. But in most processes the value of the product and the cost of the necessary energy are of the same order, and power questions become of vital importance.

It is difficult to draw definite conclusions which can be applied to our present purpose from most of the statements made in journals and articles on the cost of power-raising by different systems. In considering the matter, we must keep several points clearly in view. The first is the very high value of the *load-factor* of power used in electrochemical industries. The load-factor is defined as the ratio of the average power consumption to the maximum power consumption needed

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[1] J. W. Richards, *Electrochem. Ind.*, **5**, 168 (*1907*).

at any time. In many cases—for example, municipal electric light and power undertakings—it is 10–20 per cent., and rarely exceeds 50 per cent. But for electrochemical purposes it is generally[1] very high—about 90–95 per cent. A high load-factor means a cheaper supply, and power for electrochemical processes can thus be got on comparatively advantageous terms. Then many of the available estimates on power-production are vague as to what they really include. The running costs of a power plant, besides fuel, include charges for repairs and sundries, labour and management, which must all be brought into an estimate of any value. But there are also the capital charges for interest and depreciation of plant, including spare machines. These can be very different in different systems of power-production, and all must be taken into account when making an estimate, comparative or otherwise. Further, the charges of the different power companies are of little use in making comparisons. These companies must make their profits, which vary considerably; the published figures often include transmission charges over a long distance, and, unless otherwise explicitly stated, generally hold for power of low load-factor used intermittently for lighting or driving small machines. It is futile, as has been done, to compare the charges of a power company at £15–£25 per H.P. year with the costs of a water-power installation in the Alps or Scandinavia at 10*s.* to 20*s.* per H.P. year, and then to conclude that electrochemical industries have no future in this country because of the scarcity of suitable water-power.

Three systems of power-production must be briefly considered:—

1. Water-driven turbines.
2. Steam turbines or engines.
3. Internal-combustion engines consuming gas (and occasionally oil).

Water-power.—The cost of water-power can vary enormously, according to local circumstances and the engineering difficulties to be overcome. The price is mainly decided by the initial capital costs, the maintenance charges being comparatively low. These capital costs vary between £3 and £30 per H.P. installed, and probably average about £10. If interest and depreciation be taken as 15 per cent., the average capital charges will be £1 10*s.* per H.P. year.[2] Putting working charges at 15*s.* per H.P. year, the average total cost of water-power will come to £2 5*s.* per H.P. year (0·082*d.* per K.W.H.). Under exceptionally favourable circumstances its cost is far lower, as the following figures show:—

Svaelgfos, Norway, 8*s.* 3*d.* per H.P. year.
Notodden, Norway, 13*s.* 7*d.* per H.P. year.
Chedde, Savoy, 18*s.* 4*d.* per H.P. year.

But as a rule the figures will fall between £2–£4 per H.P. year. At

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[1] Not in certain electrothermal processes.

[2] A year is taken as 365 × 24 = 8,760 hours.

Niagara, power is supplied by the different companies to large consumers at prices between £2 2*s*. 6*d*. and £4 3*s*. per H.P. year.

Steam-power can be generated using ordinary reciprocating steam engines or else steam turbines. Both have approximately the same low thermodynamic efficiency, only converting 0·1–0·15 of the heat value of the fuel into mechanical energy. This fraction can occasionally rise to 0·18.

The capital cost of an installation of not less than 1,000 H.P. will average about £12 per H.P. Fuel and other running expenses vary considerably, according to local conditions. It is, however, fairly safe to say that the total power costs in this country will work out at £5–£8 per H.P. year (0·18*d*.–0·29*d*. per K.W.H.), and under very favourable conditions may fall still lower. The prices *charged* by English power companies for power of high load-factor vary between £9 10*s*. and £20 per H.P. year, though better terms can doubtless be obtained by large and regular consumers. When prices reach £10–£12 per H.P. year, they approach the uneconomic limit for most electrochemical industries.

Gas-power.—Gas engines are coming more and more into use at the present time for power-raising, due partly to the considerable improvements effected in them during the last few years. Their initial cost is greater than steam plant, as are also their running expenses other than fuel, but on the other hand their efficiency is from 50–100 per cent. higher, varying between 0·2–0·25, and indeed can often be still greater with engines of large size. The formation of producer gas from coal is a much more efficient process than the generation of steam in a boiler. Where blast-furnace or coke-oven gases are available as fuel, their advantages over steam plant are correspondingly increased.

The initial cost of a gas plant of fair dimensions (3,000 H.P. or more) will be about £15 per H.P. installed, including producers, etc. Assuming fuel to cost 9*s*. to 10*s*. per ton, and that an ammonia-recovery plant is operated, the total cost per H.P. year will come to £3 to £3 10*s*. (0·11*d*.–0·13*d*. per unit), of which some 40 per cent. is accounted for by capital charges, the remainder being about equally divided between fuel and other running expenses.

Comparative.—The above data would indicate that a gas-power plant without doubt works more cheaply than a steam plant. Nevertheless there is still a great deal of controversy on the point. The truth seems to be that for small installations of 1,000 H.P. or thereabouts, where ammonia recovery hardly pays, a steam plant with its lower first cost is the more economical, whereas the reverse statement holds good for plants of larger capacity. A gas plant should have a steady continuous load. A low load-factor is a point strongly in favour of steam power. Another deciding circumstance in favour of a steam plant may be the demand for waste steam, with its manifold applications in chemical works. Finally, steam plant still has a better name for proved reliability. The tendency to scrap steam engines in favour of gas engines is nevertheless a marked one at present.

If we further compare the figures for gas and water power we see that, except in certain exceptional cases, there is very little difference. Many water-powers actually *generate* their energy at a cost exceeding £3 per H.P. year, and, where large power companies are in possession, the price for electrochemical purposes can rise still higher. This disposes of the ancient argument that water-power is essential to the success of most electrochemical industries. When to that are added the facts that in Great Britain coal is cheap and markets are near, whilst many raw materials are readily available, we see on the contrary that this country offers exceptional facilities for electrochemical enterprise.

Literature

(*Power.*) Pring. *Some Electrochemical Centres.*

CHAPTER II

EQUILIBRIUM

1. General

ALTHOUGH for practical purposes chemical reactions are often divided into two classes—'reversible' and 'irreversible'[1]—no such distinction strictly exists. At room temperature hydrogen and chlorine combine practically completely, giving HCl, and HCl will of itself furnish no appreciable quantities of hydrogen and chlorine. Hence this reaction is stated to be 'irreversible.' But in reality it is just as much reversible as is the reaction

$$CH_3COOH + C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + H_2O.$$

Minute traces of hydrogen and chlorine do undoubtedly exist in the free state after the great bulk has combined, giving HCl. The difference between the two reactions is only one of *degree*, not one of *kind*.

Every chemical system, left to itself, will finally arrive at a state of **equilibrium,** when all the component substances, whether originally present or formed during the reaction, will coexist in quantities depending on the temperature and pressure of the system as well as on the amounts of the original substances taken. If the reaction is to proceed further, one or other of the products must be removed, thus disturbing the equilibrium. In the desulphurisation of steel,[2] the sulphur is converted into a form (CaS) which is insoluble in the reacting system. In the dehydration of $ZnCl_2$ melts;[3] the water is blown off by continually renewing the HCl atmosphere.

The reasons owing to which this equilibrium is often not clearly manifest are (1) the exceedingly small equilibrium concentrations of some of the substances; and (2) considerable *reaction resistances* which often prevent the equilibrium setting in.

This second point is very important. Thus, although the equilibrium state of a system is defined by the *constancy of composition* of the system over an unlimited length of time, yet constancy of composition alone

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[1] Not to be confounded with the perfectly definite conceptions of reversible and irreversible processes discussed in Chapter VII.

[2] P. 443.

[3] P. 422.

must not be taken as a criterion of the equilibrium state. Thus a H_2-O_2 mixture is apparently perfectly stable at room temperature; nevertheless it is in reality very far removed from its equilibrium state, at which minute traces of the gases exist in presence of a large excess of water-vapour. To be certain that a system is in a state of equilibrium, it must be possible to reach that state from both sides—commencing therefore with an excess of either set of the reacting substances. Thus if equimolecular quantities of C_2H_5OH and $CH_3 . COOH$ react, producing $CH_3 . COOC_2H_5$ and water, we know that the equilibrium state is reached when two-thirds of the alcohol and acid have been transformed into ester and water. And we know this to be true because, starting with $CH_3 . COOC_2H_5$ and water, CH_3COOH and C_2H_5OH are formed, and if equimolecular quantities are taken the reaction ceases when only *one-third* has been converted to acid and alcohol, two-thirds remaining unchanged. But the system has now the same composition as when alcohol and acid were originally taken, and hence is at equilibrium.

Catalysts.—These reaction resistances are often so great that they practically inhibit the commencement of reactions which would otherwise occur. A substance whose addition in such cases renders the progress of the reaction measurable, or in other cases increases the velocity with which equilibrium is reached, is termed a **catalyst.** Well-known technical catalysts are the platinum used in the SO_3 contact process, the copper salts used in the Deacon chlorine process, the sulphur and $HgSO_4$ used respectively in the chlorination and sulphonation of certain organic compounds, etc. We shall encounter many cases in this book (*e.g.* in graphitisation,[1] azotisation of CaC_2,[2] electrical oxidation,[3] etc., etc.).

The mechanism by which these catalysts act is often, as we shall see, quite unexplained. One point however must be emphasised, *i.e.* that the catalyst does not affect the final equilibrium state, but only the *velocity* with which that state is reached. A system in equilibrium can usually be regarded as in a stationary state, defined by *the equality of the velocities of two opposed reactions.* Thus, in the above example, the velocity at equilibrium of interaction between acid and alcohol giving ester and water is equal to the velocity of interaction of ester and water giving acid and alcohol. If now the velocity of one of these reactions be increased more than the velocity of the opposing reaction, it is clear that the system will no longer remain in equilibrium. It follows that a catalyst must increase the velocity of the two opposing reactions concerned to the same extent.

We will now consider the conditions of equilibrium in different types of constant temperature systems. As a first classification we can divide these into *homogeneous* and *heterogeneous* systems. A homo-

[1] P. 493. [2] P. 482. [3] P. 146.

geneous system is, both chemically and physically, of the same composition in all parts; *e.g.* a pure crystalline substance, or an aqueous solution, or a space filled with gas or vapour. A heterogeneous system can vary in chemical or physical composition in different parts, *e.g.* a saturated aqueous solution in contact with undissolved solid.

2. Homogeneous Equilibria

In a homogeneous system the conditions of equilibrium at constant temperature are essentially determined by the **Law of Mass Action.** Suppose the equilibrium point of the following reaction be considered :—

$$n_1A_1 + n_2A_2 + \text{etc.} \;.\;.\;.\; \rightleftarrows n_1'A_1' + n_2'A_2' + \text{etc.}$$

where A_1, A_2, A_1', A_2', etc., represent the different kinds of molecules involved, n_1, n_2, n_1', n_2', etc., denote the respective numbers of the same taking part in the reaction,[1] and $[C_1]$ $[C_2]$ $[C_1']$ $[C_2']$ the *molecular concentrations* or *gram-mols. per unit volume* of the different substances.[2] Then the following equation holds[3] :—

$$\frac{[C_1']^{n_1'} \,.\, [C_2']^{n_2'} \,.\,.\,.\,.\,.}{[C_1]^{n_1} \,.\, [C_2]^{n_2} \,.\,.\,.\,.\,.} = K$$

where K, a constant for any particular equilibrium at a particular temperature, is termed the *equilibrium constant* of the reaction at that temperature. We see that K is great if $[C_1']$ $[C_2']$, etc., are great compared with $[C_1]$ $[C_2]$, etc., and that therefore a high value of K corresponds to the reaction going more or less completely from left to right. If therefore K be known, and if in the equilibrium reaction mixture all but one of the values $[C_1]$ $[C_2]$ $[C_1']$ $[C_2']$, etc., can be directly determined, the remaining one can be calculated. And whatever the proportions of the different substances in the initial reaction mixture, they will finally adjust themselves so as to satisfy the above equation.

We will discuss numerically two simple examples.

The reaction

$$CH_3 \,.\, COOH + C_2H_5 \,.\, OH \rightleftarrows CH_3 \,.\, COOC_2H_5 + H_2O$$

was investigated by Berthelot and St. Gilles.[4] They started with acid and alcohol, water and ester being absent. Suppose that n mols. of alcohol were added at the start to one mol. of acid, the whole occupying a volume v. At equilibrium suppose x mols. each of water and ester

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[1] With $2H_2 + O_2 \rightleftarrows 2H_2O$, we have $n_1 = 2$, $n_2 = 1$, $n_1' = 2$. With $2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$, we have $n_1 = 2$, $n_2 = 10$, $n_3 = 8$, $n_1' = 1$, $n_2' = 2$, $n_3' = 5$, $n_4' = 8$.

[2] Thus with two $\frac{\text{grams}}{\text{litre}}$ of hydrogen $[C] = 1$; with 4·8 grams ozone per 100 litres $[C] = 0{\cdot}001$; with 20 grams KCl per 350 c.c. $[C] = \frac{20}{74{\cdot}6} \times \frac{1{,}000}{350} = 0{\cdot}766$.

[3] This result must be assumed.

[4] *Ann, Chim. Phys.* [3] **65**, 385 (*1862*), **66**, 5 (*1862*), **68**, 225 (*1863*).

to be present. Then $1-x$ and $n-x$ represent the quantities of acid and alcohol respectively present. We have:—

$$K = \frac{\frac{x}{v}\cdot\frac{x}{v}}{\frac{1-x}{v}\cdot\frac{n-x}{v}} = \frac{x^2}{(1-x)(n-x)}$$

K being independent of the volume.

The following experimental results were obtained:—

n	x	K
0·18	0·171	3·9
0·33	0·293	3·3
0·50	0·414	3·4
1·00	0·667	4·0
2·00	0·858	4·5
8·00	0·966	3·9

With the ratio $\frac{[\text{acid}]}{[\text{alcohol}]}$ varying initially between 6 : 1 and 1 : 8, the final state of the system was throughout determined by the above equation, in which K is about 3·8–3·9. With more refined experimental methods, the agreement would doubtless have been more exact.

The equilibrium

$$2SO_3 \rightleftarrows 2SO_2 + O_2,$$

of fundamental importance in the SO_3 'contact' process, was investigated by Bodenstein and Pohl. They led different mixtures of SO_2 and oxygen or SO_2 and air over platinum black at definite temperatures, when partial conversion to SO_3 took place. The gases issuing from the reaction chamber were rapidly drawn off, cooled, and analysed. That equilibrium was established was proved by starting with SO_3 and measuring the extent of dissociation into SO_2 and O_2. We can write

$$K = \frac{[C]^2_{SO_2}\cdot[C]_{O_2}}{[C]^2_{SO_3}}$$

The results of Table I. are for experiments at 727° C. (1,000° abs.).

TABLE I

T°	p in mm. of mercury	$SO_2 : O_2 : N_2$	%	$SO_2 : SO_3 : O_2$	K . 10^3
1003	770	0·42 : 1 : 0	59·6	0·132 : 0·195 : 0·673	3·49
1000	760	1·24 : 1 : 0	52·2	0·309 : 0·338 : 0·353	3·59
1000	765	2·44 : 1 : 0	42·3	0·481 : 0·355 : 0·164	3·67
1000	758	3·36 : 1 : 0	37·1	0·566 : 0·333 : 0·101	3·52
1001	760	7·94 : 1 : 0	20·8	0·775 : 0·203 : 0·22	3·67
997	764	2·46 : 1 : 3·76	35·8	0·233 : 0·130 : 0·182	3·58
1001	760	3·10 : 1 : 3·76	32·3	0·283 : 0·136 : 0·68	3·52
1000	758	1·06 (as SO_3) : 1 : 0	54·4	0·273 : 0·325 : 0·402	3·43

The various columns contain respectively (1) temperature ; (2) total pressure ; (3) composition of reaction mixture (in the last experiment SO_3 was used instead of SO_2) ; (4) percentage of original SO_2 (SO_3) present as SO_3 in equilibrium mixture ; (5) fractional concentration of equilibrium mixture ; (6) equilibrium constant, referred to 1000° abs., and, when necessary, corrected for slight temperature differences.

K is calculated as follows, the concentrations being expressed in $\frac{\text{mols.}}{\text{litre}}$ [C]. At 0° C. and 760 mm. of mercury, one mol. of any gas occupies 22·42 litres. At higher temperatures the volume is correspondingly greater. If the fractional concentrations in column 5 be denoted by *c*, we have

$$[C] = c \cdot \frac{p}{760} \cdot \frac{273}{T} \cdot \frac{1}{22{\cdot}42},$$

and

$$K = \frac{c^2_{SO_2} \cdot c_{O_2}}{c^2_{SO_3}} \cdot \frac{p}{760} \cdot \frac{273}{T} \cdot \frac{1}{22{\cdot}42}$$

Thus in the second case

$$K = \frac{(0{\cdot}309)^2 \,.\, (0{\cdot}353)}{(0{\cdot}338)^2} \cdot \frac{760}{760} \cdot \frac{273}{1{,}000} \cdot \frac{1}{22{\cdot}42}$$

The agreement between the different experiments is excellent.

3. Heterogeneous Equilibria

Phases.—A heterogeneous system is characterised by the presence of two or more homogeneous systems in contact and separated by definite limiting surfaces. The number of distinct kinds of homogeneous systems, differing either chemically or merely physically from one another, which build up a heterogeneous system, is called the number of **phases** of the system, and each of the distinct kinds of component homogeneous systems is called a phase. It will be seen that the ideas of size and shape have no part in the conception of a phase. Thus an aqueous Ag_2SO_4 solution is a single phase. If contained in an enclosed space together with some air, this air will become saturated with aqueous vapour at the pressure of the Ag_2SO_4 solution. Being homogeneous in all parts, it will constitute a second phase. Similarly a $BaCl_2$ solution is a separate phase. If the two solutions be mixed, we shall get a precipitate containing AgCl and $BaSO_4$. Each of these salts will constitute a separate solid phase, and the homogeneous mother liquor will form a third, liquid, phase.

When a heterogeneous system is in equilibrium, each separate phase, taken separately, is in equilibrium internally, and further all the phases are in equilibrium with one another. Equilibrium in a heterogeneous system is therefore characterised by the superposition of a number of homogeneous equilibrium systems, and to each of the latter, when capable of a variation in composition, the law of mass action is applicable. But the state of equilibrium in the whole heterogeneous system is *independent of the relative masses or sizes, etc.*, of the different phases.

For instance, suppose equilibrium established in a system where ZnS has been precipitated from a $ZnCl_2$ solution by H_2S. The number of phases is three—solid ZnS, liquid solution, and gas. The mass action law can be applied to the liquid phase, in which $ZnCl_2$, ZnS, HCl, and H_2S are in equilibrium. Further, all three phases are in equilibrium with one another—the liquid phase is in equilibrium with the precipitate and with the H_2S in the gas phase. But it makes no difference to the composition of the liquid phase if the actual mass of the ZnS or gas or solution is altered. If the amount of precipitate be doubled, or if the greater part of the gas phase be cut off from the rest of the system, the composition of the solution will remain unaltered.

The classification of heterogeneous equilibria is most easily done by means of the **Phase Rule.** An adequate treatment of this subject is here impossible, and readers are referred to Professor Findlay's *The Phase Rule.* For our purpose we can conveniently divide constant temperature heterogeneous equilibria into three classes.

(*a*) No single phase can vary in concentration.
(*b*) One phase only is capable of such variation.
(*c*) Two or more phases can thus vary.

Of class (*a*) we have many instances. For example, a liquid in contact with its saturated vapour. At a definite temperature, the pressure of the vapour phase is fixed, and no variation is possible except by altering the temperature. A similar example is a saturated solution in contact with excess of solid solute. At a given temperature the concentration of the solution is constant—the solubility has a definite value. Another instance is a solid in contact with its vapour phase at the sublimation pressure (*e.g.* iodine), or the very similar case of a polymerised solid in equilibrium with a gaseous phase consisting of simpler molecules. As an example may be taken the case of solid paracyanogen in equilibrium with gaseous cyanogen :—

$$(C_2N_2)_x \rightleftarrows x\, C_2N_2$$

At any given temperature the cyanogen gas pressure is constant, and is known as the *dissociation pressure* at that temperature.

Of another type of dissociation a good example is

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

Here two solid phases are in equilibrium with one gaseous phase, and once more at constant temperature the pressure is fixed, and incapable of alteration except by upsetting the equilibrium. That this in fact must be so can be shown as follows. Consider the state of equilibrium in the single homogeneous gaseous phase. In accordance with the law of mass action we can write for any temperature

$$K = \frac{[CaO] \, . \, [CO_2]}{[CaCO_3]},$$

where $[CaO]$ and $[CaCO_3]$ represent the very low molar concentrations of CaO and $CaCO_3$ in the gaseous phase. Now these low concentrations have a perfectly definite meaning. They are the *sublimation pressures* of lime and calcite, and of course constant at constant temperature. We can therefore replace $\frac{[CaO]}{[CaCO_3]}$ by k, and get

$$[CO_2] = \frac{K}{k}.$$

That is, the dissociation pressure of $CaCO_3$ is constant at constant temperature.

The fact that in such equilibrium equations as the above, the concentrations of the solid phases taking part can be considered as constant, is generally expressed by saying that the *active mass* of a solid which is taking part in a reaction is constant. This excludes the case of *solid solutions*.[1] This generalisation enables us to treat more complex cases of equilibria between solid phases and gaseous phase, the stipulation being that only one gas is involved in the reaction.

For example we can take the equilibria [2]

$$SiO_2 + 2C \rightleftarrows Si + 2CO \quad (1)$$
$$CaO + 3C \rightleftarrows CaC_2 + CO \quad (2)$$

As in both cases all the constituents but the CO are solids, we can write

$$K_1 = k_1 \, [CO]^2$$
$$K_2 = k_2 \, [CO],$$

the CO equilibrium pressures being therefore definitely fixed if the temperature be fixed. Thus Rothmund found for the second case p_{CO} at 1620° to be one-third of an atmosphere. If, by pumping off, the pressure be artificially kept below this figure, lime and carbon will react, giving carbide and CO until all are used up. If, on the other hand, CO gas be pumped in, and the pressure thus kept above the equilibrium figure, the reaction will proceed from right to left, CO being absorbed. At higher temperatures the equilibrium pressure

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[1] A solid solution is a solid phase containing two or more constituents whose composition can be *continuously* varied within certain limits. There are no boundary surfaces of supermolecular dimensions separating its different constituents: the intermixture is molecular just as in liquid solutions. Many of the commonest alloys are solid solutions (*e.g.* steels, brasses, Cu-Ag mixtures). We shall meet several examples in this book: *e.g.* pp. 121, 133, 136–139, 241, 492, etc.

[2] Pp. 469, 487.

is higher, at lower temperatures lower. If therefore the pressure be artificially kept constant at one-third of an atmosphere, and the temperature raised above 1620°, the lime and carbon will disappear and carbide will be formed. But if the temperature be lowered below 1620°, the pressure being still kept at the same figure, all the carbide will disappear; or if lime and carbon be present, no carbide will result. By a similar variation of conditions, silicon can be oxidised by CO with deposition of carbon; or silica can be reduced by carbon with evolution of CO.

We now come to the second type of heterogeneous equilibrium, where one of the phases can vary in concentration, the temperature remaining constant. If NH_4HS be gently heated, it dissociates thus:

$$NH_4HS \rightleftarrows NH_3 + H_2S,$$

giving a mixture of two gaseous dissociation products. Using pure NH_4HS, the composition of the gaseous phase is constant, always 50 per cent. H_2S : 50 per cent. NH_3. Hence at a definite temperature there will be a perfectly definite dissociation pressure—in fact the system will behave like those just discussed. But if an excess of one of the dissociation products—NH_3 or H_2S—be added, a new equilibrium state will set in, in which the composition of the gaseous phase will be different from what it was previously, whilst the solid phase will still be NH_4HS. Consider the equilibrium in the gaseous phase. We have

$$K = \frac{[H_2S] \cdot [NH_3]}{[NH_4HS]}.$$

NH_4HS being a solid, we can put $[NH_4HS]$ = constant. For ordinary purposes of calculation $[H_2S] \cdot [NH_3]$ can be replaced by $k \cdot p_{H_2S} \cdot p_{NH_3}$, and we thus get

$$K_1 = p_{NH_3} \cdot p_{H_2S}$$

i.e. the product of the partial pressures of the two dissociation products must be a constant at any given temperature. Isambert[1] made measurements at 25·1° and obtained the following results (pressures in cm. of mercury), which show a sufficiently good agreement between the values of K_1 :—

p_{NH_3}	p_{H_2S}	K_1
13·8	45·8	632
20·9	29·5	617
20·8	29·4	612
25·05	25·05	627
41·7	14·6	609
45·3	14·3	648
45·8	13·8	632

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[1] *Compt. Rend.* **92**, 919 (*1881*); **93**, 731 (*1881*); **94**, 958 (*1882*).

The mean value for K_1 is 626. Suppose then that solid NH_4HS dissociates at 25° into an atmosphere of H_2S kept at a constant partial pressure of 60 cm., the partial pressure of the NH_3 gas will be $\frac{626}{60} = 10 \cdot 4$ cm.

The solubility product of difficultly soluble salts, discussed on p. 73, is a very similar example to the above.

As another instance we may take the reaction

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2.$$

When steam acts on an excess of heated iron, Fe_3O_4 and hydrogen are formed, and finally an equilibrium state is reached with both hydrogen and steam present in the gas phase. Conversely, when hydrogen acts on an excess of heated Fe_3O_4, the metal and steam are produced, and an equilibrium state is eventually reached. The iron and the oxide, being solids of constant active mass, play no part in the gaseous equilibrium; and we get

$$K_1 = \frac{[H_2]^4}{[H_2O]^4}$$

or, as partial pressures can be substituted for concentrations,

$$\frac{p_{H_2}}{p_{H_2O}} = \text{constant.}$$

Preuner obtained the following results at 900° :—

p_{H_2}	p_{H_2O}	k
13·5 mm.	8·8 mm.	1·53
18·0	12·7	1·42
37·4	25·1	1·49
54·1	35·4	1·53
71·8	49·3	1·46

If therefore steam at any pressure be kept in contact with heated iron at 900°, it will be decomposed until the pressure of the hydrogen formed is 1·5 times the pressure of the steam remaining. If the original pressure of the steam be 750 mm., the pressure in the final equilibrium mixture will be hydrogen 450 mm. : steam 300 mm; whilst if hydrogen gas be heated with Fe_3O_4 at 900°, steam will be formed, the reaction ceasing when $\frac{p_{H_2}}{p_{H_2O}} = 1 \cdot 5$. If the original hydrogen pressure is 300 mm., the final pressures will be H_2 180 mm. : H_2O 120 mm.

In the last type of heterogeneous equilibrium which we shall discuss, two or more phases can vary in concentration at constant temperature.

Simple examples are an unsaturated aqueous solution and the corresponding aqueous vapour phase, or a solution of a gas in a liquid and the gaseous phase in equilibrium with that solution. In the former case, the concentration of dissolved substance in the solution can vary between zero and the saturation quantity, whilst, since the vapour pressure of the water is lowered by the solution in it of the dissolved substance, the concentration of the vapour phase can vary between the limits of the pressure of pure water and the pressure of the saturated solution. Similarly the gas pressure in the second case can be arbitrarily varied within certain limits, and to each pressure corresponds a definite solubility of gas in the liquid.

Any equilibria in the separate phases can be treated by the law of mass action, and we need here only consider the equilibria between the different phases. The law governing these equilibria is very simple. Neglecting complications arising when the molecules of a substance are of different complexity in different phases of the system, it can be stated as follows: *At constant temperature, the ratio of the molecular concentration of a substance in one phase to its molecular concentration in another phase is constant.* If $[C_1]$ and $[C_2]$ are the equilibrium concentrations in the two phases,

$$\frac{[C_1]}{[C_2]} = K.$$

(This constant ratio is of course different for every pair of phases.)

We will illustrate the above law by a few examples. Consider a gas in equilibrium with its solution in a liquid. For $[C_2]$, the concentration in the gaseous phase, we can substitute p, the pressure, or partial pressure, if present in a gaseous mixture. The result (known as Henry's Law) is that the solubility of a gas in a liquid is proportional to the pressure of the gas.

On p. 344 is given an instance involving the solubility of chlorine in water at different partial pressures. On p. 519 is considered the equilibrium

$$3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO,$$

which tends to set up when nitrous gases are passed into water. The concentration of HNO_3 in the liquid phase is of course directly determined (according to the mass action law) by the concentrations of NO_2 and NO in the liquid phase; and as the latter are proportional to their concentrations in the gas phase, it follows that the HNO_3 concentration will *increase* with *increasing* NO_2 and *decreasing* NO partial pressures.

Succinic acid dissolves in both water and ether. If therefore an aqueous solution be shaken up with ether, or an ethereal solution with water, some of the acid will pass from one solvent to the other until equilibrium is reached. In accordance with the equation, whatever the absolute concentration of the acid in the two liquids, their ratio will always be constant when equilibrium has been reached. The following table contains some experimental figures :—

C_1 = grams acid per 10 c.c. water.	C_2 = grams acid per 10 c.c. ether.	$K = \frac{C_1}{C_2}$
0·024	0·0046	5·2
0·070	0·013	5·4
0·121	0·022	5·4

K is termed the *partition coefficient* of succinic acid between water and ether.

On p. 443 we have a somewhat similar case, involving the distribution of sulphur between liquid steel and liquid slag in a steel-refining furnace. But the qualification caused by the presence of different molecular complexes (here chemically different molecules) in the different phases becomes very important. The law is only qualitatively, not quantitatively, followed. This is to a certain extent true of most ‘ practical ’ cases.

As a last example, consider an aqueous solution containing n' mols. of solute dissolved in n mols. of solvent. Let the vapour pressures of pure solvent and of solution be respectively p_0 and p. If the molecular concentration $\left(\frac{\text{mols.}}{\text{litre}}\right)$ of the solvent when in the pure state be [C], its molecular concentration in the solution will be $\frac{n}{n'+n}$ [C]. Applying the law, we have

$$\frac{p_0}{[C]} = K_1 \text{ and } \frac{p}{\frac{n}{n'+n}\cdot[C]} = K_1.$$

Hence

$$\frac{p}{p_0} = \frac{n}{n'+n}$$

$$1 - \frac{p}{p_0} = 1 - \frac{n}{n'+n}$$

$$\frac{p_0 - p}{p_0} = \frac{n'}{n'+n}.$$

For a dilute solution n' is small compared with n, and we can write

$$\frac{p_0 - p}{p_0} = \frac{n'}{n}.$$

That is, the ratio of the difference of vapour pressures of solution and solvent (the ‘lowering’ of the vapour pressure) to the vapour pressure of the pure solvent is equal to the ratio of the number of molecules of solute present to the number of molecules of solvent in which the solute is dissolved. This is an exceedingly important result, which we shall employ in Chapter IV.

4. Effect of Temperature

We must finally briefly discuss the effect of temperature variation on equilibrium. All chemical reactions can be divided into *endothermic*, those which absorb heat, and *exothermic*, those which liberate heat. And the manner of variation of the equilibrium constant of a reaction with temperature depends essentially on whether the reaction is exothermic or endothermic. Consider any chemical system in equilibrium, and imagine its temperature to be raised. We can readily see that, if the equilibrium changes with rise of temperature, that reaction must commence which absorbs heat, not the reverse reaction which gives out heat. Were this not so, it is evident that more heat would be added to the system, the temperature would rise, and the reaction would proceed more and more rapidly, the temperature continually rising. Such a state would be quite unstable, and could correspond to no conceivable equilibrium. We conclude therefore that increased temperature favours endothermic reactions and the production of endothermic compounds, and that, conversely, exothermic reactions and products are favoured by low temperatures. (These statements apply to equilibrium states only, not to reaction velocities.) If the reaction has practically no heat effect, the equilibrium will be almost independent of temperature, and the equilibrium constants of those reactions which are accompanied by large heat effects (positive or negative) will be most sensitive to temperature changes.

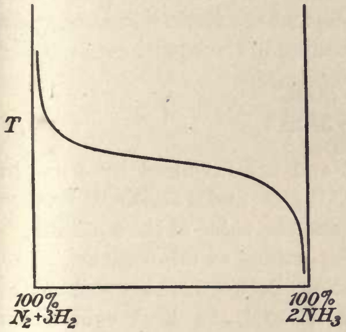

FIG. 1.

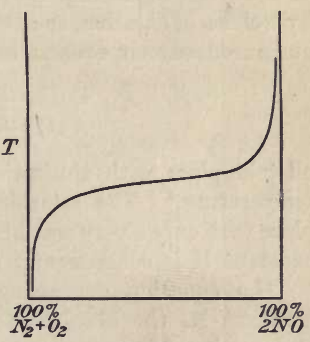

FIG. 2.

Fig. 1 shows how the equilibrium between a typical exothermic compound (NH_3) and its constituents changes with temperature.

The curve gives the relation between temperature and percentage combination or decomposition. At low temperatures the exothermic ammonia is stable; at higher temperatures it dissociates into its constituent gases. Low temperatures are therefore favourable for the synthesis of ammonia from its elements.[1] Fig. 2 shows how the composition of a system, consisting of an endothermic compound such as NO in equilibrium with its constituents, changes with temperature. Rise of temperature favours formation of the compound. NO is produced to a considerable extent at the temperature of the electric arc.[2]

Similarly the formation of HCl from hydrogen and chlorine, of SO_3 from SO_2 and oxygen, and of CuO from copper and oxygen give out heat; at higher temperatures HCl, SO_3 and CuO can all be made to dissociate. On the other hand, the production of CaC_2, whether from its elements or from lime and carbon, takes place with absorption of heat, and high temperatures are necessary for its formation.[3] The hydrolysis of chlorine, or of cuprous salts, and the formation of cuprous and aurous salts in aqueous solution according to the equations

$$CuCl_2 + Cu \longrightarrow 2CuCl$$
$$AuCl_3 + 2Au \longrightarrow 3AuCl$$

all take place with absorption of heat and are favoured by a rise in temperature.[4] The esterification of C_2H_5OH and CH_3COOH[5] takes place with only a very small heat effect, and the value of the equilibrium constant K is consequently almost independent of temperature.

The equation expressing the relation between the equilibrium constant K, the absolute temperature T, and the heat evolved in the reaction Q is

$$\log K_2 - \log K_1 = \frac{Q}{4{\cdot}57}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

K_2 and K_1 are the equilibrium constants at the temperatures T_2 and T_1, and Q (expressed in calories) is assumed to be independent of the temperature, or, if able to vary, to be the mean value over the range of temperature T_2 to T_1. From this equation, knowing K at two different temperatures, we can calculate Q; or, knowing Q and the value of K for one temperature, we can calculate it for another temperature.

For example, Thompson[6] worked on the calcium carbide equilibrium

$$CaO + 3C \rightleftarrows CaC_2 + CO.$$

Amongst other measurements, he found the CO equilibrium pressure to be 0·44 mm. at 1445° C. and 0·82 mm. at 1475° C. Q at 1460° is

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[1] See p. 479.
[2] Chap. xxvii.
[3] P. 469.
[4] Pp. 245, 246, 247, 273, 319.
[5] P. 14.
[6] P. 470.

$-$ 116,000 cals. (reaction going from left to right). We have therefore

$$\log \frac{K_2}{K_1} = -\frac{116000}{4{\cdot}57}\left(\frac{1}{1475+273} - \frac{1}{1445+273}\right).$$

As the lime, carbon, and carbide are solids, we can substitute $\frac{K_2}{K_1}$ by $\frac{p_2}{p_1}$ and get

$$\log \frac{p_2}{p_1} = \frac{116000}{4{\cdot}57} \cdot \frac{30}{1748 \times 1718}$$

whence

$$\frac{p_2}{p_1} = 1{\cdot}79.$$

The experimental value $\left(\frac{0{\cdot}82}{0{\cdot}44}\right)$ was 1·86.

Literature

Nernst. *Theoretical Chemistry.*
Mellor. *Chemical Statics and Dynamics.*

CHAPTER III

FARADAY'S LAWS—CURRENT EFFICIENCY

1. Phenomena of Electrolysis

Electronic and Electrolytic Conductors.—Conductors of electricity can be divided into two classes—*metallic* or *electronic* conductors and *electrolytic* conductors. Typical of the former class are substances like copper, graphite, and Fe_3O_4. To the latter class belong aqueous solutions of H_2SO_4, $AgNO_3$ or ammonia, fused $PbCl_2$ or cryolite, solid $BaCl_2$ or $BaSO_4$ some distance below their melting-points, and finally hot gases.

A fundamental difference exists between the two kinds of conduction, obvious when the above examples are considered. In both cases the current produces heating and magnetic effects; but in 'metallic' conductors the electricity passes through *without the accompaniment of any ponderable quantity of matter*, whereas in electrolytic conductors or **electrolytes** the movement of the electricity is *always associated with the movement of matter.* When the electricity leaves the electrolyte, it cannot take the matter with it; the latter is consequently set free, and a chemical effect is produced, which marks the chief distinction between electronic and electrolytic conduction. The study of these chemical effects and of the corresponding electrical effects necessary for their production forms the largest and most important part of the science of electrochemistry.

Electrolysis.—If two platinum plates be dipped into dilute sulphuric acid, and connected with the two poles of a battery, a current passes (the sulphuric acid being an electrolyte); **electrolysis** takes place, and it is noticed that at the platinum plate connected with the negative terminal of the battery hydrogen gas is given off, whilst at the plate connected with the positive pole of the current source oxygen is evolved. These gases are produced at the platinum plates only, and not along the path of the current through the electrolyte. If we use instead silver nitrate solution, we observe deposition of silver on one platinum plate and evolution of oxygen at the other; and whatever the solution, we notice that chemical action only takes place at the **electrodes,** or points where the current enters and leaves the electrolyte. This is characteristic of electrochemical actions. The electricity, whether positive or negative, while moving through an electrolytic conductor, is associated with some form of matter. When it leaves the electrolyte to continue its journey through an electronic conductor, it cannot carry this accompanying matter further, and the latter is therefore set free.

If now the hydrogen and oxygen from the H_2SO_4 solution are collected, it is found that they stand almost exactly in the proportions necessary to form water, the volume of hydrogen being twice that of the oxygen. Any slight deviation from this exact ratio is due to disturbing causes discussed later. Finally, if, after the electrolysis is finished, samples of acid in the neighbourhood of the two electrodes are titrated, it is found that the one from the neighbourhood of the *positive electrode* where oxygen was evolved is stronger than the one from the neighbourhood of the *negative electrode.*[1] If, however, the whole contents of the electrolysis vessel or electrolytic cell are titrated, the total amount of acid is found to be unchanged. The effects of the electrolysis are thus :—

(1) to decompose water into hydrogen and oxygen, the products being separated, not mixed ;

(2) to concentrate one portion of the sulphuric acid, at the same time diluting another portion.

Suppose similar experiments carried out with various solutions such as (*a*) $CuSO_4$, (*b*) HCl, (*c*) KOH, (*d*) $NaNO_3$. It will be found that the respective negative electrode products are (*a*) metallic copper, (*b*) hydrogen, (*c*) hydrogen, (*d*) hydrogen and NaOH. The corresponding positive electrode products are (*a*) oxygen and H_2SO_4, (*b*) chlorine, (*c*) oxygen, (*d*) oxygen and nitric acid. Concentration changes are also produced in all cases. Thus with KOH, the solution has now become stronger near the negative electrode. A consideration of these results shows that the negative electrode products are always of a metallic or basic nature, whilst the positive electrode products are always of a non-metallic or acidic nature. This again is a perfectly general result. When a current passes through an electrolyte, the *metallic or basic product* of the resulting chemical action is always set free *at the negative pole*, which is termed the **cathode,**[2] whilst the *non-metallic or acid product* of reaction is liberated *at the positive pole* or **anode.**[2] This fact is utilised when it is necessary to distinguish between

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[1] To the engineer, the negative pole of his dynamo (or secondary cell) is the pole by which negative electricity *leaves* the machine. To the electrochemist, the negative pole of his electrolytic bath is the pole by which negative electricity *enters*. This distinction must be clearly borne in mind.

[2] If the electrolyte is divided by a diaphragm or other means into cathode and anode portions, these are termed **catholyte** and **anolyte** respectively.

the two poles of a current source. Wires from these are brought a little distance apart on to a piece of pole reagent paper—filter-paper moistened with a solution of KI or a little Na_2SO_4 and phenol-phthalein. In the former case, the positive pole is shown by a brown coloration due to iodine. With the Na_2SO_4 and phenol-phthalein a pink coloration is produced at the negative pole by the liberated alkali.

2. Faraday's Laws

So far we have seen that electrolysis has two effects—the formation of two substances or groups of substances of opposite polarity and the production of concentration changes. The only quantitative relation noticed has been that, in the electrolysis of dilute sulphuric acid, hydrogen and oxygen are liberated in the proportions in which they form water. Suppose now that an electrolyte be put in the same circuit with an ammeter, and electrolysed, the time being noted and the current kept constant. When the electrolysis is finished, let the products be measured (by weight or volume) and let this procedure be repeated, using different currents during different lengths of time. It will be found that *the resulting chemical effect is directly proportional to the product of the current into the time of electrolysis, that is, to the quantity of electricity which has flowed through the electrolyte.* This is a statement of **Faraday's First Law of Electrolysis.**

Thus, if it is found that 30 grams of copper are produced by 10 amperes flowing for x hours, then the same quantity will be produced by 20 amperes in $\frac{x}{2}$ hours, or by three amperes flowing for $\frac{10\,x}{3}$ hours; and 60 grams will be produced by a current of 10 amperes flowing for $2\,x$ hours, etc.

Faraday's First Law expresses then the fundamental relation existing between quantity of electricity and quantity of any particular substance set free by or taking part in an electrolytic process. In the above statement of it, the assumption is made that one reaction only takes place at each electrode.

The question now arises, In what relation do the quantities of *different* substances liberated by the same quantity of electricity stand to one another? Suppose a number of electrolytic baths arranged in series, so that when a current is passing the same quantity of electricity flows through each of them. Let one contain copper electrodes in $CuSO_4$ solution, another silver electrodes in $AgNO_3$ solution, a third platinum electrodes in Na_2SO_4 solution, a fourth platinum electrodes in fairly strong HCl. Let current be passed through till $\frac{63{\cdot}6}{2}$ grams of copper have been deposited on the copper cathode in the first vessel, and let the effects produced at the other electrodes be measured. From the copper anode in (1), $\frac{63{\cdot}6}{2}$ grams of copper will have been dissolved. In (2), 107·9 grams of silver will have been deposited on the cathode and dissolved from the anode. 1·01 grams of hydrogen will be obtained at the cathode in both (3) and (4), and further in (3) 40 grams of NaOH. Finally, at the anode of (3) we shall obtain $\frac{16}{2}$ grams of oxygen and $\frac{98}{2}$ grams of H_2SO_4, and at the anode of (4) 35·5 grams of chlorine. *These quantities are in all cases proportional to the equivalent weights of the substances concerned.* This relation is known as **Faraday's Second Law of Electrolysis,** and together with the first law can be combined into the following formal statement :—

If a current pass through an electrolyte, bringing about chemical changes at the electrodes, the quantity of each substance formed will be directly proportional to its equivalent weight and to the time of passage of the current.

The quantity of electricity capable of bringing about the transformations described in the preceding paragraph, and of liberating one gram-equivalent of product, is termed a **faraday,** and has been found by careful experiment to be very nearly 96,540 coulombs or ampere-seconds. The ampere-hour is 3,600 coulombs. We therefore have the relation

$$\begin{aligned} 96{,}540 \text{ coulombs (ampere-seconds)} &= 26{\cdot}8 \text{ ampere-hours} \\ &= 1 \text{ faraday.} \end{aligned}$$

Conception of Ions.—To explain the regularities described, Faraday suggested that the neutral dissolved molecules of an electrolyte consist of two oppositely charged parts, which he termed **ions.** The negatively charged fraction or **anion** is composed of a non-metal or of an acid radicle, whilst the positively charged part, the **cation,** consists of a metal, of hydrogen, or of some positive radicle, such as NH_4. When the current passes, the positive ions are attracted towards the negatively charged cathode, where their charge is neutralised, and they are set free. The anions behave similarly, being discharged at the positive electrode, the anode. If the further assumption be made that the quantity of electricity—positive or negative—associated with one gram-equivalent of every kind of ion is always the same, and equal to 96,540 coulombs, all the above results, both qualitative and quantitative, can be consistently explained. This conception of Faraday's, developed in accordance with later discoveries, is now universally used. A unit positive charge is usually denoted by $^{\cdot}$, a negative charge by $'$. As the number of charges per unit will vary directly as the valency of the ion, we write $K^{\cdot}$, Cl', $Cu^{\cdot}$ (cuprous ion), $Cu^{\cdot\cdot}$ (cupric ion),

OH', SO_4'', $FeCy_6''''$ (ferrocyanide ion), etc. Corresponding neutral molecules can be written $K_2^{\cdot\cdot}SO_4''$, $Cu^{\cdot\cdot}Cl_2''$, etc., though the signs representing the charges are usually omitted.

3. Current Efficiency

The *minimum* quantity of electricity needed for the production of a gram-equivalent of an electrolytic product is 26·8 ampere-hours. We emphasise the word minimum, because in the average electrolysis more than this amount is required.

This is not due to any breakdown of Faraday's Law, which has been shown to hold over a wide range of temperatures, for electrolytes other than aqueous solutions, and for fused salts. One faraday passed through an electrolyte will always liberate one gram-equivalent of product at each electrode. But it often happens that this product is not homogeneous. Some of the electricity given up at the electrode may have been associated with one kind of ion, and some with another kind of ion. Thus, in the electrolysis of brine solutions for the production of alkali and chlorine, under certain circumstances large quantities of oxygen can be evolved at the anodes instead of chlorine.

Secondly, and more important, is the fact that the primary product of electrochemical action, when liberated from its accompanying charge of electricity, can often react partly or completely with bodies in the neighbourhood of the electrode, some thus being lost; or it is liberated in such a form that it cannot be easily collected, or it can perhaps diffuse rapidly away, and to some extent recombine with the product of electrolysis at the other electrode. If a KCl solution be electrolysed between copper electrodes, neither potassium nor chlorine is obtained as a final product. The former acts on the water, producing alkali and hydrogen, the latter attacks the copper electrode, giving cuprous chloride. When sodium is prepared, as in the Castner process, by the electrolysis of molten NaOH, a certain quantity is lost by vaporisation; more reacts with the water which is constantly formed during the process; a third source of loss is due to dissolved metal escaping to the anode, and there combining with the evolved oxygen. Or the substance itself may be chemically unstable and tend to decompose spontaneously—*e.g.* sodium hyposulphite. Good results are then best obtained by using a high **current concentration,**[1] this being defined by the ratio $\frac{\text{current}}{\text{volume of electrolyte (catholyte, anolyte)}}$. The required concentration of product is in this way quickly reached. Again, current leaks and short circuits often cause wastage, as in copper refining.

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[1] Tafel, *Ber.* **33**, 2212 (*1900*).

Consequently, the yield of material in an electrolytic process is nearly always less than that calculated from the quantity of electricity used. The ratio of yield obtained to the theoretical yield calculated on the basis of Faraday's Law is termed the **current efficiency,** and a high current efficiency is of course one of the chief aims of an electrolytic process. Sometimes it is the first thing to be considered, often its importance may be considerably modified by other factors.

Technical current efficiencies vary within wide limits. The anodic oxidation of anthracene to anthraquinone gives almost 100 per cent. In copper refining, one of 95 per cent. is the average. Alkali-chlorine cells furnish 50–100 per cent., depending on the type of cell and the concentration of alkali produced. Hypochlorite liquors are obtained at about 66 per cent. current efficiency; metallic sodium and aluminium from fused electrolytes at about 45 per cent. and 70 per cent. respectively. These figures all refer to the chief product. One should really speak of *anodic and cathodic current efficiencies.*

4. Measurement of Quantity of Electricity

The determination of current efficiency involves, therefore, two measurements—the weight or volume of product and the quantity of electricity used. The latter may be measured in two ways. The current may be observed at frequent intervals, when the mean figure, multiplied by the time, will give the number of ampere-hours expended; or this last quantity may be measured directly.

For the detection of current, and occasionally for the measurement of small currents, galvanometers are used. For heavier currents ammeters are employed. To enter here into their construction or use is unnecessary. It might, however, be mentioned that the most economical system for general experimental electrochemical work is the employment of a high-resistance milliamperemeter, together with a number of external shunts. One instrument will thus cover an enormous range. The shunt resistances are relatively cheap. The method of measuring current by employing a high-resistance voltmeter and a low resistance of known value in the main circuit is based on the identical principle. Putting the voltmeter across the ends of this resistance, we have

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

Coulometers.—For the measurement of quantity of electricity in small-scale experimental electrochemical work, **coulometers** are used. In these instruments some electrochemical product is liberated by the current in easily measurable form, and from its amount, assuming Faraday's Law, the quantity of electricity passed through can be readily calculated. In a good coulometer there must be no disturbing or secondary by-reactions, and much investigation has been devoted to this point. It has been found necessary to define carefully the conditions under which the instruments are used.

The **silver coulometer** is the most accurate[1] of all so far described. As worked out by T. W. Richards,[2] it is set up as follows (Fig. 3). The cathode consists of a platinum crucible containing the electrolyte, a freshly prepared 10 per cent. $AgNO_3$ solution. The anode is a pure silver rod, wrapped in filter paper and suspended in $AgNO_3$ solution, but separated from the cathode by a 1 mm. Pukall porous pot. The level of liquid inside this pot is lower than that outside, and diffusion of anode liquid to the cathode is thus counteracted. Richards found this necessary in consequence of substances formed at the anode which can, under varying conditions of current density, produce either too large or too small cathodic deposits. The anodic and cathodic current densities must not exceed 0·2 and 0·02 amp./cm.^{2} respectively.

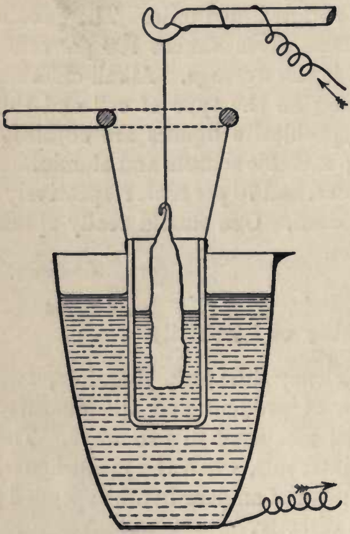

FIG. 3.—Silver Coulometer.

Where complete accuracy is not required, the **copper coulometer** can be used. It is cheaper and gives sufficiently good results. Here again certain complications occur which will be fully considered later,[3] but which are largely avoided in the form described (Fig. 4). The electrolyte consists of the following solution[4] :—

150 grams copper sulphate crystals,
50 grams H_2SO_4,
50 grams alcohol,
1 litre water.

The electrodes number three, and are conveniently hung parallel to the sides of a rectangular glass vessel. They can be kept in position by slots cut in small pieces of wood which grip on the edges of the shorter sides of the glass jar. Two of these electrodes are anodes, one the cathode. The last, a thin sheet of electro-

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[1] See p. 6.

[2] *Zeitsch. Phys. Chem.* **41**, 302 (*1902*).

[3] Pp. 245–247.

[4] F. Oettel, *Chem. Zeit.* **17**, 543 (*1893*).

lytic copper, is suspended between the anodes. Its increase in weight is the measure of the quantity of electricity passed through. The decrease in weight of the anodes is too indefinite. These anodes can be made of ordinary sheet copper, and are best enclosed in bags of parchment paper to keep impurities from the electrolyte. The size of the coulometer is determined by the currents it is designed to carry. To get good results, a cathodic current density of 0·5–2·5 amps./d.m.^{2} (taking into account both sides of the cathode) must be used. Too high values furnish a deposit dark in colour, loose, and easily rubbed off. If, on the contrary, the current density be less than the lower limit given, the weight of copper deposited is too small. During long-continued use, the electrolyte should be stirred, conveniently by a slow stream of hydrogen, which also opposes oxidising effects due to dissolved air. When the electrolysis is finished, the cathode is withdrawn, washed thoroughly with water and then alcohol, dried quickly by holding some distance above a Bunsen flame, and weighed. As 31·8 is the equivalent weight of cupric copper, if m be the increase in weight of the cathode in grams, and x the number of ampere-hours passed through,

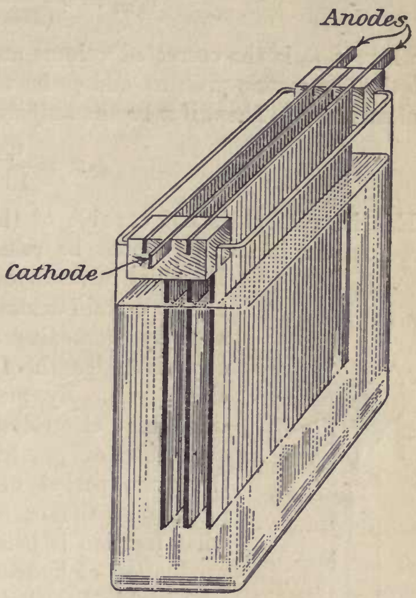

FIG. 4.—Copper Coulometer.

$$x = \frac{m}{31{\cdot}8} \cdot \frac{96540}{3600}.$$

In the **water coulometer,**[1] the volume of electrolytic gas evolved during the passage of the current is measured. This gas is produced by the electrolysis of a 15 per cent. NaOH solution (NaCl-free) between nickel electrodes. The electrolysis vessel is an ordinary glass bottle, provided with a rubber stopper. This carries a delivery tube, dipping under a graduated glass cylinder, which has been filled and inverted over water. The passage of one faraday produces one gram (11·2 litres) of hydrogen, and eight grams (5·6 litres) of oxygen—altogether

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[1] F. Oettel, *Zeitsch. Elektrochem.* **1,** 355 (*1894*).

16·8 litres of electrolytic gas at 0° and one atmosphere. One ampere-minute means therefore 10·44 c.c. of gas. To convert the volume as actually read off to standard conditions, we can use the formula

$$v_{0,760} = v\,\frac{273\,(b - p)}{(273 + \theta)\,760}$$

where $v_{0,760}$ is the corrected volume and v the observed volume in c.c., b the barometric pressure and p the vapour pressure of water in mm. of mercury. Then, if x be the ampere-minutes used,

$$x = \frac{v_{0,760}}{10{\cdot}44}.$$

This instrument is not capable of the same accuracy as the copper coulometer, in fact it cannot be relied upon beyond $\pm 0{\cdot}5$ per cent. Its chief advantage is that it enables us to follow closely certain oxidation or reduction reactions whilst actually proceeding, and to determine the yield over any given length of time without interrupting the electrolysis. By putting the coulometer in series with the electrolytic bath, and comparing the quantities of gas liberated in the two cases over the same period of time, it can be found what portion of the current is doing useful work and what fraction is being expended in the undesirable production of hydrogen and oxygen.[1]

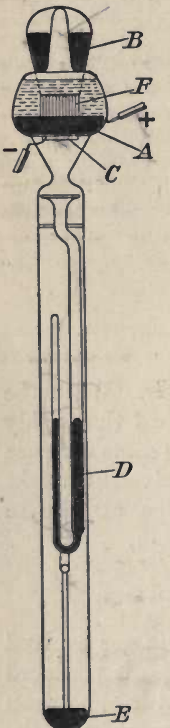

Fig. 5.—Wright Electrolytic Meter.

Wright Electricity Meter.—Large quantities of electricity can be directly measured by means of *ampere-hour* or *electricity meters*. Of these instruments one only gives reliable and accurate results. This is the Wright Electrolytic Meter, as modified by Abegg and by Hatfield, and sold in this country by the Reason Manufacturing Co. of Brighton. An accurately shunted fraction of the current passes through a ballast resistance and through the cell, shown in essentials in Fig. 5. The anode is of mercury, kept at a constant level on the ring-shaped ledge A, by means of the reservoir B. The cathode C is of iridium foil, and the electrolyte a potassium iodide solution of mercuric iodide. When the current passes, droplets of mercury are produced at the cathode. Being of iridium, no amalgamation or adhesion occurs, but the mercury falls through the funnel underneath into the U-tube D. There its volume can be read off, and gives a measure of the quantity of

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[1] See p. 36.

electricity passed. When the U-tube is completely filled the contents siphon over into the bottom of the apparatus E, where is another scale. At the anode mercury dissolves quantitatively, and the composition of the electrolyte remains absolutely unchanged. Local concentration differences at the electrodes are ingeniously nullified, and mercury is prevented from passing from the anode to the lower part of the apparatus (by shock or otherwise) by means of the fence of glass tubes F. Temperature changes are compensated by the ballast resistance. The apparatus is reset by simply inverting it, when the mercury flows again into the reservoir B. Its accuracy is within 1 per cent., though the amperage may vary from 10 per cent. to 150 per cent. of the rated figure. It is exceedingly reliable and constant, and needs no attention. Hatfield[1] has also given some interesting details of an instrument in which bromine is precipitated and measured, which promises to be still more useful for small quantities of electricity.

Calibration of Ammeters.—Large quantities of electricity are, however, still usually measured by making periodical readings of an ammeter, and the calibration of this instrument is important. It can be carried out in several ways.

(*a*) *Most conveniently with a standard ammeter.* The two instruments are connected in series, together with a variable resistance, such as the type consisting of a number of loosely packed carbon plates which can be screwed up into better contact. Current is passed through, and simultaneous readings made. A whole series can be taken by suitably regulating the current.

(*b*) *With a standard high resistance voltmeter, standard low resistance, and adjustable resistance.* The use of voltmeter and known resistance for current measurement has already been mentioned.[2] Knowing the value of the standard resistance R, the true current is given by $I = \frac{E}{R}$, where E is the voltmeter reading. A comparison series is taken as in method (*a*).

(*c*) *With a coulometer.* This method is much less rapid and convenient than (*a*) or (*b*), and can only be used for low-range ammeters. It has the advantage of needing no standard instrument of any kind. Suppose a copper coulometer to be used. It is connected in series with the ammeter and variable resistance. Until conditions are constant and the ammeter registers the required reading, the weighed cathode for actual use is not inserted, a similar auxiliary one being used. When all regulation is finished, the current is interrupted, the working cathode rapidly put in, the electrolysis restarted and the time noted. The experiment is carefully watched, and any fluctuations in the ammeter reading neutralised by adjusting the resistance. When sufficient time

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[1] *Zeitsch. Elektrochem.* **15**, 728 (*1909*).

[2] See p. 31.

(previously calculated) has been allowed for the deposition of a convenient quantity of copper, the electrolysis is again interrupted and the time noted, the increase in weight of the cathode determined, and the current calculated, assuming 26·8 ampere-hours for each 31·8 grams of copper. This is repeated for a number of ammeter readings.

5. Calculation of Current Efficiencies

Before closing this chapter, examples will be given of the calculation of current efficiencies.

1. The electrolytic reduction of carbonic acid to formic acid [1] is being studied on a small scale. The catholyte is saturated K_2SO_4 solution, through which CO_2 gas bubbles. The cathode is an amalgamated zinc plate, 2·5 d.m.^{2} in area (one side). A current of about 0·25 amp. is passed for eight hours. Water and copper coulometers are included in the circuit. Occasionally the $H_2 - CO_2$ mixture which continually passes away from the cathode is collected, and after absorbing the CO_2 by potash, the volume of the residual hydrogen is compared with the volume of the electrolytic gas evolved in the water coulometer during the same period. On two such occasions, the volume of the electrolytic gas is in each case 60 c.c.; the volume of cathodic hydrogen 10·6 c.c. and 8·7 c.c. respectively, in all cases as directly measured. The formic acid produced is estimated at the end, and amounts to 1·23 grams. The increase in weight of the cathode in the copper coulometer is 2·335 grams. Required (*a*) the current efficiencies during the periods over which the gas samples are collected and (*b*) the current efficiency during the whole run.

(*a*) Of the 60 c.c.[2] of electrolytic gas, 40 c.c. are hydrogen. This quantity would be liberated on each occasion in the electrolysis vessel itself if no gas were to be used in the reduction process. But 10·6 [2] c.c. and 8·7 [2] c.c. are the amounts actually liberated. Hence (40 — 10·6) c.c. and (40 — 8·7) c.c. respectively are used in the reduction. The current efficiencies are therefore

$$100 \cdot \frac{40 - 10{\cdot}6}{40} = 73{\cdot}5 \text{ per cent., and}$$

$$100 \cdot \frac{40 - 8{\cdot}7}{40} = 78{\cdot}25 \text{ per cent.}$$

(*b*) The increase in weight of the copper cathode is 2·335 grams. The number of ampere-hours used is consequently $\frac{2{\cdot}335}{31{\cdot}8} \cdot 26{\cdot}8$. (Average current is therefore $\frac{2{\cdot}335}{31{\cdot}8} \cdot \frac{26{\cdot}8}{8} = 0{\cdot}246$ ampere.) The equation expressing the reduction is

$$H_2CO_3 + H_2 \longrightarrow H_2CO_2 + H_2O \text{ (passage of 2 faradays).}$$

We see that to produce one mol. (46 grams) of formic acid, two faradays or 2 . 26·8 ampere-hours are needed. The theoretical yield of formic acid is therefore

$$\frac{\frac{2{\cdot}335}{31{\cdot}8} \times 26{\cdot}8}{2 \times 26{\cdot}8} \times 46 = 1{\cdot}69 \text{ grams,}$$

and the current efficiency is

$$100 \cdot \frac{1{\cdot}23}{1{\cdot}69} = 72{\cdot}8 \text{ per cent.}$$

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[1] Coehn and S. Jahn, *Ber.* **37**, 2,836 (*1904*).

[2] Note that uncorrected readings can be used.

2. A 1,000-ampere alkali-chlorine cell is being tested over a short run. The cathode liquors are intended to contain 120 $\frac{\text{grs.}}{\text{litre}}$ NaOH. The current is measured by a shunted ammeter every five minutes. After constant conditions are attained, the cell is run for six hours, during which time 70·3 litres of causticised brine are produced, containing on an average 118·0 grams NaOH per litre. The current readings run thus 970 . . . 1,008 . . . 1,021 . . . 1,002 . . . 984 . . . 987 . . . 1,011 . . . 1,020 . . . 1,005 . . . 994 . . . 1,000 . . . 1,007, etc., and average 1,002 amperes. Required, the cathodic current efficiency.

The NaOH produced $= 70{\cdot}3 \times 118 = 8295$ grams. The ampere-hours used $= 6 \times 1002 = 6012$ ampere-hours. The production of one equivalent (40 grams) of NaOH requires theoretically 26·8 ampere-hours.

Hence, the theoretical NaOH production will be

$$\frac{6012}{26{\cdot}8} \times 40 = 8973 \text{ grams,}$$

and the current efficiency

$$100 \cdot \frac{8295}{8973} = 92{\cdot}4 \text{ per cent.}$$

Literature

Le Blanc. *Electrochemistry.*
Lorenz. *Elektrochemisches Praktikum.*

CHAPTER IV

OSMOTIC PRESSURE—THEORY OF SOLUTIONS

1. Osmotic Pressure

It is well known that the particles of a dissolved substance behave analogously to those of a gas. If pure water be carefully superposed on a sugar solution, sugar can be detected after a certain time in all parts of the liquid, and the whole will ultimately attain a uniform composition. This is quite similar to the expansion of a gas into a vacuum or from a high to a low pressure. Or if solutions of KCl and $CuSO_4$ be brought into contact, diffusion will proceed until the two bases and the two acids are distributed equally throughout the whole mass, just as gaseous oxygen and hydrogen will interdiffuse until a uniform gaseous mixture results. It is natural to seek a common explanation for these parallel phenomena, and to suppose the dissolved particles to be in a state of continual spontaneous motion, like the particles of a gas, and therefore capable of *exerting a pressure*, moving against gravity, and diffusing.

The existence of this **osmotic pressure** can be easily proved. It is not manifest at the boundary surfaces of a solution, being counteracted by an internally directed pressure of the order of 1000 atmospheres, due to the surface tension of the solvent. To demonstrate its existence the influence of the solvent must be eliminated. This condition can be realised experimentally if we enclose the solution in a vessel through the walls of which the solvent molecules can freely pass, but which is *impermeable* to the particles of the solute. These particles will still exert their pressure on the walls, whereas the solvent will no longer have any effect, but will behave as an indifferent medium.

Such a *semi-permeable membrane* can be readily prepared by forming a layer of cupric ferrocyanide in the interior of the walls of an ordinary unglazed porcelain pot. K_4FeCy_6 solution is allowed to diffuse into the walls from the inside of the pot, and $CuSO_4$ solution from the outside. The precipitate forms in the structure of the wall, the pot being subsequently thoroughly freed by washing from soluble salts. (To obtain a membrane which will withstand high pressures, additional precautions must be taken.)

The apparatus is then built up as shown in Fig. 6. In the top of the porous pot, containing, for example, a sugar solution, a glass tube is cemented with sealing-wax. This is connected with a manometer, and has also an open T-piece *a*, which is sealed off after the glass tube has been cemented on. The level of the manometer liquid is indicated by *b b*. Finally the pot is immersed in a vessel of water.

What happens is as follows. At the semi-permeable membrane equilibrium is non-existent. There is a resultant pressure difference equal to the osmotic pressure of the dissolved sugar. Also the walls are permeable to the solvent. The conditions correspond to those of a gas put into communication with a vacuum. The gas tends to expand—to lower its pressure. The solution tends to dilute—to lower its osmotic pressure. The gas expands by particles entering the vacuum, the solution dilutes by solvent entering through the walls. This process tends to continue until there is no difference of osmotic pressure between the two sides of the membrane, in this case indefinitely, as there is no sugar outside the porous pot.

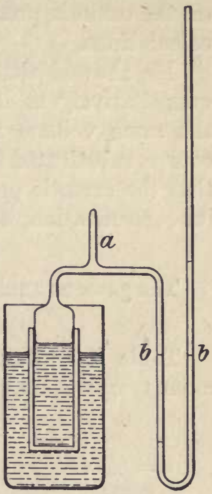

FIG. 6.—Osmometer.

But there is an opposing force acting. The gaseous analogy is a weighted piston closing a vacuum. The gas will only expand into the vacuum until its pressure falls to that exerted by the weight on the piston. Here the solvent entering the porous pot compresses the air above the solution, and this alters the level of the manometer liquid. The increased pressure in the apparatus tends to force the solvent out through the porous wall. As the process continues, the osmotic pressure of the solution decreases, owing to dilution, and the pressure in the apparatus increases. When these pressures are equal, no more solvent will enter. Equilibrium is attained, and the pressure indicated by the manometer is equal to the osmotic pressure of the solution in the cell—not equal to the osmotic pressure of the solution originally present, but to that of the more dilute solution formed at the finish. This difference can be made very small by choosing a manometer of narrow bore, and filling it with a heavy liquid.

2. Solution Laws

It was in 1885 that Van't Hoff showed the full theoretical significance of this phenomenon, though its existence had long been known to botanists. In particular, the well-known plant physiologists Pfeffer, de Vries, and Traube had done much experimental work in that field. The excellent properties of the cupric ferrocyanide membrane were first demonstrated by Traube, and it was to Pfeffer's measurements on the osmotic pressure of sugar solutions that Van't Hoff applied his calculations.

He showed that the solutions, if not too concentrated, behaved quantitatively as if the sugar were in the gaseous state, occupying the same volume as the sugar solution—osmotic pressure being, of course, substituted for gaseous pressure. To be more precise, he showed that the osmotic pressure P of the sugar solution was proportional to its concentration, or inversely proportional to its dilution v. Thus

$$\mathrm{P}v = \text{constant}.$$

The gaseous analogy is simply Boyle's Law

$$pv = k.$$

Table II contains some of Pfeffer's results for sugar solutions at room temperature.

TABLE II

n = % of sugar	P in mm. of Hg	Corresponding calculated gas pressure	$\frac{\mathrm{P}}{n}$
1	535	527	535
2	1016	1054	508
2·74	1518	1449	554
4	2082	2108	521
6	3075	3162	513

The osmotic pressure rises with increase of temperature, and Van't Hoff showed the coefficient of increase of pressure per 1° C. to be $\frac{1}{273}$—the figure observed by Gay Lussac for perfect gases heated at constant volume. The osmotic pressure is thus proportional to the absolute temperature. Table III illustrates this. It contains Pfeffer's results for a 1 per cent. sugar solution, expressed in atmospheres. The formula from which the 'calculated' values are obtained is

$$\mathrm{P} = 0{\cdot}655\ (1 + 0{\cdot}00366\ \theta).$$

TABLE III

θ	Observed pressure	Calculated pressure	Difference
6·8	0·664 atm.	0·671 atm.	+ 0·007
13·7	0·691	0·688	− 0·003
14·2	0·671	0·688	+ 0·017
15·5	0·684	0·692	+ 0·008
22·0	0·721	0·708	− 0·013
32·0	0·716	0·732	+ 0·016
36·0	0·746	0·741	− 0·005

For strengths of sugar solution other than 1 per cent., the equation becomes

$$P = 0{\cdot}655 \,.\, n \ (1 + 0{\cdot}00366 \ \theta),$$

where n is the percentage of sugar dissolved. This value n is inversely proportional to the dilution v, and we can put

$$n = \frac{k_1}{v}.$$

Substituting $\frac{1}{273}$ for 0·00366 and absolute for Centigrade temperature, we obtain

$$P = \frac{0{\cdot}655 \ k_1 T}{v \ 273}$$

or

$$Pv = k_2 T.$$

The corresponding gas equation is

$$pv = RT$$

and if one gram-molecule of gas or of dissolved substance be considered and the same units used, it is found that $k_2 = R$.

For example, a 1 per cent. sugar solution at 7° C. had an osmotic pressure of 505 mm. (Pfeffer). Then

$$P = \frac{505}{760} = \frac{2}{3} \text{ atmosphere}$$

$$T = 273 + 7 = 280°.$$

The formula of cane sugar is $C_{12}H_{22}O_{11}$, the molecular weight consequently 342. One gram occupies 100 c.c. of solution ; 342 grams would thus occupy 34·2 litres. The value of k_2 in litre-atmospheres per degree is therefore

$$\frac{34{\cdot}2 \times 2}{280 \times 3} = 0{\cdot}0814.$$

The gas constant R, expressed in the same units, is 0·0821. We can consequently write

$$Pv = RT.$$

The whole analogy between dilute solutions and perfect gases is most strikingly shown by the following statement, so very similar to Avogadro's Law. *At the same osmotic pressure and the same temperature, equal volumes of solutions contain the same number of dissolved molecules.*

The above results of Pfeffer were obtained by rather crude methods, and the agreement is often imperfect. In recent years the technique of these measurements has been fully worked out, more particularly by Morse and his collaborators in America, and possible errors have been attacked and eliminated in detail. Very high osmotic pressures can now be measured with considerable exactness. Some of the results of Morse and Frazer on sugar solutions follow. In the calculation of Pfeffer's approximate figures in the above tables, no distinction was made between weight and volume percentages. In Tables IV and V the theoretical pressures are calculated on the assumption that the sugar is gasified in a volume equal to that of the *solvent* present. Concentrations are expressed as gram-molecules per 1,000 grams of water; pressures are in atmospheres.

TABLE IV

Concentration	θ	P found	Corresponding gas pressure	Difference
0·05	20·5	1·25	1·21	−0·04
0·1	18·5	2·44	2·40	−0·04
0·2	21·5	4·80	4·85	+0·05
0·3	19·4	7·23	7·22	−0·01
0·5	20	12·08	12·07	−0·01
0·8	17·5	19·07	19·14	+0·07
0·9	20·2	21·80	21·74	−0·06
1·0	22·5	24·34	24·34	—

The figures of Table V show how Gay Lussac's Law is obeyed.

TABLE V

Concentration	$\theta = 4\text{–}5^\circ$	$\theta = 10^\circ$	$\theta = 15^\circ$
0·1	2·40	2·44	2·48
0·2	4·75	4·82	4·91
0·3	7·07	7·19	7·33
0·4	9·43	9·58	9·78
0·5	11·82	12·00	12·29
0·6	14·43	14·54	14·86
0·7	16·79	17·09	17·39
0·8	19·31	19·75	20·09
0·9	22·15	22·28	22·94
1·0	24·83	25·06	25·42
Mean *molecular* osmotic pressure	24·12	24·50	24·98

Extrapolating, we get 23·7 atmospheres as the molecular osmotic pressure at 0°. The temperature coefficient of osmotic pressure is therefore, taking the value at $\theta = 0^\circ$ as unity,

$$\frac{24{\cdot}98 - 24{\cdot}12}{23{\cdot}7 \times 10} = 0{\cdot}00363,$$

whilst the coefficient of increase of gaseous pressure per degree is 0·00366.

3. Determination of Molecular Weight of Dissolved Substances

From Osmotic Pressure Measurements.—It is clear that if we know the osmotic pressure and temperature of a solution, and also the concentration of the solute, we can calculate the molecular weight of the latter. Using the gas constant R, the equation

$$Pv = RT$$

holds for that volume of solution containing one gram-molecule of the dissolved substance. If n gram-molecules are contained in the volume v, the equation becomes

$$Pv = n\,RT.$$

Measuring P therefore, and knowing v and T, n can be calculated. But if m be the mass of solute dissolved, and M is its molecular weight, we have

$$m = nM,$$

whence M can be calculated.

For example, a solution containing 40 grams of dissolved substance per litre shows an osmotic pressure of 2·74 atmospheres at 14° C. What is the molecular weight of the dissolved substance?

We have $P = 2{\cdot}74 : v = 1{\cdot}0 : T = 287 : R = 0{\cdot}0821$.

Whence, from $Pv = nRT$, we get $n = 0{\cdot}1163$.

Substituting in the equation

$$m = Mn,$$

where m is 40, we finally have

$$M = 344.$$

From Vapour Pressure Measurements.—But in practice osmotic pressure measurements are not easily carried out. They are tedious, and a membrane that will serve for one series of measurements may be useless for another, owing to its permeability to the dissolved substance. A cupric ferrocyanide membrane is in general an efficient one, but is useless for many electrolytes, *e.g.* potassium nitrate. Other methods of ascertaining the molecular weights of dissolved substances are generally used. We have seen[1] that the vapour pressure of a solution is lower than the vapour pressure of the solvent, and that, putting

p_0 = vapour pressure of solvent,
p = vapour pressure of solution,
n' = number of molecules of solute dissolved in
n molecules of solvent,

we have the relation

$$\frac{p_0 - p}{p_0} = \frac{n'}{n' + n},$$

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[1] P. 22.

or, where n' is small compared with n, that is, when the solution is a dilute one,

$$\frac{p_0 - p}{p_0} = \frac{n'}{n}$$

If M′, m', are the molecular weight and mass of the solute, and M, m, the molecular weight and mass of the solvent, we have, as before,

$$m = \mathrm{M}n \text{ and } m' = \mathrm{M}'n',$$

and the equation becomes

$$\frac{p_0 - p}{p_0} = \frac{m'}{m} \cdot \frac{\mathrm{M}}{\mathrm{M}'}$$

Consequently by measuring p, m' and m, and knowing p_0 and M, we can calculate M′. In the particular case of a 1 per cent. solution, $\frac{m'}{m} = \frac{1}{100}$, and we get

$$\mathrm{M}' \cdot \frac{p_0 - p}{p_0} = \frac{\mathrm{M}}{100} = \rho$$

or, expressed fully, the product of the molecular weight of a dissolved substance into the relative lowering of vapour pressure of the solvent in a 1 per cent. solution is equal to the molecular weight of the solvent divided by one hundred. In accordance with this the values of ρ for solutions of perchlorethane, turpentine, cyanic acid, benzoic acid, trichloracetic acid and benzaldehyde in ether were found to be 0·71–0·72 (molecular weight of ether 74). Similarly for water the figure is 0·185 (theoretical value 0·18).

From Freezing-point and Boiling-point Measurements.— But vapour-pressure measurements, like osmotic-pressure measurements, are not readily carried out. In practice, *freezing-point* and *boiling-point* determinations are made. In Fig. 7, AB represents the sublimation curve of ice, and BC the vaporisation curve of water. The point B corresponds to the freezing-point T. Let DE represent the vapour pressure curve of a solution. It cuts the curve AB at D. At this point and the corresponding temperature T′, the solution and ice have the same vapour pressure, and consequently T′ is the freezing-point of the solution. The freezing-point of a solvent is therefore *lowered* by the presence of a solute.

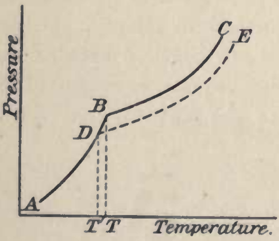

FIG. 7.

And we can easily see that, as in the immediate neighbourhood of the freezing-point, the different curves can be regarded as straight lines, this depression is proportional to the lowering of vapour pressure of the solvent. Thus if DE and D′E′ (Fig. 8) denote the vapour pressure curves for two different solutions of freezing-points respectively D and D′, BF and BF′ will be the two lowerings of vapour pressure, and DG and DG′ the two depressions of freezing-point. Then we see at once that

$$\frac{\mathrm{BF}}{\mathrm{BF}'} = \frac{\mathrm{BD}}{\mathrm{B'D'}} = \frac{\mathrm{DG}}{\mathrm{D'G'}}$$

Hence *the freezing-point of a solution is lower than that of the solvent by an amount directly proportional to the molecular concentration of the solute.* If $d\mathrm{T}$ represents the depression of freezing-point,

$$d\mathrm{T} = k\frac{n'}{n} = k\frac{m'}{m} \cdot \frac{\mathrm{M}}{\mathrm{M}'}.$$

A similar proposition can be proved for the boiling-point, which is higher, not lower, for the solution than for the solvent.

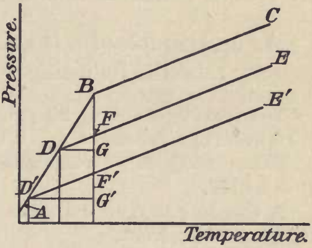

FIG. 8.

These relations were discovered empirically by Raoult, and employed by him to determine the molecular weights of many substances in solution. Van't Hoff succeeded in deducing them thermodynamically, in showing their connection with the osmotic pressures of the solutions, in actually calculating Raoult's empirical constants for many solvents from latent-heat and freezing-point or boiling-point data,—in a word, in putting the whole subject on a sound theoretical basis.

If we rewrite the last equation, referring the freezing-point depression to a quantity of solution containing 100 grams of the solvent, we get

$$d\mathrm{T} = k \cdot \frac{n'\mathrm{M}}{100}$$
$$= k' \cdot n'$$

It was the value of the constant k' which Van't Hoff calculated. His calculation cannot here be considered in detail, but it will suffice to give the final result, which is

$$k' = \frac{\mathrm{RT}^2}{100\ \mathrm{L}},$$

or, putting R = 2 cals.,

$$k' = 0{\cdot}02\,\frac{\mathrm{T}^2}{\mathrm{L}}$$

where T is the freezing-point and L the latent heat of fusion per gram of the pure solvent.

Table VI shows how closely the values of k' thus calculated agree with the same found by freezing-point measurements.

TABLE VI

Substance	T	L	$0{\cdot}02\,\frac{T^2}{L}$	k' experimental
Water	273	80·3	18·6	18·4
Acetic acid	290	43·2	38·8	39·6
Formic acid	281·5	55·6	28·4	27·7
Benzene	278	29·1	53·0	50·0
Nitrobenzene	278·3	22·3	69·5	70·7

As an example of a freezing-point molecular weight determination, we may take the following :—

The freezing-point of 20 grams of water is lowered 0·362° by dissolving in it 0·3 gram of a substance A. What is the molecular weight of A ?

Substituting $dT = 0{\cdot}362$ and $k' = 18{\cdot}4$ in the equation $dT = k'n'$ we get $n' = 0{\cdot}0197$.

A concentration of 0·3 gram per 20 c.c. corresponds to $m' = 1{\cdot}5$ grams per 100 grams of solvent.

Whence by substitution in

$$m' = M'n'$$

we get

$$M' = \frac{1{\cdot}5}{0{\cdot}0197} = 76.$$

The relation connecting an *increase of the boiling-point* of a solvent and the gram-molecular concentration of the solute is very similar. These equations have been verified for many solvents and solutes, and have proved of great service in the measurement of the molecular weights of the latter. Like the osmotic-pressure equations, they only hold strictly for dilute solutions ; with strong solutions complications arise, similar to those occurring in the theory of highly compressed gases. But even in the field of dilute solutions, there is a large and important class of apparent exceptions.

4. Anomalous Behaviour of Electrolytes

All solutions of strong electrolytes (strong acids, bases, and their salts) show an anomalous behaviour, giving abnormally large osmotic pressures, lowerings of vapour pressure and of freezing-point. Such solutions behave in fact as if they contain a larger number of molecules than would be calculated from the weighed amount of substance dissolved. Thus, instead of the equation

$$Pv = RT$$

holding for the osmotic pressure of that amount of solution which contains one chemical gram-molecule of solute, the relation

$$Pv = iRT$$

must be used, where *i—the Van't Hoff factor*—is always greater than unity, though seldom exceeding three. Similarly the lowering of vapour pressure is given by

$$\frac{p_0 - p}{p_0} = \frac{in'}{n}$$

and the lowering of freezing-point by

$$dT = k \,.\, i \,.\, \frac{n'}{n}$$

Moreover, for the same solution, the same value of i must be introduced into these various equations. With increasing dilution of the solution, it becomes greater, and finally approaches some simple integral limiting value.

To illustrate this abnormal behaviour, we may take vapour pressure measurements of aqueous solutions of electrolytes. We have seen[1] that for a 1 per cent. solution, the product of the molecular weight of the dissolved substance into the relative lowering of vapour pressure of the solvent should equal the molecular weight of the solvent divided by one hundred. For water the value of this constant (ρ) should be 0·18, and has been found by experiment to be 0·185 for non-electrolytes. With electrolytes the values of Table VII are obtained.

TABLE VII

Solute	ρ	i
KAc	0·326	1·76
LiCl	0·359	1·94
LiBr	0·367	1·98
KCNS	0·327	1·77
$Ca(NO_3)_2$	0·432	2·34
$CaCl_2$	0·423	2·29

When similar behaviour is encountered in the measurement of gaseous vapour densities, the abnormal values are attributed to *dissociation* of the normal molecules into simpler constituents, *e.g.* PCl_5 into PCl_3 and Cl_2. In precisely the same way the abnormal results discussed above are explained by the dissociation of the molecules of the electrolyte into simpler constituents, each of which can act as a separate individual in determining the osmotic pressure or vapour pressure of

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[1] P. 44.

the solution. This dissociation is greater in dilute solution, just as the dissociation of gaseous substances, when taking place with an increase in the number of molecules, is greater at low pressures.

The factor i gives the ratio of the total number of particles in solution to the number that would be expected to be present, judging from the molecular weight and quantity dissolved of the substance. What the nature of these simpler constituents is will be shown in Chapter VI.

Literature.

Le Blanc. *Electrochemistry.*

CHAPTER V

IONIC TRANSPORT DURING ELECTROLYSIS

1. Mechanism of Migration of Ions

In Chapter III we dealt with the phenomena occurring at the electrodes when electricity enters or leaves an electrolyte, and saw how proportionality exists between the quantity of electricity and the quantity of matter with which it is associated. In Chapters V and VI we must consider the mechanism of the passage of electricity *through* the electrolyte.

Views of Grotthuss.—Our present ideas on this subject sprang originally from Grotthuss. Previously to him, the view was that when a current passed through an electrolyte, liberating positive and negative constituents at the electrodes, these positive and negative constituents arose from the *same* molecules. Each molecule of the electrolyte was therefore separately decomposed, and furnished its decomposition products simultaneously at the electrodes.

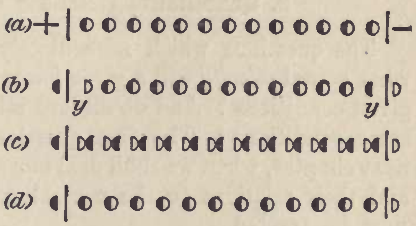

Fig. 9.

But according to Grotthuss this was incorrect. On applying a voltage to electrodes dipping in an electrolyte, the molecules were first polarised, all their positive parts becoming turned towards the negative pole, and *vice versa*, as in Fig. 9 (*a*). When the voltage exceeded a certain value, decomposition commenced, and the positive and negative ions nearest the negative and positive poles respectively were torn away from their molecules, the charge passing off through the electrodes, and the material part being liberated, as in Fig. 9 (*b*).

The next stage was an interchange of the different ions along the whole series of polarised molecules, resulting in the neutralisation of the free ions *y y* according to Fig. 9 (*c*). Lastly the molecules were twisted round under the influence of the electric field, and assumed the position (*d*), similar to (*a*), ready for the cycle to recommence.

Views of Faraday. — In Grotthuss' conception, therefore, the opposed attractive and repulsive actions of the two poles form the essential feature. Faraday modified this idea and made it less rigid. He regarded the applied voltage as simply influencing the forces of affinity which play between the electro-positive and electro-negative parts of the molecules, and causing the oppositely charged ions to wander more markedly in one direction than another. *The essential cause of the passage of electricity through the electrolyte lies as much, therefore, in the nature of the dissolved substance as in the presence of the electrodes*, which are regarded by Faraday merely as 'doors' by which electricity enters or leaves the electrolyte, and only capable of influencing the *direction* of motion of the different ions.

According to him, it is simplest and 'most philosophical' to state that, during electrolysis, such substances as oxygen, chlorine, and iodine wander (*migrate* or are *transported*) towards the positive pole, and bodies like hydrogen and the metals towards the negative pole. This is virtually the view adopted to-day of the transport of electricity through an electrolyte.

2. Quantitative Relations of Ionic Migration I

The questions which immediately arise are the following. With what actual *velocity* will a given ion migrate towards an electrode under given conditions ? And do all ions migrate *at the same rate* under the same conditions ? The first question cannot be answered until the next chapter, when we shall deal more fully with the nature of the ions, and their relations to the neutral molecules. The second point will now be treated.

Effect of Differing Ionic Velocities. — There is no reason *a priori* for assuming that the different ions will migrate at the same rate under the same conditions. As a matter of fact they do not. Let Fig. 10 (*a*) represent the successive stages of an electrolysis, supposing that the ions *do* all move at equal rates, and let the vertical dotted line represent a diaphragm, dividing the cell into two parts. Then we see that the diminution of concentration is the same at any moment in the two parts of the cell. Thus, when two molecules have been discharged, the concentration in both anolyte and catholyte has fallen by one molecule ; with four molecules discharged, the concentration has decreased by two molecules in each compartment. If, therefore, the ions taking part in the electrolysis move at the same rate under the electric field, and if nothing takes place at anode and cathode beyond the mere discharge of ions, the concentration changes produced at the electrodes will be identical.

But suppose, on the contrary, that the oppositely charged ions move at different rates, as actually occurs. Let the positive ions have twice the velocity of the negative ions. Then Fig 10 (*b*) will represent the course of electrolysis. And we see that the diminution in concentration in the anode liquid from which the more rapidly moving positive ions are migrating is greater than the diminution in the catholyte. Moreover, the ratio of these two diminutions of concentration is 2 : 1, identical with the ratio of the relative velocities of the ions. Thus, when three molecules have been discharged, the catholyte concentration has decreased by one molecule, the concentration at the anode by two molecules.

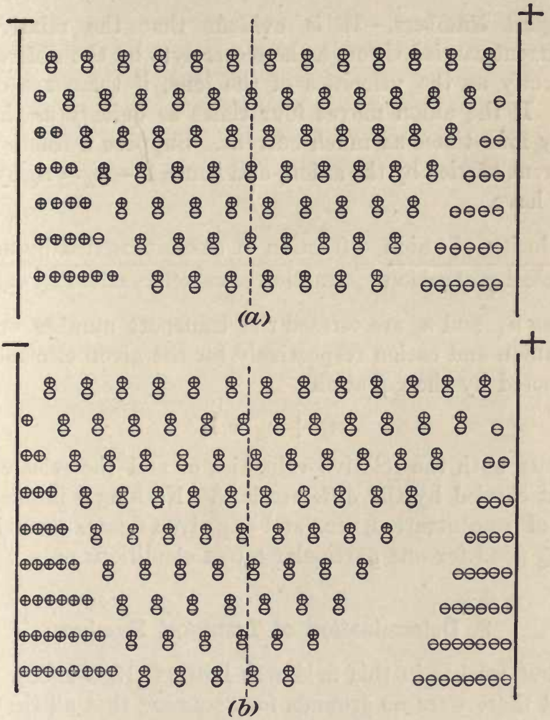

FIG. 10.

This is a perfectly general result. If the cation moves five times as fast as the anion, the diminution in concentration in the anode compartment will be five times as great as that in the cathode compartment, and we can write

$$\frac{\text{Diminution in concentration at cathode}}{\text{Diminution in concentration at anode}} = \frac{\text{velocity of anion}}{\text{velocity of cation}} = \frac{u_A}{u_C}$$

In this way, therefore, by measuring the concentration changes at the electrodes during electrolysis, we can get a value for the ratio of the velocities of the different ions.

If, for example, in the electrolysis of hydrochloric acid at platinum electrodes, it were found that the diminution of acidity in the anolyte corresponded to a normality of 0·21 and in the catholyte to a normality of 0·046, we should have

$$\frac{u_A}{u_C} = \frac{0{\cdot}21}{0{\cdot}046} = 4{\cdot}56.$$

Transport Numbers.—It is evident that the relative fractions of the current carried through the electrolyte by the different ions will vary directly as the velocities of the ions, if these are of the same valency. If the anion moves four times as quickly as the cation, it will carry four times as much current. Suppose a fraction n_A of the total current carried by the anion, and hence $1 - n_A = n_C$ by the cation. Then we have

$$\frac{u_A}{u_C} = \frac{\text{velocity of anion}}{\text{velocity of cation}} = \frac{\text{fraction of current carried by anion}}{\text{fraction of current carried by cation}} = \frac{n_A}{n_C}$$

The values n_A and n_C are termed the **transport number** or **migration ratio** of anion and cation respectively for the given electrolyte. They are connected by the equation

$$n_A + n_C = 1,$$

and express both the relative velocities of and the relative fractions of current carried by the different ions. Nothing is implied as to the influence of concentration, etc., and any given figures must be regarded as holding good for one particular set of conditions only.

3. Determination of Transport Numbers

The first worker in this field was Hittorf (1853–1859), who recognised that there were no grounds for assuming that all the ions would move at the same rate. He carried out many careful determinations of transport numbers, and was able to make important deductions on the constitution of aqueous solutions of certain salts. The principle on which his measurements were based is essentially the one discussed—the determination of concentration changes produced near the electrodes during electrolysis. The forms of apparatus he used have now been superseded by more accurate and convenient ones. Hittorf had no high voltages at his command, and was unable therefore to use long columns of liquid in his experiments. To avoid diffusion effects, he employed diaphragms, the use of which is open to objection. And he was further unable to produce large differences in concentration.

A more modern but nevertheless simple type of apparatus, used by

Nernst and Loeb,[1] is shown in Fig. 11. Suppose the transport numbers of a silver nitrate solution are being determined. The cathode, contained in the bulb on the right, consists of silver foil. The anode is a spiral of silver wire, fused into a thin glass tube. It is introduced into the limb on the left through the rubber stopper A. The level of the electrolyte is indicated in the figure. The apparatus is put in series with a current source and a silver coulometer, and a suitable quantity of electricity, measured by the coulometer, passed through. When the experiment is completed, the heavy anode liquor in the bottom of the long limb is blown off through C by means of the tube at B, and collected separately. The 'middle' liquor, which in an actual experiment might occupy the space between *a* and *b*, and finally the lighter cathode liquor are withdrawn and collected, in each case separately. These three fractions are then weighed and analysed. Other types of apparatus have been employed. That of H. Jahn and Hopfgartner[2] might particularly be mentioned.

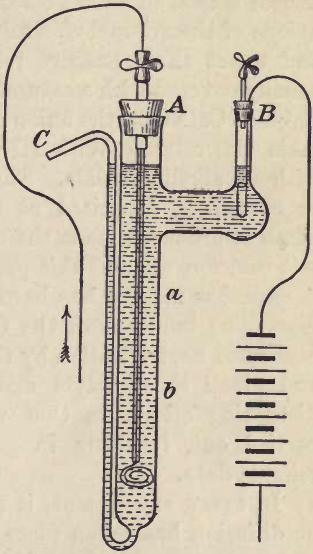

Fig. 11.—Transport Number Apparatus.

Before considering some actual determinations in detail, there are certain points to be noted. It is undesirable for accurate determinations that gases should be evolved at either electrode, as the different parts of the electrolyte may thereby be mixed. If the migration ratios are being determined for a substance like silver nitrate or copper sulphate, obviously no question arises of disturbances occurring at the cathode. But if an insoluble anode be used, free acid will be formed, and oxygen evolved. As the $H^{\cdot}$ ion of the acid travels far more quickly than any other cation, the relations may be obscured not only by mixing due to the gas, but also by an appreciable fraction of the current being carried by the $H^{\cdot}$ instead of by the $Ag^{\cdot}$ or $Cu^{\cdot\cdot}$ ions.

The remedy is to use a soluble anode of the metal whose ion is already in solution—in the present case silver or copper. The complication thereby introduced must be allowed for in the subsequent calculation. Sometimes it is impossible to use such an anode, as in the determination of the transport numbers of a salt of an alkali metal. In

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[1] *Zeitsch. Phys. Chem.* **2**, 948 (*1888*).

[2] *Zeitsch. Phys. Chem.* **25**, 119 (*1898*).

that case an anode of amalgamated zinc or cadmium is used, a device employed by Hittorf. Both zinc and cadmium ions, more particularly the latter, move very slowly in the electric field, will not catch up the alkali metal ions, and consequently will not disturb the transport relations.

Similar complications can occur at the cathode if the transport numbers of an acid or of a salt of an alkali metal are being determined. The evolved hydrogen stirs up the liquid, and any free OH' ions produced, which, like the $H^{\cdot}$ ions, can travel very quickly, catch up the anions of the original electrolyte which are moving towards the anode, and upset the transport relations. To avoid this, the cathode is usually covered with a saturated layer of some very soluble salt, such as $ZnCl_2$ or $Cu(NO_3)_2$, the anion of the salt being identical with that in the main electrolyte. With HNO_3, $Cu(NO_3)_2$ would be used, and $ZnCl_2$ with an alkaline halide. This done, no hydrogen is formed, as zinc or copper is deposited at the cathode; and consequently no free alkali is produced, as is the case in the electrolysis of an alkali metal salt solution without this precaution.

Another method has been introduced by Noyes,[1] to counteract the disturbing influence of the OH' and $H^{\cdot}$ ions. This consists in their continued neutralisation by the addition of measured quantities of acid and alkali to catholyte and anolyte respectively. By eliminating disturbing effects in that way, long-continued experiments can be carried out, resulting in greater concentration changes and more reliable data.

In every experiment, it must be definitely shown that no mixing or diffusion has taken place between the anode and cathode liquors; and consequently the middle layer must always be unchanged in composition after the experiment, otherwise the results of the determination must be rejected.

Examples.—We append a couple of examples. The second shows the type of calculation which exact experiments furnish.

1. In the determination of the transport numbers of a dilute $AgNO_3$ solution (1·98 grams $AgNO_3$ in 100 grams solution) it was found that the increase of silver in the anolyte was 0·1298 gram (using a silver anode) and the decrease of silver in the catholyte 0·1300 gram. The middle solution was unchanged in composition. 0·2470 gram of silver was deposited in a silver coulometer placed in circuit. What are the transport numbers for the given solution?

As 0·2470 gram of silver has been deposited in the silver coulometer, the same weight has been deposited in the cathode compartment of the migration apparatus. But the decrease in the catholyte is only 0·1300 gram. Hence $(0·2470 - 0·1300 = 0·1170)$ gram has migrated into the cathode compartment from the anolyte. Similarly 0·2470 gram of silver has been dissolved from the anode, and as the increase of silver in the anode compartment is only 0·1298 gram, it follows that $(0·2470 - 0·1298 = 0·1172)$ gram of silver has migrated to the cathode. Taking a mean of these values, we find that as a result of the experiment, the electrode reactions being eliminated, 0·1171 gram Ag has been transferred

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[1] *Zeitsch. Phys. Chem.* **36**, 63 (*1901*).

from anode to cathode compartment. If the $Ag^{\cdot}$ ions had carried the total current, 0·2470 gram of silver would have been transported. Therefore

$$\frac{n_A}{n_A+n_C}=\frac{n_{Ag}}{n_{NO_3}+n_{Ag}}=\frac{0{\cdot}1171}{0{\cdot}2470}=0{\cdot}474$$

Hence
$$n_{Ag}=0{\cdot}474$$
$$n_{NO_3}=1{\cdot}0-0{\cdot}474=0{\cdot}526.$$

2. The transport numbers of a dilute K_2SO_4 solution are determined by the method of Noyes. The catholyte analysed after the experiment contained 8·4394 grams K_2SO_4, and weighed 493·12 grams. Of this weight 60·78 grams represent dilute H_2SO_4 added to maintain neutrality, and to compare the final K_2SO_4 concentration with that at the start of the experiment this is subtracted.

Then another correction must be made. $K^{\cdot}$ ions have entered the cathode compartment, SO_4'' ions have left it, hydrogen gas has been evolved. The net result of these effects is calculated to be a decrease in weight of 0·14 gram, and is therefore an additive correction. The corrected weight of the catholyte comes to $(493{\cdot}12-60{\cdot}78+0{\cdot}14=432{\cdot}2)$ grams. The amount of K_2SO_4 originally present in this was $(432{\cdot}2\times0{\cdot}017247=7{\cdot}4591)$ grams. Hence the increase of K_2SO_4 in the cathode compartment is $(8{\cdot}4394-7{\cdot}4591=0{\cdot}9803)$ gram, or, plus another small correction, 0·9816 gram. The equivalent weight of K_2SO_4 is 87·13, and hence the increase, expressed in equivalent weights, is $\frac{0{\cdot}9816}{87{\cdot}13}=0{\cdot}01126$.

During the experiment 2·4594 grams of silver were precipitated in the silver coulometer. Expressed as equivalents, this is $\frac{2{\cdot}4594}{107{\cdot}9}=0{\cdot}02279$. If n_K were unity, the increase in the equivalent concentration of the K_2SO_4 would have been the same. Thus

$$n_K=\frac{0{\cdot}01126}{0{\cdot}02279}=0{\cdot}4941.$$

4. Quantitative Relations of Ionic Migration II

Migration ratios have been studied in recent years by Noyes and by H. Jahn and his pupils (Bein, Tower, etc.), and many have also been measured by Steele and Denison, using a method essentially different in principle from the one described above. The results of these investigations substantially confirm Hittorf's work of half a century earlier.

Before undertaking any extensive measurements, Hittorf investigated the effect of current strength, concentration, and temperature on the transport numbers of certain salts. He found first of all that the influence of changes in current strength, when diffusion and heating effects were eliminated, was negligible. Thus with a certain copper sulphate solution, using currents of ratios 113 : 420 : 958, he found as values of n_{Cu} — 0·291, 0·285, 0·289. The quantity of any ion transported in an experiment depends only then on the quantity of electricity which passes through the electrolyte, not on the rate at which it is sent through. Hittorf then showed that with certain very simple salts, such as the alkaline halides, the transport ratios were only very slightly dependent on concentration, but that as a rule they showed variation in the stronger solutions, and only became constant at a certain limiting dilution. Thus potassium chloride and silver nitrate solutions gave the following values :—

Parts of water to 1 part KCl	n_{Cl}	Parts of water to 1 part $AgNO_3$	n_{Ag}
6·6	0·516	2·48	0·532
18·4	0·514	5·18	0·505
39·4	0·515	14·5	0·475
		49·44	0·474
254	0·515	104·6	0·474
		247·3	0·476

Sometimes the change in the transport numbers with change in concentration was very marked, and we shall presently see the important deductions Hittorf was able to make in those cases. He also investigated the effect of temperature on transport numbers. Owing to his method being insufficiently exact, he could detect no marked effect. From later measurements, however, it is now known that, as the temperature is raised, the rates of migration of most ions, particularly monovalent ones, tend to become equal to one another, and consequently the transport numbers of the salts tend to become more nearly 0·5 at higher temperatures (Kohlrausch).

A table of the general numerical results obtained by different workers is given in Appendix I. Here we need only remark on the low value of n_A for acids, indicating a very high velocity for the hydrogen ion, and also how high the value of n_{OH} is compared with n_A for other anions.

5. Applications of Ionic Migration Phenomena

All the above considerations relate to electrolytes containing one salt only in solution. The important question of how the current is carried in solutions containing a mixture of two or more salts will be referred to in the next chapter, after dealing more fully with the condition of the dissolved molecules in an electrolyte. Our chief interest in the subject of ionic migration lies, indeed, in the light it throws on this matter and in the essential rôle it has played in the development of the theory of electrolytes, as we now know it.

Application to Chemical Questions.—But, that apart, the study of transport relations has also often led directly to very important deductions concerning the constitution of electrolytic solutions. Thus Hittorf determined the transport ratios for a solution of $SnCl_4$, which is acid in reaction. He found the value of n_{Cl} to be practically identical with the value it would have if the $SnCl_4$ were completely hydrolysed according to the equation

$$SnCl_4 + 4H_2O \rightleftarrows Sn(OH)_4 + 4HCl$$

and concluded that such was the case. His view was later confirmed by another (thermochemical) method.

Again, when electrolysing potassium ferrocyanide solutions, Daniell found that the iron concentrated at the anode, and therefore must be associated with negative, not positive electricity. He accordingly gave the salt the formula $\overset{++++}{K_4}\ \overset{----}{(FeCy_6)}$ which it still retains, in place of the previously used double salt formula $4KCy, FeCy_2$.

Similarly Hittorf found that the platinum in sodium chloroplatinate wandered to the anode during electrolysis, and proposed for the salt the modern formula Na_2PtCl_6, in place of the old $2NaCl, PtCl_4$. And by observing in each case the movement of the blue colour during electrolysis, it can be demonstrated that the copper in an ammoniacal copper sulphate solution is present as a complex cation, but in an alkaline copper tartrate solution as a complex anion.

Finally, changes in constitution accompanying changes in concentration can be followed by the same method. Thus a dilute copper bromide solution is blue; as it is concentrated it becomes green, brownish green, and finally, in very strong solutions, a dark brown. Denham[1] has shown this variation to be accompanied by a simultaneous change in the value of n_{Cu}. This is about 0·44 for dilute solutions, but rapidly decreases, changes sign, and reaches a value of about $-0{\cdot}4$ in a 5 N. solution. It has been shown that the value of n_c is given by the diminution of the cation concentration around the anode (disturbances due to electrode reactions eliminated). A negative transport number can only mean that the copper concentration increases at the anode during electrolysis. As in the above cases, we therefore conclude that in these solutions a portion of the copper, greater the stronger the solution, is present as complex anion.

It is seldom that transport relations have any *direct* bearing on a technical electrochemical process. If electrolysis takes place in a solution which is kept at rest, concentration changes result near the electrodes, partly due to unequal rates of migration. But such concentration differences are undesirable. They increase the voltage required by the cell, and may further lead to the production of impure products at the electrodes. For these reasons (and others) the electrolyte is nearly always continually circulated through the cells, or in some other way mixing is effected. Concentration changes are thus as far as possible destroyed, and hence calculations involving transport numbers usually find no application. In a few cases this is not so.[2]

Literature

Le Blanc. *Electrochemistry.*

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[1] *Zeitsch. Phys. Chem.* **65**, 641 (*1909*).

[2] See theory of alkali-chlorine cells, p. 357.

CHAPTER VI

CONDUCTIVITY OF ELECTROLYTES—THEORY OF ELECTROLYTIC DISSOCIATION

1. Specific Conductivity

When a current flows through an electrolyte, a certain amount of energy is consumed and degraded into heat, quite apart from what happens at the electrodes. This is due to the resistance of the electrolyte. Since all ways in which electrical energy is consumed during an electrolysis are of importance to the technical electrochemist, the subject of the resistance of electrolytes, apart from its wider theoretical significance, demands a thorough treatment.

The resistance of an electrical conductor depends not only on the material of which it is made, but also on its dimensions, and before the resistances of two substances can be compared all questions of relative size or shape must be eliminated. The resistance of a conductor of uniform cross section is given by

$$R = r \cdot \frac{l}{a},$$

where r is a constant, depending on the particular material and on the units used, l the length, and a the cross-section. If l and a be made unity, we have

$$R = r;$$

r is therefore the resistance of a unit cube of the conductor, and is termed the **specific resistance** of the substance. If the ohm and the centimetre be employed, it expresses the resistance of the material in ohms per centimetre cube.

But generally electrolytes are not so much compared by means of their specific resistances as by their **specific conductivities.** Certain important theoretical relations are thereby rendered clearer. Just as the conductivity of a substance is the reciprocal of its resistance, so is its specific conductivity the reciprocal of its specific resistance.

If the latter be denoted by r and the specific conductivity by κ, we have

$$\kappa = \frac{1}{r}$$

where κ is given in reciprocal ohms. Just as the specific resistance of a substance is the voltage which must be applied to two opposite faces of a centimetre cube in order that a current of one ampere may flow across the cube, so the specific conductivity is the current which would flow across such a cube on application of a potential difference of one volt to two opposite faces. It is in fact given by

$$\frac{\text{current per unit area}}{\text{potential fall per unit length}} = \frac{\text{current density}}{\text{potential gradient}}.$$

2. Determination of Conductivity

General.—Conductivity determinations are readily carried out by means of Wheatstone's Bridge, shown in Fig. 12. ACB and ADB are two paralleled circuits through which current flows from a source E. The resistance R between A and C is known (usually a resistance box) and can be regulated; the resistance x is unknown.

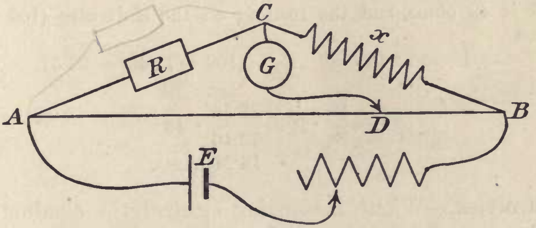

FIG. 12.—Wheatstone's Bridge.

The branch CD containing a galvanometer or some other form of current detector is fixed at C, but makes connection by means of a sliding contact D with the stretched uniform graduated wire AB. This usually consists of platinum-iridium or of constantan, a hard, untarnishable, copper-nickel alloy, and is one metre in length. By moving D, the relative sizes of the resistances AD and DB can be altered at will.

Now the two ends of the circuits ACB and ADB have common potentials. Hence, if the potential at A be higher than that at B, there will be a gradual potential fall along both circuits in the direction of A to B, and every point in the circuit ACB will have a corresponding point in the circuit ADB at the same potential. Suppose now the contact D is moved along the wire AB. As long as the potentials of C and D differ, a current will flow one way or another through the circuit CD, and will be indicated by the instrument G. When the potentials of C and D are identical no current will flow. In making a measurement, this point is found by suitably regulating R and by moving D, and the reading on the slide-wire scale taken. The wire being uniform, the relative resistances of the branches AD and DB are at once obtained. Let them be R_1 and R_2 respectively, and suppose the currents in the branches ACB and ADB to be I_1 and I_2 respectively. Then, if E_1 and E_2 are the potential falls AC = AD, and CB = DB, we have

$$E_1 = I_1R \qquad E_2 = I_1x$$
$$E_1 = I_2R_1 \qquad E_2 = I_2R_2$$

Or

$$\frac{I_1}{I_2} = \frac{R_1}{R} \text{ and } \frac{I_1}{I_2} = \frac{R_2}{x}$$

And finally

$$\frac{R_1}{R_2} = \frac{R}{x}$$

from which equation x is calculated.

Thus if R is 48 ohms, and the reading on the slide-wire (100 divisions) is 72·46, we have

$$R_1 = 72{\cdot}46 \qquad R_2 = (100 - 72{\cdot}46) = 27{\cdot}54,$$

and therefore

$$x = \frac{R_2}{R_1} \cdot R = \frac{27{\cdot}54}{72{\cdot}46} \cdot 48$$
$$= 18{\cdot}24 \text{ ohms.}$$

Of Electrolytes.—When measuring electrolytic conductivities by this method, several special precautions must be taken. The use of direct current would decompose the electrolyte. Its actual resistance would thereby change; but, more important still, its apparent resistance would alter very considerably owing to losses of potential at the electrodes caused by decomposition. These *polarisation*[1] effects would entirely destroy the accuracy of a conductivity determination. A small induction coil (only needing two volts at its primary terminals) which furnishes *alternating current* is consequently employed. With alternating current, a galvanometer is of course useless. A convenient current detector is furnished by an ordinary telephone. On reaching the equipotential point on the slide-wire, a very sharp minimum of sound can be obtained, using a good coil. As the movement of the sliding contact tends to obscure this, it is customary to connect the

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[1] See Chap. IX.

telephone to the ends of the slide-wire, and to put the coil between C and the sliding contact. The final arrangement, therefore, is as in Fig. 13, where F represents the primary cell, H the induction coil, and K the telephone. The alternating E.M.F is applied at C and D, the current traversing the parallel circuits CAD and CBD. R and D are adjusted until the telephone indicates a null potential difference between A and B. Then

$$\frac{\mathrm{AD}}{\mathrm{BD}} = \frac{\mathrm{R}}{x}.$$

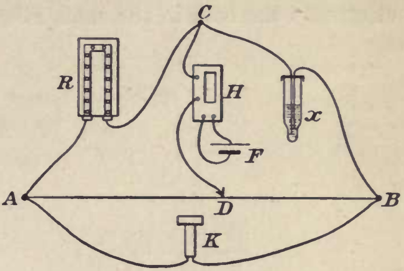

FIG. 13.—Apparatus for measuring Electrolytic Conductivities.

To deduce the specific conductivity of a solution directly from a measurement carried out on it, the vessel used must be of exact geometrical shape, its dimensions very exactly determined, and the electrodes very carefully inserted. This is tedious, and there are further slight uncertainties as to whether the current is passing through the liquid quite uniformly over the measured path, etc. For these reasons it is best to use a more convenient vessel whose dimensions need not be exactly known, but in which the experimental conditions can be subsequently reproduced without fail. Its conductance is measured, using a solution whose specific conductivity has been determined once for all. This done, a further determination and a comparison will furnish the specific conductivity of any other solution. If the conductance of the vessel filled with the standard and the unknown electrolyte be respectively A and A′, and if the specific conductivity of the standard electrolyte be known to be κ_0, we have for κ the unknown specific conductivity

$$\kappa = \frac{\kappa_0}{\mathrm{A}} \cdot \mathrm{A}' = \mathrm{KA}'.$$

K is termed the *cell constant* for the particular vessel. When once determined, the specific conductivity of any liquid can be directly calculated from a conductivity measurement, using the above equation. Various solutions are used as standards. The commonest are N. potassium chloride and maximal or best conducting sulphuric acid. This is 30 per cent. by weight and of $\delta = 1{\cdot}223$ at 18°, at which temperature the specific conductivities of these two solutions are respectively 0·09822 and 0·7398 reciprocal ohms per centimetre cube.

Resistance vessels of various types are used, two being illustrated in Fig. 14. In (*a*) the body is of hard glass, which is only slightly attacked by aqueous solutions. The electrodes are of stout platinum, cemented into glass tubes, and lie horizontally, one above the other. The tubes pass through the ebonite lid, where they are securely cemented and are further connected by sealing-wax at A. In this way the electrodes are held in the same relative positions to one another, and the cell-constant is prevented from altering. Before use, the electrodes are platinised with a solution containing 3 per cent. of chlorplatinic acid and $\frac{1}{40}$ per cent. of lead acetate, freed from platinum salts by electrolysis with dilute sulphuric acid, and finally thoroughly washed with distilled water. Polished platinum electrodes give a far poorer sound minimum with the telephone when at the right point on the bridge, particularly with solutions of good conductivity. Fig. 14 (*b*) represents a type of vessel that can be conveniently dipped into a large working electrolysis tank, when determinations must be made on the spot.

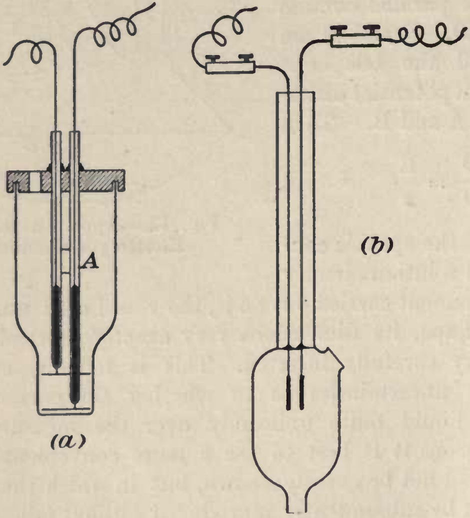

FIG. 14.—Conductivity Vessels.

In carrying out precision conductivity measurements, great care must be taken to purify the water used. Even when all dissolved salts, ammonia, and carbon dioxide have been removed, there still remains a very slight residual conductivity. This is due to the water molecules furnishing minute traces of $H^{\cdot}$ and OH' ions which carry the current.

Conductivity of a Working Cell.—The internal resistance of a cell which has no current passing through it can be measured in the way described. If, however, the internal resistance of a cell through which current is passing or of a cell which is actually furnishing current is desired, a different arrangement must be used. The most important methods for effecting this are those of Block[1] and of Nernst and Haagn.[2] Fig. 15 illustrates the former method applied to a primary cell which is furnishing current. A is the cell; B, C, D, resistances of

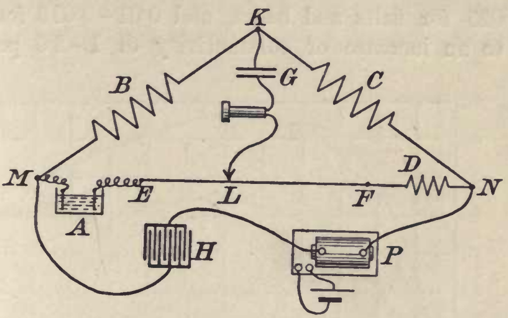

FIG. 15.—Conductivity Measurement on a Working Cell.

known value, capable of regulation. EF is the slide-wire. G and H are condensers in the telephone and induction coil circuits respectively. The direct current from A travels along the circuit ABCDFE, but cannot enter the branches KL and MHN because of the condensers G and H. These condensers, however, do not hinder the passage of the alternating current from P, and thus the measurement of conductance is carried out quite independently of the direct current from A. When a balance is obtained by moving L as usual, we have the following relation of resistances :—

$$\frac{B}{A + (EL)} = \frac{C}{D + (LF)}$$

from which the resistance of A is directly got.

Conductivity, Concentration and Temperature.—The technique of conductivity measurements has been chiefly worked out by Kohlrausch, to whom we also owe the great bulk of our existing data, and the discovery of several very important relations dealing with conductivities. Besides depending on the nature of the electrolyte and the solvent, the conductivity of a solution also depends on its concentration and on the temperature.

The general effect of an increase of concentration is an increase in specific conductivity up to a maximum point and a subsequent decrease.

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[1] *Zeitsch. Phys. Chem.* **58**, 442 (*1907*).

[2] *Zeitsch. Phys. Chem.* **23**, 97 (*1897*). *Zeitsch. Elektrochem.* **2**, 493 (*1896*).

This behaviour is well shown in Fig. 16. Its significance will be seen later.

The specific conductivity of an electrolyte increases almost linearly with temperature. We can write

$$\kappa_\theta = \kappa_{18}[1 + a(\theta - 18)].$$

a is 0·02–0·025 for salts and bases, and 0·01 – 0·016 for acids, corresponding to an increase of conductivity of 1 – 2·5 per cent. per degree. This relation holds good for temperatures considerably above 100° (Noyes). For exactly comparable measurements, identity of working temperature must be carefully ensured. It is also obvious that, from the point of view of lessened resistance, it is advantageous in a technical electrolytic process to work at as high a temperature as possible.

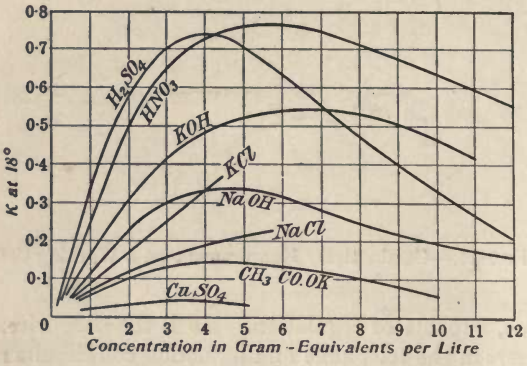

FIG. 16.

The values of a few specific conductivities and specific resistances are given in Table VIII. They hold good for 18°.

TABLE VIII

Electrolyte	κ in reciprocal ohms	r in ohms
1 N. H_2SO_4	0·20	5·0
5 N. H_2SO_4	0·68	1·47
1 N. KOH	0·185	5·41
2 N. KOH	0·25	4·0
4 N. NaCl	0·197	5·08
1 N. $AgNO_3$	0·068	14·7
1 N. $CuSO_4$	0·025	40
2 N. Na_2CO_3	0·079	12·7

3. Equivalent Conductivity

The consideration of specific conductivities suffices for practical purposes. When known, we can tell whether much Joule heat or not will be produced on passing a current through an electrolyte. But for a closer consideration of the mechanism of electrolytic conduction, and the wider question of the constitution of electrolytes, it is better to use a different unit for expressing conductivities, that of **equivalent conductivity,** the conductivity due to one equivalent weight of dissolved substance. If for a given solution we denote by η the number of equivalents per c.c. (it will of course be a small fraction), and if Λ represents equivalent conductivity, we have

$$\Lambda = \frac{\kappa}{\eta},$$

or better, if v is the number of c.c. of solution containing one gram-equivalent—that is the dilution in c.c.—we have

$$\Lambda = \kappa v.$$

To render the relations of these different magnitudes quite plain, let us consider a conductivity vessel consisting of a tall vertical rectangular prism of unlimited length, open at the top, and one centimetre square in plan section ABCD (Fig. 17). Suppose two opposite vertical sides ADE and BCF to be constructed of platinum and to act as electrodes, the other two sides being of some non-conducting material (glass). If one c.c. of electrolyte be poured into this vessel, and the conductance measured, the result will be the *specific conductivity* of the solution, as the height of the liquid in the vessel is one cm. and the current consequently passes across a centimetre cube. If more solution be poured in, the conductance of the vessel will continually increase, proportionally to the quantity added. When finally the height of liquid in the cell becomes v cm., v c.c. of electrolyte, and therefore one gram-equivalent of dissolved material, are present. The conductance of the vessel will be v times its original value (the specific conductivity), equal therefore to the *equivalent conductivity* in accordance with the above equation.

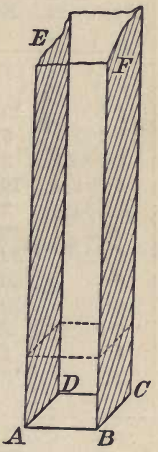

FIG. 17.

Equivalent Conductivity at Infinite Dilution.—We can see that Λ has a twofold dependence on v. Not only is it directly proportional to the latter, but its other factor, the specific conductivity κ, decreases as v increases, except in very strong solutions.[1] As a matter of fact the work of Kohlrausch and others has shown

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[1] See p. 64.

that the equivalent conductivity increases with the dilution, at first quickly, then less rapidly, and finally in many cases asymptotically reaches a maximum and becomes practically constant. In other cases the final figure cannot be experimentally observed, the solutions becoming too dilute for accurate measurement. This maximum value is termed the **equivalent conductivity at infinite dilution,** and is denoted by Λ_∞. We can write in fact

$$\Lambda = a\Lambda_\infty$$

where a is a fraction less than unity, altering with the dilution and expressing the ratio of the equivalent conductivity to the maximum possible equivalent conductivity, that at infinite dilution.

Table IX contains a number of values of Λ_∞ and Λ for different electrolytes at various dilutions at 18°.

TABLE IX

Normality of solution	v in litres	KCl	$AgNO_3$	H_2SO_4	HCl	Acetic Acid	KOH
	∞	130·1	115·80	398·5	395·2	—	238·7
0·0001	10^4	129·07	115·01	—	—	107	—
0·0002	$5{\cdot}10^3$	128·77	114·56	—	—	80	—
0·0005	$2{\cdot}10^3$	128·11	113·88	368	—	57	—
0·001	10^3	127·34	113·14	361	377	41	234
0·005	$2{\cdot}10^2$	124·41	110·03	330	373	20·0	230
0·01	10^2	122·43	107·80	308	370	14·3	228
0·02	50	119·96	105·60	286	367	10·4	225
0·05	20	115·75	99·50	253	360	6·48	219
0·1	10	112·03	94·33	225	351	4·60	213
0·5	2	102·41	77·5	205	327	2·01	197
1	1	98·27	67·6	198	301	1·32	184
2	0·5	92·6	—	183	254	0·80	160·8

The conducting power then of a gram-equivalent weight of electrolyte increases with the dilution, finally reaching a maximum value measured by Λ_∞, the equivalent conductivity at infinite dilution.

Ionic Conductivity.—The next step—one of first importance—was taken by Kohlrausch. He showed that these equivalent conductivities at infinite dilution split up into two additive parts, which can be referred to cation and anion respectively. Moreover, the **equivalent ionic conductivity** thus deduced for a particular ion from measurements on certain salts is independent of the salts and *characteristic of that ion,* and if used to calculate the equivalent conductivity at infinite dilution of other different salts will give correct results. That is, Kohlrausch showed that Λ_∞ for every electrolyte is an additive function of the ionic conductivities of the different ions. Denoting these ionic conductivities by l_A and l_C, we have

$$\Lambda_\infty = l_A + l_C.$$

The values of a number of ionic conductivities at 18° are given below :—

$Li^{\cdot}$	33·4	$H^{\cdot}$	318 ?	ClO_3'	55
$Na^{\cdot}$	43·6	OH'	174 ?	NO_3'	61·8
$K^{\cdot}$	64·7	Cl'	65·4	$\frac{1}{2}\,SO_4''$	68·4
$Ag^{\cdot}$	54·0	Br'	67·6	$\frac{1}{2}\,Mg^{\cdot\cdot}$	46
$NH_4^{\cdot}$	64	I'	66·4	$\frac{1}{2}\,Ca^{\cdot\cdot}$	51·8
				$\frac{1}{2}\,Cu^{\cdot\cdot}$	47·3
				$\frac{1}{2}\,Pb^{\cdot\cdot}$	61·3

Table X contains values of Λ_∞ calculated from the above figures, and values extrapolated from experimental results. The agreement is excellent.

TABLE X

Salt	l_A	l_C	$l_A + l_C$	Λ_∞ extrapolated
KBr	67·6	64·7	132·3	132·3
KOH	174	64·7	238·7	not < 234
$KClO_3$	55·0	64·7	119·7	119·7
NaCl	65·4	43·6	109·0	108·99
$AgNO_3$	61·8	54·0	115·8	115·8
NH_4NO_3	61·8	64	125·8	not < 126·1
$\frac{1}{2}Na_2SO_4$	68·4	43·6	112·0	not < 110·5
$\frac{1}{2}MgCl_2$	65·4	46	111·4	not < 109·4 not < 115·1
$\frac{1}{2}CaCl_2$	65·4	51·8	117·2	not < 115·2

4. Electrolytic Dissociation Theory

Before proceeding further, a brief review of what we already know of the constitution of electrolytes and the mechanism of conduction may be given. We regard dissolved molecules of electrolytes as composed of two oppositely charged halves—the ions—of opposed chemical nature.[1] When a current passes, these ions travel towards the electrodes, and lose their electricity, the material part being set free. The velocities with which different kinds of ions travel towards their respective electrodes under otherwise identical conditions are not usually the same ; the *relative* velocities of the oppositely charged

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[1] Chap. III.

[2] Chap. V.

ions in any salt can be determined by migration experiments. The conducting power of a gram-equivalent of an electrolyte increases with the dilution, finally reaching a maximum.[1] (Arrhenius, one of the chief workers on conductivities, divided the dissolved molecules in an electrolyte into two classes, the *active*, which conducted the current, and the *inactive*, which did not. The proportion of active molecules increased with increasing dilution, and this fraction he termed the *coefficient of activity*, and measured it by the ratio $\frac{\Lambda}{\Lambda_\infty}$. It was therefore identical with a in the equation $\Lambda = a\Lambda_\infty$.[2]) The values of Λ_∞ for different electrolytes are additive functions of characteristic equivalent ionic conductivities belonging to the different ions.[3] Finally solutions of strong electrolytes have abnormally high osmotic pressures,[4] indicating that a dissociation of the dissolved molecules into simpler ones has taken place, a dissociation moreover which increases with the dilution and appears to reach a limiting value, in both respects just as the equivalent conductivity does.

These different facts were correlated by Arrhenius in 1887 by means of his **Electrolytic Dissociation Theory**—a generalisation of the utmost importance and fruitfulness. Several physicists (Clausius, Helmholtz, Planck) had already suggested that solutions of electrolytes contained *free charged ions*, and that only such ions were capable of conducting the current. At the same time, the number of ions so split off from the neutral molecules was regarded as comparatively small. Arrhenius extended this conception, stated that the dissolved molecules were often *very largely* dissociated into their charged ions, which could then act to a great extent independently, pointed out several independent means of measuring the degree of this dissociation, and showed that values obtained by these different methods gave concordant results.

The first essential point in Arrhenius' theory is that the fraction of the dissolved molecules thus dissociated is often very great. Small in concentrated solutions, it increases with the dilution (just as a purely chemical dissociation taking place with increase in number of molecules increases with decreased pressure), and finally approaches the limiting value of 100 per cent. Binary salts formed from monobasic acid and monacid base—as KNO_3, NaCl, $AgClO_3$—are the most strongly dissociated. The corresponding simple acids and bases—HCl, NaOH, NH_4OH—vary enormously. Salts such as $CuSO_4$ and $ZnSO_4$ are dissociated far less than the simpler ones given above, whilst with more complex examples, as $Ba(NO_3)_2$, H_2SO_4, and H_3PO_4, the dissociation takes place step by step—two ions only being formed in moderately

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[1] P. 66.

[2] P. 66.

[3] P. 67.

[4] Chap. IV.

strong solutions and a greater number in dilute solutions. Thus H_2SO_4 at first gives

$$H_2SO_4 \longrightarrow H^{\cdot} + HSO_4{}';$$

the dissociation

$$HSO_4{}' \longrightarrow H^{\cdot} + SO_4{}''$$

will set in later.

The dilution necessary to reach the same degree of dissociation—say 80 per cent.—varies therefore considerably with the electrolyte. It is smaller the less complex the undissociated salt and the stronger the component base and acid. We have the following approximate values for 18°:—

KCl	is 80 per cent.	dissociated in	0·4 N.	solution.
KAc	,,	,,	0·1 N.	,,
$BaCl_2$	,,	,,	0·05 N.	,,
$CdCl_2$	,,	,,	0·005 N.	,,

Like other electrical phenomena, *electrolytic dissociation*, often loosely termed *ionisation*, is only very slightly affected by temperature.

Now, as current is carried solely by these free ions, which increase in number with the dilution, it follows that the conducting power of a gram-equivalent of electrolyte will also increase with dilution and will tend towards a maximum value, corresponding to complete ionic dissociation. The conductivity of any solution will depend then, firstly on the number of ions present, and secondly on the velocity with which they move under the electric field. The osmotic pressure of an electrolyte will be determined by the total number of osmotically active particles in solution, and, as many molecules are dissociated into two or more ions, will be greater than the amount calculated not allowing for dissociation. This discrepancy will be more marked in dilute solutions where the dissociation is more complete than in strong solutions, which corresponds to facts. At very great dilutions, the ratio of observed to normal osmotic pressure will be given by the total number of ions the salt can furnish—will always therefore tend towards a small integral number. With NaCl and $CuSO_4$, it will be two; with K_3FeCy_6, four; etc., etc.

A last important qualitative agreement with theory is the fact that most of the properties of dilute solutions can be regarded as additive functions of the properties of the component ions, instead of as the properties of the undissociated salts. Thus a dilute $AgNO_3$ solution has one set of properties which we associate with the $Ag^{\cdot}$ ion and another set which we associate with the $NO_3{}'$ ion, but no properties which we can put down as peculiarly due to silver nitrate. A dilute solution containing equivalent quantities of KCl and Na_2SO_4 has the same properties as a dilute solution containing equivalent quantities of K_2SO_4 and NaCl. The properties of both solutions are the sum of properties attributed to the $Na^{\cdot}$, $K^{\cdot}$, Cl', and $SO_4{}''$ ions. These statements hold good for such properties as colour, specific gravity, refractivity, specific heat, etc., etc., and go to show that in dilute solutions the ions act practically independently of one another.

Degree of Dissociation.—The most important evidence, however, presented by Arrhenius was of a quantitative nature. In particular he was conspicuously successful in showing that the extent of dissociation of an electrolyte calculated by two absolutely independent methods—osmotic pressure and conductivity—was equal or nearly so. Suppose a molecule of electrolyte can dissociate into n ions, and that the fraction dissociated, its **degree of dissociation,** is a for a particular solution. Let i as before[1] be the Van't Hoff factor, *i.e.* $\frac{\text{observed osmotic pressure}}{\text{calculated chemical osmotic pressure}}$. The *degree of dissociation* is identical with Arrhenius' *coefficient of activity,*[2] and we can write

$$a = \frac{\Lambda}{\Lambda_\infty}.$$

If now a be the fraction of dissociated molecules, the undissociated fraction will be $1 - a$. As each molecule on dissociating furnishes n ions, the total number of ions will be na, and the total number of osmotically active particles $na + (1 - a)$. Therefore

$$i = \frac{na + (1 - a)}{1}$$
$$= 1 + a(n - 1).$$

That is, a value for i has been calculated from conductivity data only. Conversely, if i be known from osmotic measurements, the degree of dissociation a can be calculated.

Table XI contains values for i calculated from three different series of measurements.

TABLE XI

Substance	Molecular normality	i from osmotic pressure	i from freezing-point data	i from conductivity
Cane sugar	0·3	1·00	1·08	—
Acetic acid	0·33	—	1·04	1·01
KCl	0·14	1·81	1·93	1·86
$LiCl$	0·13	1·92	1·94	1·84
$MgSO_4$	0·38	1·25	1·20	1·35
$Ca(NO_3)_2$	0·18	2·48	2·47	2·46
$SrCl_2$	0·18	2·69	2·52	2·51
K_4FeCy_6	0·356	3·09	—	3·07

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[1] Chap. IV.

[2] P. 68.

Cane sugar, a non-conductor, and acetic acid, a weak acid and feeble electrolyte, have values of i nearly approaching unity. With KCl and LiCl, strong electrolytes of simple constitution, i is already nearly two in $\frac{1}{7}$–$\frac{1}{8}$ molecular normal solutions. With $MgSO_4$, another binary electrolyte, but in stronger solution and containing a weaker base, i is less, but still between one and two. With the two ternary salts, it tends towards three, whilst with K_4FeCy_6, a complex salt in fairly strong solution, the maximum value of five is far from being attained. The figures Arrhenius himself calculated (from freezing-point and conductivity measurements) did not agree so well, as the existing experimental data were rather unreliable. Yet they were sometimes very striking. Thus, for $BaCl_2$, i calculated from Raoult's freezing-point measurements is 2·63. A solution of the same concentration gives $a = 0{\cdot}77$, calculated from conductivity measurements. The possible number of ions, n, is three. Hence

$$i = 1 + 0{\cdot}77(3 - 1) = 2{\cdot}54.$$

Another important consequence of the electrolytic dissociation theory which is capable of quantitative verification is the following. The equivalent conductivity of an electrolyte at infinite dilution is, as we have seen, composed of the sum of two constants which are characteristic of the cation and anion present. Further, as the conductivity of a solution depends on the rates at which the ions travel to the electrodes through the electrolyte, it is obvious that these constants, already termed equivalent ionic conductivities, must represent the relative velocities[1] with which the ions move under the same conditions in an electric field. But these relative velocities are also the cause of the different *transport* numbers of different salts; and hence, knowing the necessary ionic conductivities, we can calculate these transport numbers. If l_A and l_C represent the ionic conductivities for anion and cation respectively, then the fraction of the current carried by the anion will be

$$\frac{l_A}{l_A + l_C} = n_A.$$

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[1] The *actual* velocities with which ions will move under given conditions are directly proportional to their ionic conductivities. The methods by which these **ionic mobilities** are measured cannot be treated here. The following figures will give some idea of their magnitudes. They hold good for a potential fall of 1 volt per cm.

U_K	0·000669 cm./sec.
U_{Na}	0·000450 cm./sec.
U_H	0·003415 cm./sec.
U_{NO_3}	0·000640 cm./sec.
U_{Cl}	0·000677 cm./sec.
U_{OH}	0·001802 cm./sec.

Their velocity is proportional to the voltage gradient.

Similarly

$$\frac{l_C}{l_A + l_C}$$

will be equal to n_C. Table XII contains values of n_A directly determined by migration experiments and values calculated[1] using the figures for ionic conductivities on p. 67.

TABLE XII

Salt	$\frac{l_A}{l_A + l_C}$	n_A
KI	0·505	0·506
LiCl	0·65	0·63
$AgNO_3$	0·522	0·528
HCl	0·172	0·172
NaOH	0·80	0·81

The agreement is excellent.

Dilution Law.—The application of the equilibrium laws to solutions of electrolytes gives interesting results. First consider the dissociation equilibrium of an electrolyte of formula $C_n\,A_m$, where C and A represent cation and anion respectively. Suppose the molecule to dissociate electrolytically according to the equation

$$C_nA_m \rightleftarrows nC + mA.$$

Then we can write[2] (substituting S = salt for $C_n\,A_m$)

$$K \times [C_S] = [C_C]^n \times [C_A]^m.$$

If one gram-molecule of the original salt be contained in v litres, and the degree of dissociation at equilibrium is a, we have

$$[C_S] = \frac{1-a}{v}$$

$$[C_C] = \frac{na}{v}$$

$$[C_A] = \frac{ma}{v}$$

And therefore

$$K = \frac{(na)^n \,.\, (ma)^m}{1-a} \,.\, v^{1-m-n}$$

To test this equation, we will take the simplest case, the dissociation of a binary electrolyte. Here $n = m = 1$, and K becomes

$$\frac{a^2}{(1-a)v},$$

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[1] These values depend ultimately on an accurate migration experiment for *one salt only*.

[2] Law of Mass Action.

a formula which has been shown to hold very exactly for the dissociation of weak acids or bases, such as CH_3COOH and ammonia. The two following Tables, XIII and XIV, contain for $CH_2Cl . COOH$ and for ammonia constants calculated using values of α obtained from conductivity measurements.

TABLE XIII

Monochloracetic Acid at 14°.

Dilution v	Equivalent conductivity	α from conductivity	K
20	51·6	0·166	$1{\cdot}65 \times 10^{-3}$
205	132	0·423	1·52
408	170	0·547	1·61
2,060	251	0·806	1·62
4,080	274	0·881	1·60
10,100	295	0·948	1·71
20,700	300	0·963	1·21
∞	311	1·000	—

TABLE XIV

Ammonia at 25°.

Dilution v	Equivalent conductivity	α from conductivity	K
8	3·20	0·0135	$2{\cdot}3 \times 10^{-5}$
16	4·45	0·0188	2·3
32	6·28	0·0265	2·3
64	8·90	0·0376	2·3
128	12·63	0·0533	2·3
256	17·88	0·0754	2·4
∞	237	1·000	—

If we try to apply this relation, discovered by Ostwald and Planck, and known as Ostwald's **Dilution Law,** to the dissociation of strong electrolytes except in very dilute solutions, it breaks down.

Solubility Product. — Another interesting application of the electrolytic dissociation theory deals with the solubility of sparingly soluble salts. A solid salt brought into contact with a solvent will dissolve until the solution is saturated. When this happens, we have two equilibria to consider. Firstly the solid salt is in equilibrium with the undissociated salt molecules in the solution. Secondly, these undissociated molecules are in equilibrium with their ions. We can write

$$C_{\text{solid}} \times k_1 = [C_{\text{undissociated}}]$$
$$[C_{\text{undissociated}}] \times k_2 = [C_{\text{cation}}]^n \times [C_{\text{anion}}]^m$$

supposing a molecule of salt to contain n cations and m anions. Now, as the active mass of a solid is constant,[1] we can put $C_{\text{solid}} = k_3$, and obtain the result

$$[C_{\text{cation}}]^n \times [C_{\text{anion}}]^m = k_1 \cdot k_2 \cdot k_3 = K.$$

K is termed the *solubility product* of the salt in question.

If we again take a simple case, and suppose the salt to be a binary one, $n = m = 1$, and the equation becomes

$$[C_{\text{anion}}] \cdot [C_{\text{cation}}] = K.$$

That is to say, when a solution is saturated with a binary salt, the product of the molecular concentrations of the two ions concerned is a constant.

As a concrete case, imagine that, to a solution already saturated with $CaSO_4$, a little Na_2SO_4 is added.[2] The concentration of the SO_4'' ion is thereby increased. But as

$$[C_{Ca}] \cdot [C_{SO}] = K$$

it follows that C_{Ca} must decrease. Calcium sulphate is consequently precipitated from the solution until the condition given by the equation is once again fulfilled. This is the explanation of the well-known fact that the solubility of a salt is decreased by the addition to the solution of another salt having a common ion.

The above equation allows us to calculate the magnitude of this influence in different cases. If this is done, good agreement is obtained when the salt concerned is only slightly soluble, but a much poorer one with moderately or easily soluble salts. Thus Noyes[3] studied the effect of the addition of small quantities of $AgNO_3$ and $KBrO_3$ on the solubility of $AgBrO_3$. Table XV contains some of his results. All concentrations are in gram-molecules per litre.

TABLE XV

Quantity of $AgNO_3$ or $KBrO_3$ added	Solubility of $AgBrO_3$		
	On addition of $AgNO_3$	On addition of $KBrO_3$	Calculated from solubility product
0·0	0·00810	0·00810	(0·00810)
0·0085	0·00510	0·00519	0·00504
0·0346	0·00216	0·00227	0·00206

The agreement is very satisfactory.

The conductivity of a solution containing two or more different salts is now seen to be determined by the ionic equilibria in the electrolyte. The quantities of the different ions and of the different

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[1] P. 18.

[2] A larger quantity may introduce other effects.

[3] *Zeitsch. Phys. Chem.* **6**, 241 (*1890*).

undissociated salts will adjust themselves in accordance with the dissociation constants of the salts. This done, each single ion will contribute independently to the conductivity of the electrolyte, which will then be determined by the ionic conductivities and the quantities of the different ions present.

Such calculations as those on the last few pages afford the best justification for the use of the conception of electrolytic dissociation as a working theory in electrochemistry. A good working hypothesis should fulfil two conditions. It should be capable of explaining existing facts and figures and also of guiding investigators to the discovery of new phenomena and laws. In both respects, Arrhenius' hypothesis has proved satisfying and fruitful. The enormous strides made during the last twenty years in electrochemistry, both pure and applied to other branches of chemistry, are due directly to its use. Certain chemists still refuse to accept it, imagining it to involve, for example, the belief that a solution of common salt contains free particles of sodium metal and chlorine gas floating about unattacked in the liquid. It seems superfluous to point out that this is not so; what are present are *very highly charged atoms* of sodium *element* and chlorine *element*—quite a different matter. As Le Blanc has pointed out, the quantity of electricity (100 coulombs) which is associated with one milligram only of hydrogen in the ionic condition, would suffice to charge up to discharging point an air condenser of several square kilometres in area. And there are no grounds for assuming that, when sodium chloride dissociates, giving *elementary atomic* sodium and chlorine, these substances must necessarily possess the properties of metallic sodium and liquid or gaseous chlorine.

The necessity of the assumption of the existence of charged current-carriers or ions in an electrolyte under ordinary conditions can be seen from the following considerations. If the molecules of the solute must be decomposed before they will conduct the current, a certain definite amount of energy will be absorbed before any current can pass. But it can be experimentally shown that, if absorption of energy is avoided at the electrodes, the current passing varies directly with the voltage applied. Ohm's Law is obeyed, and no minimum voltage is required for the passage of current. Thus with copper electrodes in copper sulphate solution, where converse reactions take place at anode and cathode, the current passing varies directly as the potential difference used, however small the latter. Hence, no energy is consumed before conduction starts in decomposing $CuSO_4$ into $Cu^{\cdot\cdot}$ and SO_4'' ions, and these conducting particles must exist normally in the solution.

There is no doubt, of course, that Arrhenius' hypothesis needs modification and extension in order to account fully for all the phenomena of electrolytes. We have already pointed out that for strong electrolytes it is only capable of representing the equilibria in very dilute solutions. Abegg considered that many discrepancies would be explained by the further study of the ionisation of ternary and other complex salts. Undoubtedly, in such salts, we are often not dealing with simple ions, but with complex ones similar to those present in the extreme cases investigated by Denham.[1] But it is unlikely that complicated ionisation causes all the lack of agreement between experiment and theory.

Noyes[2] has put forward the view that the process of ionisation is primarily of an electrical nature, quite unlike ordinary chemical dissociation, and that the laws of mass action cannot with justification be applied to it, as the electrical forces which govern the formation of ions obey quite different laws. He supports this view by considerations based on the slight influence of temperature on ionisation, the practical independence of the concentration shown by the optical properties of electrolytes, etc. It is probable that his conception is to a great extent correct. In the dissociation of *strong* electrolytes, electrical phenomena may play a more important part than chemical phenomena. The ionisation of weak electrolytes, which obeys the mass action law, is, on the other hand, more of a chemical than an electrical process.

Literature.

Le Blanc. *Electrochemistry.*
Lorenz. *Elektrochemisches Praktikum.*

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[1] P. 57.

[2] *Jour. Amer. Chem. Soc.* **30**, 351 (*1908*).

CHAPTER VII

ENERGY RELATIONS

1. Total Energy and Maximum External Work

In this chapter we must consider the energy changes which take place in an electrochemical cell, and their relations to the energy changes of the corresponding chemical reaction. As a concrete case we can take the Daniell cell working at constant temperature. This cell consists of a copper electrode dipping into a solution of $CuSO_4$ which is separated by a porous partition from a solution of $ZnSO_4$ containing a zinc electrode. Written briefly, it is

$$\mathrm{Zn} \mid \mathrm{ZnSO_4} \mid \mathrm{CuSO_4} \mid \mathrm{Cu}.$$

When the zinc and copper poles are joined externally by a wire, a positive current flows through this wire from copper to zinc, zinc goes into solution as zinc sulphate, and copper is deposited on the copper electrode. If, on the contrary, current be forced through the cell in the opposite direction, zinc will be deposited on the zinc electrode, and copper enter solution at the copper electrode. The corresponding chemical reaction is

$$\mathrm{Zn} + \mathrm{CuSO_4}\,.\,aq. = \mathrm{Cu} + \mathrm{ZnSO_4}\,aq.$$

to be read from left to right when the cell spontaneously furnishes current, and from right to left when current is forced through the cell from outside. At first we will limit our considerations to the direct action—left to right in the above equation.

Change of Total Energy.—When copper sulphate solution and zinc are brought together, the formation of copper and zinc sulphate solution is accompanied by an evolution of heat. Suppose this reaction carried out in such a calorimeter (*e.g.* an ice calorimeter) that the temperature of the system is the same before and after the reaction, and let the heat liberated be measured. Then we shall have changed copper sulphate and zinc into zinc sulphate and copper at the same temperature, and, as no other changes involving energy transformation have taken place, it follows that the heat measured is equal to the **decrease of total energy** of the system. This value is usually denoted by U. In the present case, it is the difference of the heats of formation of zinc sulphate and copper sulphate solutions, and for the concentrations $CuSO_4$, $100H_2O$ and $ZnSO_4$, $100H_2O$ is 50110 cals. per gram-mol. at 0°.

Maximum External Work.—The matter which immediately concerns us is the following. When the reaction is carried out, not as above, but in such a way that useful (*i.e.* completely controllable and transformable) external work results,[1] what is the relation between the maximum amount of work so obtainable and U, the decrease of total energy of the system ? If they are exactly equivalent, then it is clear that the electromotive force of an electrochemical cell can be directly calculated from thermo-chemical data. For if U be the number of calories liberated by the interaction of n gram-equivalents, we have

$$4{\cdot}19 \times U = n \times 96{,}540 \times E$$

$$E = \frac{4{\cdot}19\ U}{96{,}540\ n}$$

With the Daniell cell, $n = 2$ and $U = 50{,}110$, whence $E = 1{\cdot}087$ volts.

The above assumption was at first regarded as correct, and this method of calculating the E.M.F. of a cell, known as the *Helmholtz-Thomson rule*,[2] is still widely applied. But though it often leads to approximately correct results, it rests on an erroneous basis. The decrease of total energy of a working system U, and the **decrease of free energy or the maximum useful work obtainable**, denoted by A, are not identical. Instead of writing $U = A$, we must write

$$\underset{\text{Decrease of total energy}}{U} = \underset{\text{Maximum work obtainable}}{A} + \underset{\text{heat evolved}}{q}$$

q can be small or great, positive or negative. If positive, the maximum useful work obtainable during the process is less than U, and the balance, set free as heat, tends to warm the system up. If q is negative, then $U < A$. The working system, besides doing external work equivalent to the decrease in total energy, also abstracts heat from its surroundings, and converts it into useful work, thus tending to cool down during operation.

2. Reversible Processes

The next point is, Under what conditions must a galvanic cell give current in order that the electrical energy produced may be equivalent to A, the maximum external work obtainable from the corresponding

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[1] In the present case, as electrical energy.

[2] Both of these investigators soon recognised the incorrectness of their assumption.

chemical change? Let us again consider a Daniell cell working *isothermally* (at constant temperature), and with the current capable of regulation by means of an external resistance. Let the cell furnish a moderate current until one gram-atom of copper has been deposited and one gram-atom of zinc dissolved. A certain amount of electrical energy will be liberated, mostly in the external circuit, but partly in the cell, owing to the resistance of the latter not being negligible. Let this amount of electrical energy be measured and equal to a_1.

Then we can represent the total change of the system by

$$\mathrm{Zn} + \mathrm{Cu}^{\cdot\cdot} \longrightarrow \mathrm{Zn}^{\cdot\cdot} + \mathrm{Cu} + a_1.$$

When the process is finished, let the current be reversed, and forced in the opposite direction through the cell by means of an external source of voltage, until the original chemical conditions have been regenerated, one gram-atom of copper in this case dissolving, and one gram-atom of zinc depositing. Let the current passing be the same as in the first operation, differing in direction only. Correcting again for the resistance of the cell, the energy used will be the product of the voltage between the electrodes and the quantity of electricity passed through (two faradays). We can denote this quantity of energy, which will be somewhat greater than a_1, by a_2, and the equation representing the process becomes

$$\mathrm{Cu} + \mathrm{Zn}^{\cdot\cdot} + a_2 \longrightarrow \mathrm{Cu}^{\cdot\cdot} + \mathrm{Zn}.$$

The condition of the Daniell cell is now in all respects the same as before. It has not altered chemically, and its temperature throughout has been kept constant. The sum result of the whole cycle is therefore given by

$$[\mathrm{Cu}^{\cdot\cdot} + \mathrm{Zn}] - [\mathrm{Cu} + \mathrm{Zn}^{\cdot\cdot} + a_2] - [\mathrm{Cu}^{\cdot\cdot} + \mathrm{Zn}] + [\mathrm{Cu} + \mathrm{Zn}^{\cdot\cdot} + a_1] \\ = a_1 - a_2$$

and, as $a_2 > a_1$, the result is a loss of available or useful energy (in this case electrical energy, which has been converted into heat in the cell).

Suppose the cycle to be repeated, using a much smaller current, perhaps one-tenth as great. Let the quantities of electrical energy given out and absorbed in the two partial processes (decrease and increase of free energy respectively) be denoted by a_1' and a_2'. If these magnitudes be compared with a_1 and a_2, it will be found that $a_1' > a_1$ and $a_2' < a_2$. It follows that $(a_2' - a_1') < (a_2 - a_1)$. As before $(a_2' - a_1')$ represents the result of the cycle, a decrease in power of doing useful work. If further experiments were made with ever-diminishing current densities, we should find the difference between the external work done during the first operation and the external work absorbed during the second operation becoming ever smaller, and finally negligible. At an infinitely small current density, $a_2 - a_1$ is zero. A process carried out under such conditions is known as a

reversible process, because it is possible to return to the original state of the system by a path which is in all respects the reverse of that previously taken, and, when again at the starting-point, the system is in all respects, *including the very important one of energy relations*, the same as it was before the process commenced.

The electrical energy furnished by a primary cell when working isothermally and reversibly is equal to A, the decrease of free energy or the maximum external work obtainable from the corresponding chemical change. The truth of this statement follows from the Second Law of Thermodynamics, and cannot be proved here. Similarly the increase in free energy of an electrochemical system when current is passed through it from outside is equal to the energy absorbed by the cell, working reversibly and isothermally.

3. Irreversible Processes

An isothermal reversible process is characterised by the fact that the power the system has of doing useful work suffers no actual diminution—only the *form* in which this work can manifest itself is changed. Thus, in the above example, the only change is the transference of available chemical energy into the same amount of available electrical energy and *vice versa*. In an **irreversible** process, on the other hand, the capacity of the system for useful external work *decreases*, owing to irreversible heat effects. As the above consideration of the Daniell cell indicated, the extent of this degradation of useful energy to heat is greater, the greater the velocity of the process. This is true generally, and not only of electrochemical systems. In mechanical processes, the amount of useful energy converted into heat by friction increases rapidly with the rate of working. Generally speaking, no processes of any kind are reversible in practice. It is obviously impossible to let them take place sufficiently slowly, and friction or similar passive resistances must always be overcome, causing a certain amount of energy to be lost as heat.

Electrochemical processes often take place nearly reversibly, and again are often irreversible. This irreversibility may not only be quantitative, but can extend itself to the qualitative aspect of the process. If, in the above case, the $ZnSO_4$ be replaced by H_2SO_4, zinc will go into solution as before when the cell gives current spontaneously. But when current is passed through it, zinc is not deposited, as in the Daniell cell, but hydrogen is evolved; that is, instead of the reaction

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

being reversed, the reaction

$$Cu + H_2SO_4 \longrightarrow CuSO_4 + H_2$$

is brought about. Such a cell is irreversible.

Quantitative irreversible effects are very general,[1] though often only of slight magnitude. The cathodic discharge of hydrogen needs widely different potentials at different electrodes; when metals dissolve anodically, there are often considerable irreversible losses. The cathodic deposition of metals absorbs more energy when a high current density is employed—when the velocity of deposition is great—than with a low one. Just as with any other change, the greater the working speed, the greater the irreversibility and the energy losses. A system doing useful work gives less than is represented by A; a system absorbing energy needs to take up more than is represented by A to bring about a certain change.

4. Relations in Reversible Galvanic Cells

But in many cases, the electrical energy given out or absorbed by a cell working at a low current density corresponds closely to A. And if the E.M.F. of the cell be measured when no current is passing,[2] and the result in volts be multiplied by 96,540, the value of A per gram-equivalent of the substances transformed will be given in joules. In cases where a cell behaves practically reversibly at a convenient working current density, the relations between the various magnitudes U, A, and q may be demonstrated as follows. Let the cell, with an internal resistance as small as possible, be placed in a calorimeter (preferably an ice-calorimeter, so that it will work isothermally) and allow it to discharge through an external circuit consisting of a suitable coil of wire in a second calorimeter. Then, as the electrical energy developed at constant temperature represents, in the case of a reversible galvanic cell, the maximum work obtainable at constant temperature from the corresponding chemical reaction, and as this in its turn is transformed into heat energy in the wire, the amount of heat set free in the second calorimeter will be a measure of A, the maximum external work obtainable from the change. In the first calorimeter (apart from the small quantity of heat produced by the current) the heat effect is equal to q. If $U > A$, then q is positive and heat is liberated in the calorimeter. If, on the other hand, $U < A$, then q is negative, and heat is absorbed from the calorimeter by the cell. Further, as $U = A + q$, the algebraic sum of the heat effects in the two calorimeters gives U, the change of total energy, and this must be equal to the heat liberated when the reaction is carried out thermochemically in a single calorimeter.

We will now see by examples in what way U and A differ in typical cases. The values of U are determined thermochemically; the values of A are calculated from the E.M.F.s of the different cells.

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[1] Chap. IX.

[2] P. 90.

1. Daniell Cell at 0°.

$$Zn \mid ZnSO_4 100H_2O \mid CuSO_4 100H_2O \mid Cu.$$

Chemical reaction:

$$Zn + CuSO_4, aq. \longrightarrow Cu + ZnSO_4, aq.$$

$$U = 50{,}110 \text{ cals.} \qquad E = 1{\cdot}096 \text{ volt.}$$

Hence
$$A = \frac{1{\cdot}096 \times 2 \times 96{,}540}{4{\cdot}19}$$
$$= 50{,}510 \text{ cals.}$$

and
$$q = U - A = -400 \text{ cals.}$$

2. Lead Accumulator at 17°.

Electrolyte 1 H_2SO_4 : 20 H_2O.

Chemical reaction:

$$PbO_2 + Pb + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$$

$$U = 87{,}200 \text{ cals.} \qquad E = 2{\cdot}01 \text{ volts.}$$

Hence
$$A = \frac{2{\cdot}01 \times 96{,}540 \times 2}{4{\cdot}19}$$
$$= 92{,}630 \text{ cals.}$$

and
$$q = U - A = -5{,}430 \text{ cals.}$$

3. Hydrogen-chlorine Cell at 30°.

Electrolyte 4·98 N. HCl.

Chemical reaction:

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 \longrightarrow HCl$$

$$U = 22{,}000 \text{ cals.} \qquad E = 1{\cdot}190 \text{ volt}$$

Hence
$$A = \frac{1{\cdot}190 \times 96{,}540}{4{\cdot}19}$$
$$= 27{,}420 \text{ cals.}$$

and
$$q = U - A = -5{,}420 \text{ cals.}$$

4. Clark Cell at 18°.

Zn | saturated zinc sulphate solution | Hg_2SO_4 | Hg.

Chemical reaction:

$$Zn + Hg_2SO_4 + 7H_2O \longrightarrow ZnSO_4, 7H_2O + 2Hg$$

$$U = 81{,}320 \text{ cals.} \qquad E = 1{\cdot}429 \text{ volt.}$$

Hence
$$A = \frac{1{\cdot}429 \times 2 \times 96{,}540}{4{\cdot}19}$$
$$= 65{,}850 \text{ cals.}$$

and
$$q = U - A = +15{,}470 \text{ cals.}$$

5. Cell Ag | AgBr | $ZnBr_2$, $25H_2O$ | Zn at 0°.

Chemical reaction:

$$2AgBr + Zn + aq. \longrightarrow 2Ag + ZnBr_2\ aq.$$

$$U = 39{,}764 \text{ cals.} \qquad E = 0{\cdot}828 \text{ volt.}$$

Hence
$$A = \frac{0{\cdot}828 \times 2 \times 96{,}540}{4{\cdot}19}$$
$$= 38{,}160 \text{ cals.}$$

and
$$q = U - A = +1604 \text{ cals.}$$

These results clearly show that, as has been already stated, U and A are not equivalent. In the Daniell cell they are very nearly equal. But in the other cases there are considerable differences. A is greater than U both for the lead accumulator and the hydrogen-chlorine cell. When these two cells are in action, they absorb heat from their surroundings, and convert it into useful work in the form of available electrical energy, tending to become cooled in the process. On the other hand, the last two combinations do not convert all the energy set free during the process into useful external work, but a certain amount of it, given by q, is set free as heat. Such cells tend to warm up when working. In the Clark cell, some 19 per cent. of the total energy change appears as heat. It follows that the E.M.F. of a cell cannot be directly calculated from the corresponding change of total energy U. In some cases a very close agreement would be got; *e.g.* for the Daniell cell the value is correct to within 1 per cent. But usually this is not so. A calculation for the lead accumulator would give a result 6 per cent. too low, for the hydrogen-chlorine cell discussed a result 20 per cent. too low, for the Clark cell a figure 19 per cent. too high, and for the last combination mentioned an E.M.F. 4 per cent. too great.

By applying the Second Law of Thermodynamics to changes of temperature and the corresponding changes of the different terms of the equation $U = A + q$ we arrive at the celebrated *Gibbs-Helmholtz equation*

$$A - U = T \cdot \frac{dA}{dT}.$$

This result (which must be taken for granted here) differs from the equation already used in that q is replaced by $- T \cdot \frac{dA}{dT}$, where T is the absolute temperature, and $\frac{dA}{dT}$ the rate of change with temperature of the maximum work obtainable from the process under consideration. Applying this equation to the particular case of galvanic cells, we can substitute for A $96{,}540nE$, where n is the number of gram-equivalents transformed during a change of total energy of U calories. Then $\frac{dA}{dT}$ becomes $96{,}540n\,\frac{dE}{dT}$, and we finally have

$$n96{,}540E - 4{\cdot}19\,U = Tn96{,}540\,\frac{dE}{dT},$$

all terms being expressed in joules. From this we see that, knowing E and U, $\frac{dE}{dT}$, the coefficient of increase of electromotive force with temperature can be calculated. Moreover, the sign of $\frac{dE}{dT}$ depends on the relative magnitudes of A and U. If the maximum work which can be performed by the cell exceeds the corresponding change of total energy (in which case we remember the cell tends to cool when working), then the E.M.F. rises with increase of temperature. If on the other hand $U > A$, and the cell tends to heat up when giving current, $\frac{dE}{dT}$ is negative, and the E.M.F. diminishes with rising temperature.

We will calculate the temperature coefficient of the Daniell cell, taking U as 50,110 and the E.M.F. at 0° as 1·0962 volt.

We have

$$(2 \times 96{,}540 \times 1{\cdot}0962) - (4{\cdot}19 \times 50{,}110) = (273 \times 2 \times 96{,}540)\frac{dE}{dT}$$

$$\frac{dE}{dT} = \frac{211{,}700 - 210{,}000}{5{,}271 \times 10^4} = +\,0{\cdot}000032\,\frac{\text{volt}}{\text{degree}}.$$

The value of the temperature coefficient determined by experiment[1] is $+\,0{\cdot}000034\,\frac{\text{volt}}{\text{degree}}$, the agreement being very close.

Similarly, knowing the E.M.F. and its temperature coefficient for a given cell, we can calculate U, the change in total energy or heat of reaction. We have

$$U = \frac{96{,}540nE}{4{\cdot}19} - \frac{96{,}540nT}{4{\cdot}19} \cdot \frac{dE}{dT}.$$

For example, take the element

$$\text{Cu} \mid \text{Cu}_2\text{O NaOH} \mid \text{H}_2.$$[2]

The corresponding chemical reaction is $Cu_2O + H_2 \rightarrow 2Cu + H_2O$, and the thermochemical value of U is 27,400 cals. at 18°. The E.M.F. at 18° is 0·461 volt, and its temperature coefficient $-\,0{\cdot}00066\,\frac{\text{volt}}{\text{degree}}$. We get then:—

$$U = \frac{96{,}540 \times 2}{4{\cdot}19}[0{\cdot}461 + 291 \times 0{\cdot}00066] \text{ cals.}$$
$$= 27{,}530 \text{ cals.}$$

Table XVI[3] contains in the first column the combination dealt with, in the second column the E.M.F., and in column 3 its temperature coefficient; in the fourth column U (in cals.) calculated by the above

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[1] H. Jahn, *Wied. Ann.* **28,** 21 (*1886*).

[2] Allmand, *Trans. Chem. Soc.* **99,** 840 (*1911*).

[3] H. Jahn, *Wied. Ann.* **28,** 491 (*1886*); **50,** 189 (*1893*). Donnan and Allmand, *Trans. Chem. Soc.* **99,** 845 (*1911*). Bugarszky, *Zeitsch. Anorg. Chem.* **14,** 145 (*1897*).

equation from the data in columns 2 and 3; in the fifth column the thermochemical value of U, and in the last column the value of U calculated from E by the incorrect 'Helmholtz-Thomson rule.'

TABLE XVI

Cell	E in volts	$\frac{dE}{dT}\left(\frac{\text{volts}}{\text{degree}}\right)$	U (calculated) in cals.	U (experimental) in cals.	$\frac{96{,}540nE}{4 \cdot 19}$
Cu | $Cu(C_2H_3O_2)_2$ solution | $Pb(C_2H_3O_2)_2$, $100H_2O$ | Pb at 0°	0·4764	+0·000385	16,900	17,533	21,684
Ag | $AgClZnCl_2 . 100\ H_2O$ | Zn at 0°	1·015	−0·000402	51,989	52,046	46,907
Hg | HgO n.NaOH | H_2 at 18°	0·9243	−0·00031	46,750	46,700	42,590
Hg | HgCl 0·01 N. KCl | N. KNO_3 | 0·01 N. KOH Hg_2O | Hg at 18·5°.	0·1656	+0·000837	−3,710	−3,280	7,566

The values of U calculated from the Gibbs-Helmholtz equation are in all cases much nearer the experimental figures than are the values in the sixth column. The last case is particularly remarkable as the calculation of the heat of reaction according to the 'Helmholtz-Thomson rule' gives a value which actually differs in *sign* from the true value.

5. Relations during Reversible Electrolysis

The examples given above all refer to primary cells. The same relations hold for the converse phenomena of *reversible electrolysis*, and need no further detailed consideration. The minimum quantity of electrical work necessary for any electrolysis is the product of the quantity of electricity passed through, and the minimum reversible voltage at which the electrolysis will take place. This, as before, is connected with the change of total energy of the system and with the heat absorbed or given out in the cell when the electrolysis is isothermally conducted by the equation

$$U = A + q.$$

As A and U are defined respectively as *decrease* of capacity of doing useful work and *decrease* of total energy, A always and U generally will be negative in such cases, for the capacity of the system to perform useful work *increases* when electricity is passed through it. Similarly, if U − A be positive, or if more electrical energy be passed into the cell than corresponds to the change of total energy in the chemical substance present, q will be positive and heat will be liberated in the cell. And if U – A be negative, heat will be absorbed during working.

As an example we can take the electrolysis of 5n. HCl between platinised platinum electrodes, which takes place practically reversibly if carried out at a very low current density. 1·190 volts are necessary at 30°. For the reaction $HCl \longrightarrow \frac{1}{2}H_2 + \frac{1}{2}Cl_2$, one faraday is required. Hence

$$A = -\frac{1{\cdot}190 \times 96{,}540}{4{\cdot}19} = -27{,}420 \text{ cals.}$$

The change in total energy, as given by the heat of reaction, is – 22,000 cals. Hence

$$q = U - A = +5{,}420 \text{ cals.}$$

Heat will be given out in the cell during electrolysis, and the voltage required to carry out the electrolysis will increase with rising temperature.

We shall have occasion further to consider the conditions necessary for reversible electrolysis and the causes bringing about irreversible electrolysis in succeeding chapters.

6. Maximum Work and Affinity

It should be pointed out in conclusion that A, the maximum external work which can be obtained from a process, is also a measure of the *driving force* or *affinity* of the reaction. The tendency for a reaction to take place depends on, and is measured, not by the diminution in total energy (U) which would occur, but by the amount of useful external work (A) which could be done. No chemical or electrochemical reaction will set in spontaneously unless the value of A corresponding to it is positive. The nearer a system approaches the equilibrium point the smaller A becomes, until under equilibrium conditions A reaches the value zero. Then there is no tendency for any kind of change to set in. A cell with a voltage of zero will furnish no current.

CHAPTER VIII

ELECTROMOTIVE FORCE

1. Necessary Conditions for Electrochemical Reactions

In this and the following chapters we shall consider in detail the free-energy changes which take place in electrochemical systems—that is, the reciprocal transformations of chemical and electrical energy. We have seen the important part that irreversible effects play in electrochemical processes. But at present, on account of simplicity, they will be ignored, and subsequent considerations and deductions in this chapter, unless otherwise specifically stated, refer to reversible processes only. It will be convenient if we first discuss the transformation of chemical into electrical energy, before considering the more important reverse case.

We are at once faced by the following questions : Can all chemical changes accompanied by a decrease of free energy liberate this energy as electrical energy ? If not, what types of chemical change are capable of so doing ? And what conditions must be fulfilled in order that the chemical energy shall appear as electrical energy, and not, as generally happens, as heat ?

The first question we can at once answer in the negative. A large number of reactions which proceed very easily chemically cannot be carried out electrolytically. The combustion of carbon and sulphur to their oxides, the absorption of CO by NaOH giving H.COONa, and many organic reactions are examples.

The next two points can be taken together. As electrolytic reactions all involve the combination of matter with, or its separation from, electricity, and as these processes generally take place in aqueous solution, the first necessary condition is that the substances partaking in such a reaction must be capable of *ionising*. Copper can be electrolytically refined, because it can combine with electricity, forming the ion $Cu^{\cdot\cdot}$, which in its turn can give up its electricity and reproduce metallic copper. Chlorine can be electrolytically prepared because of its ion Cl', which exists in aqueous solution together with such ions as $Na^{\cdot}$ and $Zn^{\cdot\cdot}$. On the other hand, carbon cannot ionise, and therefore carbon dioxide cannot be formed electrochemically at a low temperature from carbon and oxygen. Similarly nitrogen does not ionise, and the electrolytic combination of nitrogen and hydrogen is thus rendered impossible. Possibility of ionisation is consequently necessary. A second point common to electrolytic reactions is that they all involve processes of an oxidising or reducing character. When zinc enters solution anodically as zinc ions,[1] it has really been oxidised, just as much as when $Fe^{\cdot\cdot}$ ions have been changed anodically to $Fe^{\cdot\cdot\cdot}$ ions. When Cl' ions are discharged to gaseous chlorine, the process again is one of oxidation. We recognise this when speaking of the *oxidation* of HCl, in which the chlorine is in the ionic condition, to chlorine gas by MnO_2. On the other hand, when $H^{\cdot}$ ions are discharged to gaseous hydrogen or $Ag^{\cdot}$ ions to metal, the process is one of reduction. Generally, an increase in the number of positive charges or a decrease in the number of negative charges associated with a substance means oxidation : the cuprous ion $Cu^{\cdot}$ is oxidised to the cupric ion $Cu^{\cdot\cdot}$, the ferrocyanide ion $FeCy_6''''$ is oxidised to the ferricyanide ion $FeCy_6'''$. And a decrease in the number of positive charges or an increase in the number of negative charges means reduction : $Au^{\cdot\cdot\cdot}$ ions are reduced to metallic gold Au, and permanganate ions MnO_4' reduced to manganate ions MnO_4''. Now, as all electrode reactions consist essentially in a change in the quantity of electricity associated with matter, we see that electrochemical processes must necessarily all be of an oxidising and reducing character. In fact, all anodic reactions must oxidise, all cathodic reactions reduce something or other.

The final condition necessary for an electrolytic process is that the reacting substances must be kept apart, but connected by two conducting paths, one the electrolyte, the other an external circuit of a metallic nature. In that way the irreversible effects of ordinary chemical reactions, where the free energy liberated appears as heat, are avoided. Instead, the positive electricity set free at the cathode (one of the electrolyte-metallic circuit junctions) by the reduction process will proceed to the other electrode through the external circuit, there recombine with matter, thus effecting oxidation, and re-enter the electrolyte. On its way through the outside circuit, it can be usefully employed by driving a suitable motor, thus utilising the free

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[1] The chemical solution of zinc by sulphuric acid is expressed by the equation $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$; or, as SO_4'' ions are present both before and after the reaction, by $Zn + 2H^{\cdot} \longrightarrow Zn^{\cdot\cdot} + H_2$. Metallic zinc has been *oxidised* to zinc ions, hydrogen ions have been *reduced* to gaseous hydrogen. Or we can suppose that zinc is first oxidised by the water, giving zinc hydroxide and hydrogen, and that the acid and hydroxide subsequently combine.

energy liberated in the chemical reaction. As examples take the three simple reactions:—

(*a*) $Au + \frac{3}{2}Cl_2 \longrightarrow AuCl_3$

(*b*) $Zn + CuSO_4 \longrightarrow Cu + ZnSO_4$

(*c*) $Fe + 2FeCl_3 \longrightarrow 3FeCl_2$.

The arrangements for bringing these about electrolytically are shown in Fig. 18. In (*a*), if chlorine water be added to the vessel containing the gold, the latter will very slowly dissolve, and no current will pass. But if it be poured over the platinum, the gold will dissolve, the chlorine water disappear, and a current will flow through the wire. Similarly in (*b*) the $CuSO_4$ solution must be added to the right-hand vessel, when copper will be deposited and zinc will dissolve. Whilst with (*c*) the $FeCl_3$ solution must be pipetted on to the platinum electrode, when it will be reduced to ferrous chloride, and iron from the iron electrode will enter solution as $Fe^{\cdot\cdot}$ ions. *For a chemical reaction to be carried out electrochemically, it must be of an oxidation-reduction nature, the substances taking part must be capable of ionisation, and must be spatially separated, but in electrical connection.*

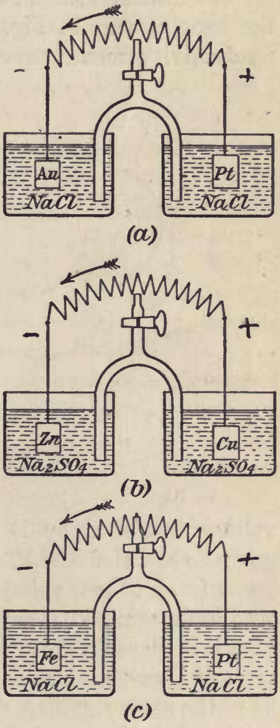

FIG. 18.

An actual *chemical* change is not necessary for the generation of an E.M.F. Two silver nitrate solutions of unequal concentrations, if mixed, suffer a loss of free energy. They can be so arranged as to produce an E.M.F. depending solely on this concentration difference, and not on any kind of chemical change. The E.M.F. is determined by the osmotic pressure difference of the two solutions, just as the work done by a gas expanding into a space at low pressure depends on the pressure difference between the two spaces.[1]

The E.M.F. of any cell is the result of all the potential differences existing in the cell. We must invariably consider at least two—the

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[1] For more on these cells, see p. 103.

potential difference between cathode and catholyte and that between anode and anolyte. When catholyte and anolyte differ, we may further take account of the *liquid potential difference* between them. This is, however, usually very small, rarely exceeding 0·02—0·03 volt, and can be neglected for most purposes, as will subsequently be done in this book.

2. Measurement of Electromotive Force

The measurement of the E.M.F. of a cell is easily carried out with the arrangement in Fig. 19. AB is a fine uniform wire, as used in conductivity measurements,[1] provided with a sliding contact C. A voltage furnished by D is applied to the ends of AB. It must be greater than the E.M.F. to be measured. One or more lead accumulators (each of two volts) will suffice. The cell x, of which the E.M.F. is to be determined, is connected to one end, A, of the bridge. In series with it is placed a galvanometer, which is also connected with C. The poles of D and x which are attached to the same end of the bridge must be of the same sign. A standard cell[2] F is also connected to A, and by means of the key H either x or F can be put into series with G. Now the cell (or cells) D produces a uniform fall of potential along AB. If the standard cell F be put into series with G, we have two opposing E.M.F.s acting along the circuit AFGC. One is the potential difference produced by D between A and C. This tends to drive positive electricity in the direction AFC, whilst the E.M.F. of the standard cell tends to send a current in the reverse direction CFA. As long as these two potential differences are unequal, a current will flow through G. When, by moving C up and down, the potential difference between A

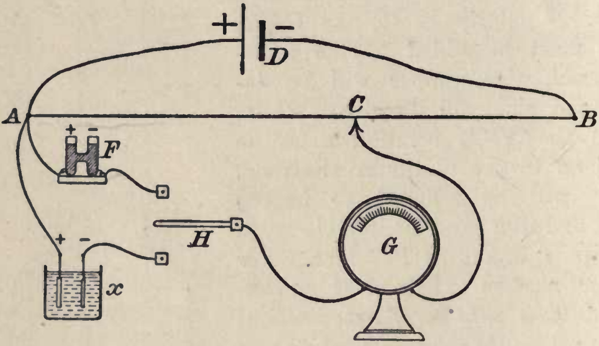

FIG. 19.

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[1] P. 59.

[2] See p. 6.

and C has become equal to the E.M.F. of the standard cell, no current will flow through G. The position of C is therefore adjusted in this way, and when the correct point has been found we know that the potential fall between A and C is equal to the E.M.F. of F, from which result we can calculate the potential drop per mm. of AB. By means of H, the unknown cell x is now thrown in, and C again moved until no current passes through G. Reading the new length of AC, and knowing the potential drop per mm., we arrive directly at the value of the E.M.F. of x. This method is exact, easily carried out, and capable of great flexibility.

The only standard cell for E.M.F. measurements needing consideration is the *cadmium cell*. The *Clark cell*, which was formerly much used, has a far too high temperature coefficient. The cadmium cell is generally constructed as in Fig. 20. One limb of the H-vessel contains mercury, and this is covered with a paste of mercurous sulphate and hydrated cadmium sulphate. The other limb contains a 12·5 per cent. Cd amalgam, which is readily made by warming the right proportions of the ingredients in a test-tube. The electrolyte consists of saturated cadmium sulphate solution, filled with 3 $CdSO_4$, 8 H_2O crystals. A small air-space is left above the liquid level, and the vessel is closed by successive layers of paraffin wax, cork, and sealing wax. All materials used must be very carefully purified. The E.M.F. of a cell is given by the expression

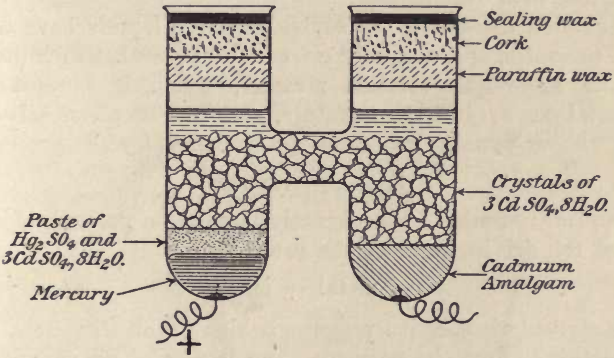

FIG 20.—Standard Cadmium Cell.

$$1{\cdot}0184 - 0{\cdot}00004\ (\theta - 20)\ \text{volt}.$$

The temperature coefficient is seen to be exceedingly small, $\frac{1}{25}$ millivolt per degree, and the E.M.F. remains constant if none but very small currents are allowed to go through it.[1]

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[1] For measurement of single potential difference, see p. 104.

3. Electrolytic Solution Pressure

The most important type of electrode process, anodic or cathodic, is that in which a metal and its corresponding ions in the electrolyte take part, and a conception of Nernst's enables us clearly to picture what happens in such cases. Every metal has a certain tendency to oxidise, and, as we have seen, this is equivalent to a tendency to take up positive electricity and enter solution as positively charged metallic cations. With the noble metals—gold, platinum etc.—this tendency is very slight; with metals such as copper and lead greater, with iron and zinc greater still, with the strongly electro-positive alkali metals very high indeed. An analogy is furnished by the different tendencies of different liquids to vaporise or give out gas molecules—small at room temperature with mercury, higher with water, very considerable with ether.

We express these facts by saying that the liquids have different vapour pressures, and similarly we can suppose that each metal has a definite **electrolytic solution pressure,** which is a constant for that metal at a given temperature, and with a given solvent. A liquid's vapour pressure measures the tendency for the process

$$\text{liquid} \rightarrow \text{vapour}$$

to take place; similarly the electrolytic solution pressure of a metal measures the driving-force of the process

$$\text{metal} \rightarrow \text{ion.}$$

This electrolytic solution pressure is high for alkali metals, low for noble metals. Now the presence of molecules of its vapour in the space above it counteracts the tendency of a liquid to vaporise; if the space is supersaturated with vapour, liquid will deposit until equilibrium is reached and the pressure above the liquid equals the pressure of saturated vapour. Any ions of the metal already in solution will act analogously. The tendency to deposit metal and give up positive electricity will be greater, the greater the concentration of those ions, and will be measured by their osmotic pressure. If that is very high, or if the electrolytic solution pressure of the metal is low, the latter will be overcome, and the net tendency will not be for metal to ionise, but for ions to discharge. In this case the metal will become positively, and the solution negatively, charged, whilst if the electrolytic solution pressure of the metal overpowers the ionic osmotic pressure, the metal will become negatively, the solution positively, charged.

The two cases are simply illustrated by copper in normal copper sulphate and zinc in normal zinc sulphate. In the former case the electrode, in the latter case the solution, is positively charged (Fig. 21). As the ionic concentrations in the two solutions are practically equal, this difference is entirely due to differences in the electrolytic solution pressures of the two metals. That of copper is low, and is overpowered by the osmotic pressure of the $Cu^{\cdot\cdot}$ ions, whilst the tendency of the strongly electropositive zinc to ionise overcomes the opposing action of the zinc ions already in solution.

Electrical Double Layer.—One could object that, if an equilibrium of the kind indicated, analogous to the equilibrium between a liquid and its vapour, does really exist between a metal and its dissolved ions, then, when a metal is dipped into solutions of its salts of different strengths, it should either dissolve or ions should deposit, until in every case the metal ion concentration in the solution has reached the value corresponding to equilibrium with the electrolytic solution pressure at that temperature. This, of course, does not occur. The electrolytic solution pressure of silver is low, but strong solution of silver salts do not deposit silver when in contact with a silver electrode, nor conversely does zinc enter solution as zinc ions in detectable amounts when immersed in a solution poor in zinc.

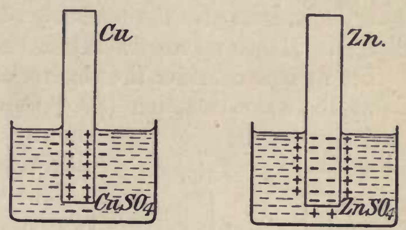

FIG. 21.

The reason for this apparent discrepancy is that, whereas with a liquid and its vapour we are dealing with electrically neutral molecules, in the present case we are concerned with charged ions. If we consider zinc in zinc sulphate, the first action is certainly the passage of positively charged zinc ions into solution leaving behind an equal number of negative charges on the metal. But this action ceases practically instantaneously, owing to the very powerful electrostatic action set up between the separated positive and negative charges, and preventing any further separation. When we remember that 96,540 coulombs are associated with one gram-equivalent of ionic matter, this fact is not surprising. The **electrical double layer**, such as is shown in Fig. 21, hinders any further formation or discharge of ions, which can only proceed continuously if the opposite charges are somehow constantly withdrawn.

We will now see, for a concrete case, how Nernst's theory explains (*a*) the chemical replacement of one metal by another, (*b*) the production of current in a galvanic cell. If we place a piece of zinc in dilute copper sulphate, zinc sulphate will be formed and copper deposited, whilst if copper be dipped into a zinc sulphate solution nothing happens. The explanation is simple. Zinc strongly tends to ionise, and, when placed in an electrolyte, assumes a high electrostatic negative charge, the corresponding positive portion of the electrical double layer being in the liquid. Copper ions tend powerfully to give up their positive charge. The strong negative electrostatic charge on the zinc enables them to do so. The negative charge on the zinc and the positive charge of the Cu¨ ions neutralise one another and metallic copper results. The electrical double layer at the zinc surface is renewed by more zinc ions passing into solution, and the process thus continues. With copper in zinc sulphate, the electrostatic negative charge on the metal is very low, as is also the tendency of zinc ions to lose their positive charges. Hence no neutralisation or chemical replacement.

Let us now consider the electrochemical arrangement for bringing about the same reaction ($Zn + CuSO_4 \longrightarrow Cu + ZnSO_4$), the well-known Daniell cell. This is shown diagrammatically in Fig. 22.

The containing vessel is divided into two parts by the porous diaphragm. One compartment contains a $ZnSO_4$ solution in which is suspended a strip of zinc, and the other copper in $CuSO_4$ solution. We have already seen that zinc in $ZnSO_4$ is negatively charged with respect to the solution, and that copper is positively charged with respect to $CuSO_4$. The potential difference between the two liquids is negligible, and it therefore follows that the copper is at a positive potential with respect to the zinc. If these two electrodes are joined externally by a wire, positive electricity will therefore flow along it from copper to zinc. The electrical double layers are thus destroyed, and will reform through more Cu¨ ions discharging and more zinc ions dissolving. The result will be a continuous current flowing through the cell and around the circuit, whilst the copper sulphate solution will become weaker, depositing copper, and the zinc sulphate solution stronger at the expense of the zinc anode. The E.M.F. of the cell is given by the potential difference between the copper and zinc strips with open external circuit, *i.e.* equal to the difference of the single electrode potentials. In this case it is (copper potential—electrolyte potential) *minus* (zinc potential—electrolyte potential). As both terms increase with an increase in the concentrations of the respective electrolytes, the E.M.F. of the cell should increase with increase of copper sulphate concentration and with decrease of zinc sulphate concentration. This deduction is borne out by facts.

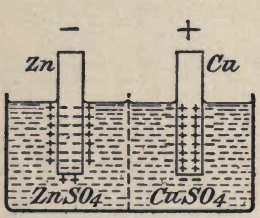

FIG. 22.—Daniell Cell.

4. Quantitative Relations at Ionising Electrodes

Electrolytic Potential.—As the E.M.F. of such a cell is determined essentially by the two electrode potential differences, these in their turn depending on the concentrations of the electrolytes which are variable, and the electrolytic solution pressures of anode and cathode, which are constants for the substance concerned (at constant temperature and with the same solvent), it is important that these latter values, or measures of them, should be known and tabulated. A suitable measure of the electrolytic solution pressure is the potential difference between electrode and electrolyte, rendered comparable with values for other substances by eliminating effects due to concentration differences between the different solutions. As standard electrolyte, one containing always *one gram-ion* per litre of the ion concerned is taken: thus a concentration of 35·5 grams Cl' ion, 56 grams $Fe^{\cdot\cdot}$ ion, 96 grams SO_4'' ion per litre. The potential difference in that case is known as the **electrolytic potential** (E.P.) of the electrode reaction concerned.[1]

Before giving any numerical figures we must decide on the conventions of sign and potential zero to be used. *The potential of an electrode will always be regarded as (potential of electrode minus potential of solution)*, never as (potential of solution minus potential of electrode), as is done by some writers. This will hold both for electrodes which give off positive ions, such as those we have discussed, and for electrodes furnishing negative ions.

There are two scales for potential measurement in common use. The first is termed the *absolute scale*, and potentials expressed on this scale, written $\mathcal{E}_a$, are certainly near the actual absolute values. Unfortunately it is not quite certain how close they are, although most of the evidence available indicates that the difference is small. This fact has led to the introduction of another scale of potential measurement, in which the zero is quite arbitrarily fixed, and reproducible with accuracy.[2] This scale is the *hydrogen scale* (potentials written $\mathcal{E}_h$), the electrode potential of a platinised-platinum electrode, half dipping in 2n. H_2SO_4, and half surrounded by an atmosphere of pure hydrogen, which bubbles at atmospheric pressure through the sulphuric acid, being taken as zero-point. This electrode is termed the *normal hydrogen electrode*, the 2n. H_2SO_4 being very nearly 1n. with respect to $H^\cdot$ ion, and the hydrogen dissolved in the platinised platinum behaving as if it had a definite electrolytic solution pressure.

The potential of the same electrode on the absolute scale is + 0·277 volt. This difference, of course, holds for all potential values expressed on the two scales. Hence we have the relation

$$\mathcal{E}_a = \mathcal{E}_h + 0{\cdot}277.$$

The advantage of using the absolute scale is, of course, that the single

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[1] Wilsmore, *Zeitsch. Phys. Chem.* **35**, 291 (*1900*).

[2] Similar considerations led to the choice of O = 16 as the basis of atomic weights, instead of H = 1.

potential value at once tells us whether a certain electrode process takes place with decrease or increase of free energy. But, on the other hand, the uncertainty mentioned above has led to the more general adoption of the hydrogen scale, which is the one used throughout this book, unless otherwise mentioned.

Voltage Series.—Table XVII contains the more important of these electrolytic potentials, and the equations expressing the electrochemical processes of which they measure the driving force.

TABLE XVII

Electrochemical Process.	Electrolytic Potential = potential of electrode minus potential of solution containing 1 gram-ion dissolved per litre.	
	$\mathcal{E}_h$ in volts.	$\mathcal{E}_a$ in volts
$Na^{\cdot} \longrightarrow Na + \oplus$	$-2·72$	$-2·44$
$Mg^{\cdot\cdot} \longrightarrow Mg + 2\oplus$	$-1·55$	$-1·27$
$Zn^{\cdot\cdot} \longrightarrow Zn + 2\oplus$	$-0·76$	$-0·48$
$Fe^{\cdot\cdot} \longrightarrow Fe + 2\oplus$	$-0·43$	$-0·15$
$Cd^{\cdot\cdot} \longrightarrow Cd + 2\oplus$	$-0·40$	$-0·12$
$Ni^{\cdot\cdot} \longrightarrow Ni + 2\oplus$	$-0·22$	$+0·06$
$Pb^{\cdot\cdot} \longrightarrow Pb + 2\oplus$	$-0·12$	$+0·16$
$Sn^{\cdot\cdot} \longrightarrow Sn + 2\oplus$	$-0·10$	$+0·18$
$H^{\cdot} \longrightarrow \frac{1}{2} H_2 + \oplus$	$\pm 0·00$	$+0·277$
$Cu^{\cdot\cdot} \longrightarrow Cu + 2\oplus$	$+0·33$	$+0·61$
$\frac{1}{2} O_2 + H_2O \longrightarrow 2OH' + 2\oplus$	$+0·41$	$+0·69$
$\frac{1}{2} I_2 \longrightarrow I' + \oplus$	$+0·54$	$+0·82$
$Hg_2^{\cdot\cdot} \longrightarrow 2Hg + 2\oplus$	$+0·78$	$+1·06$
$Ag^{\cdot} \longrightarrow Ag + \oplus$	$+0·80$	$+1·08$
$\frac{1}{2} Br_2 \longrightarrow Br' + \oplus$	$+1·08$	$+1·36$
$\frac{1}{2} Cl_2 \longrightarrow Cl' + \oplus$	$+1·36$	$+1·64$
$Au^{\cdot} \longrightarrow Au + \oplus$	$+1·5$	$+1·78$

Two kinds of equilibria are represented in this table :—

(*a*) between metal and ion,

(*b*) between non-metal and ion.

For the former class the electrolytic potential measures the tendency for ions to discharge their electricity and assume the metallic state. To get a measure of the electrolytic solution pressure, or the tendency for metals to ionise, we must simply reverse the signs of the above figures. Then we see that for easily oxidisable metals, such as Mg, Zn and Fe, we have high positive values, and for the noble[1] metals silver and mercury large negative values, indicating a very small ionising tendency.

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[1] A positive *potential* is very often spoken of as a *noble* potential.

The examples given of equilibria between non-metals and ions all deal (except oxygen) with the halogens and the anions of the halogen acids. Like the metals, the halogens tend to send into solution ions, which are negatively charged, corresponding to the electronegative character of the neutral substance. We can ascribe to each halogen an electrolytic solution pressure, just as we did to the metals, and the explanation of the potential difference at a halogen electrode,[1] the formation of an electrical double layer, etc., will be the same as before. The greater the ionising tendency, the more negative the solution becomes, and the more positive the electrode, differing in this way from the relations at a metal electrode. As the electrolytic potential always measures the driving-force of that reaction which tends to charge the electrode positively, in the case of anions it will be equivalent to the electrolytic solution pressure, and will give a measure of the tendency to ionise, not of the tendency to discharge. The more reactive the halogen, *i.e.* the more easily it enters the ionic condition, the higher will be its E.P. Thus, we find that the values of E.P. for iodine, bromine, and chlorine successively increase.

The above table sheds light on certain chemical reactions, more particularly on the action of metals in displacing hydrogen from acids, or other metals from salt solutions. We can make the general statement that a metal will replace another of lower electrolytic solution pressure from solutions of its salts.[2] As the metals stand in the table in the order of decreasing electrolytic solution pressures, each metal should be able to displace from solution all those below it. Consequently we find that zinc will displace lead, iron will displace copper, and copper turn out silver. Further tin and all metals above it should be able to liberate hydrogen from dilute acids. Copper, silver, and mercury, on the other hand, should be precipitated by hydrogen.

The facts are generally in agreement, and apparent exceptions can be readily explained. A piece of very smooth pure zinc does not dissolve in pure dilute H_2SO_4, very probably because of a thin film of hydrogen, which is unable to form bubbles and so escape. If the same pure zinc be roughened, it readily dissolves. Lead does not dissolve in dilute H_2SO_4 or HCl because of insoluble coatings of the respective salts which prevent further action.[3] Hydrogen gas will not precipitate copper from solution, because it cannot ionise. If, however, a piece of palladium be placed in the solution, the hydrogen dissolves in it, is able to ionise, and readily precipitates copper.

Effect of Ionic Concentration.—We have seen that an electrode potential partly depends on the concentration in the electrolyte

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[1] See p. 99.

[2] This is not always true with metals of nearly equal electrolytic solution pressures, as the relative concentrations of the different metallic ions in the electrolyte will then play a part.

[3] Overvoltage (p. 118) also plays a part.

of the ion concerned. If the ion is positive, the potential difference becomes more positive with increase of concentration. If the ion is negative, as Cl′, then the potential becomes more negative or less positive with increase of concentration. In dealing with the quantitative aspect of these relations we can attempt no proof of the simple equations finally reached, but will merely state the results. For a metallic electrode in a solution containing the corresponding cation we have

$$\mathcal{E} = \text{E.P.} + \frac{0{\cdot}0002\text{T}}{n} \log [\text{C}],$$

an equation connecting single electrode potential, electrolytic potential, and ionic concentration. [C] is the gram-ionic concentration and *n* the valency of the ion. If we further simplify matters by assigning a definite value to T—say 290°, which is room temperature—we obtain

$$\mathcal{E} = \text{E.P.} + \frac{0{\cdot}058}{n} \log [\text{C}].$$

From this simple formula can be calculated the single potential of an electrode for different concentrations of electrolyte.

For example, what will be the potential of a zinc electrode immersed in n. $ZnSO_4$ at 17° ? We have for this solution $a = 0{\cdot}2$. Hence [C] is $0{\cdot}5 \times 0{\cdot}2 = 0{\cdot}1$. We can put E.P. for $Zn^{\cdot\cdot} \rightarrow Zn + 2 \oplus$ as $-0{\cdot}765$ volt. Also *n* is 2. Hence

$$\begin{aligned} \mathcal{E} &= -0{\cdot}765 + \frac{0{\cdot}058}{2} \log 0{\cdot}1 \\ &= -0{\cdot}765 - 0{\cdot}029 \\ &= -0{\cdot}794 \text{ volt.} \end{aligned}$$

(The experimentally determined figure is $-0{\cdot}795$ volt.)

If the electrode reaction involves an anion, instead of a cation, we have a similar formula, only with an altered sign. The electrode potential—*i.e.* potential of electrode minus potential of solution—will be higher the lower the ionic concentration. That is, we have

$$\mathcal{E} = \text{E.P.} - \frac{0{\cdot}0002\text{T}}{n} \log [\text{C}].$$

And at 17°,

$$\mathcal{E} = \text{E.P.} - \frac{0{\cdot}058}{n} \log [\text{C}].$$

Thus, for example, what will be the electrode potential at 18° of a chlorine electrode in $\frac{1}{10}$ *n* . KCl ? We have *a* for $\frac{1}{10}$ *n* . KCl $= 0{\cdot}85$, and therefore $[\text{C}] = 0{\cdot}085$. Also E.P. is $+ 1{\cdot}363$ volt, and $n = 1$. Hence

$$\begin{aligned} \mathcal{E} &= 1{\cdot}363 - \frac{0{\cdot}058}{1} \log 0{\cdot}085 \\ &= 1{\cdot}363 - 0{\cdot}058\,(-1{\cdot}07) \\ &= 1{\cdot}425 \text{ volt.} \end{aligned}$$

A general formula for the E.M.F. of cells in which both electrodes consist of substances in equilibrium with their corresponding ions follows at once, being simply given by the difference of the two single electrode potentials.[1] The formula will naturally vary somewhat, depending on whether the electrodes give out anions or cations. We will again take the Daniell cell as example. Our formula (at 17°) will be

$$E = \mathcal{E}_1 - \mathcal{E}_2 = (\text{E.P.})_1 + \frac{0{\cdot}058}{n_1} \log [C_1]$$
$$- (\text{E.P.})_2 - \frac{0{\cdot}058}{n_2} \log [C_2].$$

The cathode is the copper electrode, which is more positively charged than the zinc. We therefore write

$$(\text{E.P.})_1 = \text{E.P.}_{\text{Cu}^{\cdot\cdot} \rightarrow \text{Cu}} = + 0{\cdot}33 \text{ volt.}$$
$$(\text{E.P.})_2 = \text{E.P.}_{\text{Zn}^{\cdot\cdot} \rightarrow \text{Zn}} = - 0{\cdot}76 \text{ volt.}$$
$$n_1 = n_2 = 2.$$

And

$$E = 0{\cdot}33 + 0{\cdot}76 + 0{\cdot}029 \log \frac{[C_{\text{Cu}^{\cdot\cdot}}]}{[C_{\text{Zn}^{\cdot\cdot}}]}$$
$$= 1{\cdot}09 + 0{\cdot}029 \log \frac{[C_{\text{Cu}^{\cdot\cdot}}]}{[C_{\text{Zn}^{\cdot\cdot}}]}.$$

As we have already seen, E increases with $[C_{\text{Cu}^{\cdot\cdot}}]$, but is lessened by an increase in $[C_{\text{Zn}^{\cdot\cdot}}]$. It can also be decreased by lowering $[C_{\text{Cu}^{\cdot\cdot}}]$. If KCN be added to the $CuSO_4$ solution, the $Cu^{\cdot\cdot}$ ions are almost completely removed and converted into $Cu(Cy)_2'$ anions, cyanogen gas being evolved. $[C_{\text{Cu}^{\cdot\cdot}}]$ thus assumes an extraordinarily low value, so much so that E not only falls to zero, but actually becomes negative. That is to say, *copper dissolves and zinc ions are discharged.*

5. Gas Electrodes

Hitherto we have chiefly dealt with the electrode reactions between metal electrodes and metal ions. There are other kinds of electrode reactions which also need discussion. Gas electrodes have already been mentioned. Besides hydrogen and the halogens, oxygen can also ionise, the corresponding equation being $\frac{1}{2}O_2 + H_2O \longrightarrow 2OH'$. Nitrogen does not ionise. To render these gases electromotively active, they are best bubbled through an electrolyte containing the ion concerned in which dips a piece of platinised platinum, half immersed in the solution. The gas will dissolve to some extent in the platinum and can then ionise. Bromine and iodine ionise just like hydrogen and chlorine, but in the case of oxygen the matter is not so

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[1] Neglecting the small liquid potential difference.

simple. An oxide of platinum plays an intermediate rôle, the process being partly irreversible. Smooth platinum can be used in all cases, but is far less effective. The electrolytic solution pressure of a gas dissolved in platinum is greater the higher the content of gas in the metal, which in its turn is greater the greater the gas pressure in the surrounding space. The potential of a gas electrode depends therefore on the pressure of the gas, but, as moderate variations of pressure only produce very slight effects, we need not further consider the matter.

6. Oxidation—Reduction Electrodes

We have seen that all reactions which can take place electromotively are divisible into two parts—an oxidation process and a reduction process, which take place electrochemically at anode and cathode respectively. The oxidation process is characterised by an increase in the number of positive charges associated with the substance oxidised, and the reverse statement holds of the reduction process. $Ag \longrightarrow Ag^{\cdot}$ is an oxidation, and $Zn^{\cdot\cdot} \longrightarrow Zn$ or $\frac{1}{2}Cl_2 \longrightarrow Cl'$ a reduction. In all cases so far considered, these single electrode reactions involve the transference of electricity between an ion and an electrically neutral substance, as in the above examples. But many reactions, when resolved into their constituent oxidation and reduction processes, give electrode reactions which involve transference of electricity from ion to ion, no electrically neutral substance taking part. For example, let us consider the reactions

$$Cu + Fe_2(SO_4)_3 \longrightarrow CuSO_4 + 2FeSO_4$$

or

$$Cu + 2Fe^{\cdot\cdot\cdot} \longrightarrow Cu^{\cdot\cdot} + 2Fe^{\cdot\cdot}$$

and

$$\begin{aligned} 2\,KMnO + 10FeSO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 &+ 2MnSO_4 \\ &+ 5Fe_2(SO_4)_3 + 8H_2O, \end{aligned}$$

also expressed by

$$MnO_4' + 5Fe^{\cdot\cdot} + 8H^{\cdot} \longrightarrow Mn^{\cdot\cdot} + 5Fe^{\cdot\cdot\cdot} + 4H_2O.$$

The former can be regarded as composed of the reactions

$$\begin{array}{ll} & \left.\begin{array}{r} Cu + 2\oplus \longrightarrow Cu^{\cdot\cdot} \\ 2Fe^{\cdot\cdot\cdot} \longrightarrow 2Fe^{\cdot\cdot} + 2\oplus \end{array}\right\} \\ \text{and} & \end{array}$$

and the latter of

$$\begin{array}{ll} & \left.\begin{array}{r} 5Fe^{\cdot\cdot} + 5\oplus \longrightarrow 5Fe^{\cdot\cdot\cdot} \\ MnO_4' + 8H^{\cdot} \longrightarrow Mn^{\cdot\cdot} + 4H_2O + 5\oplus \end{array}\right\}. \\ \text{and} & \end{array}$$

In three out of these four electrode processes we have ions taking part on both sides of the equation.

Now such chemical reactions can also generally proceed electromotively. In the first case, the following cell would be set up :

$$\begin{array}{c|c|c|c} + & & & - \\ \mathrm{Pt} & \mathrm{Fe_2(SO_4)_3} & \mathrm{CuSO_4} & \mathrm{Cu} \\ & \mathrm{FeSO_4} & & \end{array}$$

The platinum acts as a cathode, by means of which positive electricity can leave the solution; otherwise it is unchanged. The copper is the anode, and the electrode reactions will be as given. At the platinum $Fe_2(SO_4)_3$ will be reduced to $FeSO_4$, whilst the copper anode will dissolve to $CuSO_4$. The arrangement for the second case would be

$$\begin{array}{c|c|c|c} + & & & - \\ \mathrm{Pt} & \mathrm{KMnO_4} & \mathrm{Fe_2(SO_4)_3} & \mathrm{Pt} \\ & \mathrm{MnSO_4} & \mathrm{FeSO_4} & \\ & \mathrm{H_2SO_4} & & \end{array}$$

The electrode on the left acts as cathode, and at it $KMnO_4$ is reduced to $MnSO_4$, and H_2SO_4 neutralised. At the other electrode, $FeSO_4$ is oxidised to $Fe_2(SO_4)_3$. In both these arrangements the diminution of free energy of the chemical reaction, usually dissipated as heat, is utilised as electrical energy.

Such cells are termed *oxidation-reduction cells*, and the corresponding electrode systems *oxidation-reduction electrodes*. As in the types of electrode already discussed, the essential reaction is an increase or decrease in the amount of electricity associated with a substance. We can imagine potential differences to be produced at the electrodes in the same way as before. Thus, with nickel in $NiSO_4$, the two opposing tendencies are the electrolytic solution pressure of the nickel, tending to send $Ni^{\cdot\cdot}$ ions into solution, and the osmotic pressure of the $Ni^{\cdot\cdot}$ ions tending to discharge metallic nickel. If the former tendency predominates the electrode becomes charged negatively, and positively if the contrary holds. Similarly with a platinum electrode in a mixture of $FeSO_4$ and $Fe_2(SO_4)_3$, the opposing tendencies are that of $Fe^{\cdots}$ ions to give up positive charges to the electrode, and the tendency of $Fe^{\cdot\cdot}$ ions to take up positive electricity from the electrode and become oxidised to ferric ions. If the driving force of the reaction

$$Fe^{\cdots} \longrightarrow Fe^{\cdot\cdot} + \oplus$$

exceeds that of

$$Fe^{\cdot\cdot} + \oplus \longrightarrow Fe^{\cdots},$$

the electrode will become positively charged. Increase of the $Fe^{\cdots}$ ion concentration will increase this positive charge, an increase of $Fe^{\cdot\cdot}$ ions will diminish it. The formula expressing the variation of potential difference with ionic concentration is of the same type as before. At 18° it is

$$\mathcal{E} = \text{E.P.} + \frac{0{\cdot}058}{n} \log \frac{[C_1]}{[C_2]}.$$

Here $[C_1]$ is the concentration of the more positively charged ion, $[C_2]$ that of the other ion, and n is again the number of faradays involved in the electrode reaction. In the case of $Fe^{\cdot\cdot\cdot} \longrightarrow Fe^{\cdot\cdot} + \oplus$, n is 1, and we have

$$\mathcal{E} = \text{E.P.}_{Fe^{\cdot\cdot\cdot} \rightarrow Fe^{\cdot\cdot}} + 0{\cdot}058 \log \frac{[C_{Fe^{\cdot\cdot\cdot}}]}{[C_{Fe^{\cdot\cdot}}]}.$$

E.P., the electrolytic potential, is the potential of the electrode when $[C_1] = [C_2] = 1$, *i.e.* when the second term on the right hand of the equation is zero. In the case of $Fe^{\cdot\cdot\cdot} \longrightarrow Fe^{\cdot\cdot} + \oplus$, the electrolytic potential is + 0·71 volt, indicating that a ferrous-ferric sulphate mixture has a strong tendency to give up positive charges, and hence to oxidise other systems.

With more complicated electrode reactions, involving several ions, the formula is less simple. The equation expressing the electrode reaction must first be written in such a way that

left-hand side + positive electricity ⟶ right-hand side.

Thus, with the permanganate electrode

$$Mn^{\cdot\cdot} + 4H_2O + 5\oplus \longrightarrow MnO_4' + 8H^{\cdot},$$

and not as

$$MnO_4' + 8H^{\cdot} \longrightarrow Mn^{\cdot\cdot} + 4H_2O + 5\oplus,$$

or as

$$MnO_4' + 8H^{\cdot} + 5\ominus \longrightarrow Mn^{\cdot\cdot} + 4H_2O.$$

If then the mass action chemical equilibrium constant of this reaction [1] be taken as K, the single electrode potential at 18° is given by

$$\mathcal{E} = \text{E.P.} + \frac{0{\cdot}058}{n} \log \text{K}.$$

E.P. being the electrode potential in a solution of gram-ionic concentration unity for all the ions taking part. In the present case n is five and

$$K\,\cancel{\mathcal{E}} = \frac{[C_{MnO_4'}] \cdot [C_{H^{\cdot}}]^8}{[C_{Mn^{\cdot\cdot}}]}.$$

Thus we have

$$\mathcal{E} = \text{E.P.} + \frac{0{\cdot}058}{5} \log \frac{[C_{MnO_4'}] \,.\, [C_{H^{\cdot}}]^8}{[C_{Mn^{\cdot\cdot}}]}.$$

The tendency to give up positive charges—*i.e.* to oxidise—increases with

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[1] P. 14.

the acid and permanganate concentrations, and decreases with the manganous salt concentration.[1]

A great advantage of considering oxidising and reducing agents (and reactions) in this way is the fact that we can plainly see that there is no sharp line of demarcation between them. The oxidising power of a solution is directly measured by the potential difference between a platinum electrode placed in it and the solution itself. The more positive the electrode, the more strongly oxidising the solution; if the electrode assumes a high negative charge, the solution is a strong reducing agent. Alkaline $SnCl_2$, or alkaline pyrogallol, gives a negative charge to the electrode, and $NaClO$ and $KMnO_4$ will charge it positively. Between these extremes are electrolytes giving every conceivable value of single potential difference. Generally speaking, *a solution will oxidise any other solution which charges an indifferent electrode to a lower positive value*, exactly as a metal will displace from solution other metals of lower electrolytic solution pressure.

7. Concentration Cells

We have now discussed the different types of reversible electrode reactions, and can understand how any two electrode systems, provided they are at different potentials, when put together will give a primary cell. If joined by an external wire, positive electricity will flow through this circuit from the more positively charged electrode (cathode) to the less positively charged one (anode), and back again through the cell, whose E.M.F. will be given by the difference of the two single electrode potentials.

One type of cell, rather different from those hitherto considered, should be briefly mentioned—the **concentration cell.**[2] Consider the general equation for the E.M.F. of an element

$$\begin{aligned} E &= \mathcal{E}_1 - \mathcal{E}_2 \\ &= (\text{E.P.})_1 - (\text{E.P.})_2 + \frac{0{\cdot}058}{n_1} \log [C_1] - \frac{0{\cdot}058}{n_2} \log [C_2] \end{aligned}$$

(this form when both electrodes give cations). If the two electrodes

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[1] It might be pointed out that the mechanism of these apparently complex processes is really simple. Thus the reduction of MnO_4' to $Mn^{\cdot\cdot}$ ions can be split into two stages

$$MnO_4' + 4H_2O \longrightarrow Mn^{\cdot\cdot\cdot\cdot\cdot\cdot\cdot} + 8OH'$$
$$Mn^{\cdot\cdot\cdot\cdot\cdot\cdot\cdot} \longrightarrow Mn^{\cdot\cdot} + 5 \oplus$$

The first reaction takes place without ionic transference—so that the process is essentially the reduction of hepta-valent to di-valent manganese, and falls into line with the reduction of tri-valent to bi-valent iron. Similarly the oxidation of $Cr^{\cdot\cdot\cdot}$ to CrO_4' (chromate) can be regarded as essentially the oxidation of tri-valent to hexa-valent chromium.

[2] See also pp. 89, 115, 163, 207.

(and the two ions) are identical, then $(E.P.)_1 = (E.P.)_2$ and $n_1 = n_2$, and we get

$$E = \frac{0{\cdot}058}{n} \log \frac{[C_1]}{[C_2]},$$

that is, the E.M.F. of the cell is determined by the ratio of the ionic concentrations at the two electrodes.[1] It increases as this ratio increases, and is in fact a measure of the diminution of free energy occurring when the two unequally concentrated solutions are mixed. Except when the concentration ratio is enormous these E.M.F.s never reach large values.

8. Measurement of Single Electrode Potentials

The measurement of single potential differences is carried out very simply with the apparatus in Fig. 19. The electrode to be measured is opposed to a **standard electrode,** the potential of which is known, thus producing a galvanic cell, and the E.M.F. of this cell is measured exactly as described on page 90. Suppose it to be E. Then $E = \mathcal{E}_1 - \mathcal{E}_2$, the difference of the two single potentials. Knowing the standard potential difference, and having determined E, the unknown single potential at once follows. Fig. 23 shows a convenient form of vessel in which to set up electrodes, whether standard or experimental. It is about 6 inches high, and provided with a siphon-shaped side-tube. The electrode itself is sealed into a glass tube passing through a rubber stopper, or else is directly inserted through the stopper. When making up a cell, the siphon side-tubes of the two electrode vessels are filled by blowing at A, and dipped into a small vessel containing an electrolyte in order to make electrical contact. When this vessel contains a saturated $AmNO_3$ or a saturated KCl solution, the potential difference at the cell's liquid junction is practically eliminated if the electrolytes concerned are neutral or not too strongly acid.

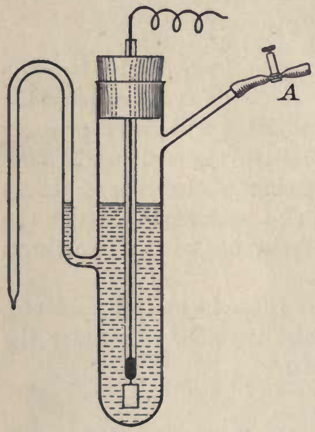

FIG. 23.—Electrode Vessel.

The standard electrodes most commonly used are the *normal* and *deci-normal calomel electrodes.* Their electrode system is Hg | KCl solution saturated with HgCl. They are readily made up. Into a vessel of the type described, half an inch of pure mercury is poured.

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[1] The liquid potential difference in the cell is not considered.

This is covered with a fine paste made by shaking up calomel and mercury several times with some of the standard KCl afterwards employed, throwing away the liquid every time. The vessel is then filled up with KCl which has already been saturated with HgCl, and the electrode is at once ready for use. The potential of the normal calomel electrode (Hg | HgCl n . KCl) is $\mathcal{E}_h = +\ 0{\cdot}283$ volt at 18°; that of the deci-normal electrode (Hg | HgCl $\frac{1}{10}$ n . KCl), $\mathcal{E}_h = +\ 0{\cdot}336$ volt at 18°.

For use with alkaline solutions, the electrodes Hg | HgO n . NaOH and Hg | HgO $\frac{1}{10}$ n . NaOH are the best. The HgO must be made by the thorough and careful ignition of pure mercuric nitrate. The same type of vessel is used as for the calomel electrode. Pure mercury is put in first, a layer of oxide added, and the NaOH solution poured on. The potentials (constant after three days) are for the normal electrode $\mathcal{E}_h = +\ 0{\cdot}114$ volt, and for the deci-normal electrode $\mathcal{E}_h = +\ 0{\cdot}169$ volt at 18°.

For use with acid solutions, the hydrogen standard electrode of potential difference $\pm\ 0{\cdot}0$ volt,[1] works very well. But more convenient is the use of the system Hg | Hg_2SO_4 n . H_2SO_4. This mercurous sulphate electrode is made up similarly to the others quoted, and has a potential $\mathcal{E}_h = +\ 0{\cdot}689$ volt at 18°.

If, as sometimes happens, it is necessary to measure the potential difference at an electrode in an electrolysis tank or vessel whilst current is passing, the siphon side-tube of the vessel containing the standard electrode is very much lengthened, bent horizontally at the end, and drawn out to a fine point, which is gently pressed up immediately against the electrode in question.[2] Working thus, the error introduced owing to the potential fall produced by the current is very low, seldom exceeding 0·002 volt in extreme instances.

Literature

Le Blanc. *Electrochemistry.*

[1] See p. 95.

[2] Haber, *Zeitsch. Phys. Chem.* **32**, 207 (*1900*). Also Foerster and Müller, *Zeitsch. Elektrochem.* **9**, 200 (*1903*).

CHAPTER IX

ELECTROLYSIS AND POLARISATION—ENERGY EFFICIENCY

1. Polarisation

In the last chapter we discussed the electrochemical processes occurring in different types of primary cells, the result of spontaneous chemical reactions accompanied by a decrease in free energy. We must now consider those cells in which the chemical energy of the system increases during action, owing to electrical energy led in from outside. Such cells are technically the most important.

The relations here existing are best understood by first considering the behaviour of the primary Daniell cell under varying conditions. We know that normally the copper electrode is about 0·3 volt positive to the solution, and the zinc electrode 0·8 volt negative to the $ZnSO_4$. The cell E.M.F. is consequently 1·1 volt, and we express the potential difference relations as in Fig. 24. Suppose now the cell is short-circuited by connecting the electrodes A and C with a wire. Positive electricity will flow along the wire from A to C. A becomes less positive, and the potential difference AB becomes less and falls below its equilibrium value. C becomes more positively charged, and the potential difference BC becomes less negative and changes from its equilibrium value. In order to restore the electrode equilibria, copper ions deposit on A, increasing its positive charge, and zinc ions pass into solution at C, thus tending to regenerate the original potential difference BC. But the supply of $Cu^{\cdot\cdot}$ ions in the electrolyte is

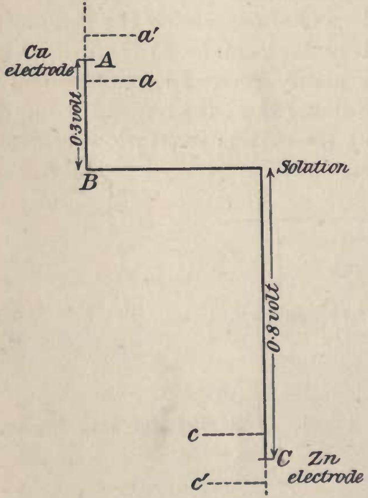

Fig. 24.

only a limited one, whilst the Zn¨ ions accumulate; hence the potential differences AB and BC must both gradually diminish. The E.M.F. of the cell given by AC will thus decrease. The process will continue until A and C are at the same potential, when electricity can no longer flow from one to the other, and the cell ceases to act.

This final state is represented in Fig. 25. A′B is the potential difference between copper and copper sulphate, C′B between zinc and zinc sulphate. As zinc ions have been continually dissolving, the zinc sulphate concentration has increased until the electrolyte has become saturated. As the Zn¨ ion concentration cannot further increase beyond this point, the potential difference BC′ cannot decrease any further, which is the reason of the far greater change of potential at the copper electrode. The copper sulphate concentration after the discharge of the cell is practically zero. The fundamental point to be noticed is that when an electrode potential becomes less positive than its equilibrium value, positive ions will be discharged (or in other cases negative ions will pass into solution). When on the contrary it becomes more positive than the equilibrium value, positive ions will enter solution (or negative ions will discharge), the tendency being in every case to neutralise the equilibrium shift.

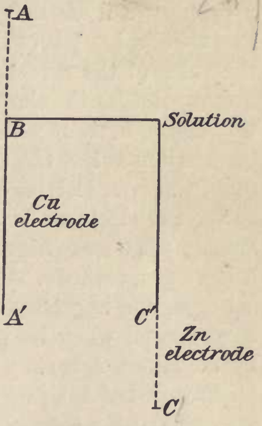

FIG. 25.

To return to the Daniell cell. Suppose that instead of short circuiting, and thus allowing the cell to work with a loss of free energy, corresponding to the chemical reaction

$$Zn + CuSO_4 \longrightarrow Cu + ZnSO_4$$

—suppose electrical energy to be led into the cell from outside, reversing the above reaction, and causing an *increase* in the power of the system to perform useful work. This is done by making the potential of the copper electrode more positive than its equilibrium value by connecting it with some outside source of positive current, and at the same time similarly rendering the potential of the zinc electrode more negative than its equilibrium value. Reactions tending to restore the electrode equilibria will set in. They will be, at the zinc electrode discharge of positive Zn¨ ions, at the copper electrode formation of positive Cu¨ ions. With the external circuit closed so that the applied source of current (and electrical energy) can steadily act, these processes will continue uninterruptedly. The copper electrode will dissolve, and zinc will be deposited on the zinc electrode. The corresponding chemical reaction is, as we have seen,

$$Cu + ZnSO_4 \longrightarrow CuSO_4 + Zn,$$

and the necessary increase of free energy is supplied as electrical energy.

When current is passed in this way into a cell from outside, raising the voltage of the cell terminals above its static value and increasing the free energy of the system, the cell is said to be **polarised,** and the phenomena observed are those of **polarisation.** Similarly, when a primary cell discharges in such a way that the voltage falls below its static value (the E.M.F.) the cell is polarised. It is evident that the value of the reversible electrode potential represents a true equilibrium point for the electrode concerned. If the potential is raised above this figure, current will tend to flow one way; if lowered beneath the equilibrium value, the tendency will be in the other direction. Generally, when an electrode potential is more positive than its equilibrium value, the electrode will attract negative charges, and function as an anode; when more negative than the equilibrium value the electrode will behave as a cathode. Just as a cell is said to be polarised when electrical energy is impressed into it from outside, so an electrode is said to be polarised when its potential is altered from the equilibrium value by an external agency or some other cause.

From what has just been said, it follows that an electrode is *anodically polarised* when its potential is made more *positive* than the equilibrium value, and *cathodically polarised* when made more *negative* than that figure. We speak correspondingly of *anodic and cathodic polarisation.* Strictly speaking, the polarisation of an electrode should be measured by the difference between the actual value of the electrode potential and the equilibrium value, but the term is often loosely applied to the actual total value of the electrode potential. The conception of anodically and cathodically polarised electrodes will be used continually in this book, and it will be well to thoroughly grasp its significance before proceeding further.

2. Energy Efficiency

Decomposition Voltage.—When the single potentials of the Daniell cell have the values corresponding to *a* and *c* (Fig. 24), and the electrodes are joined externally by a conductor, current will flow from copper to zinc *through this external circuit.* If, on the contrary, the electrode potentials be kept at *a′* and *c′* and the external circuit be closed, current will flow from copper to zinc *through the cell,* and the chemical reaction $ZnSO_4 + Cu \longrightarrow CuSO_4 + Zn$ takes place. The potential difference AC (1·1 volt) does not therefore only represent the E.M.F. of the Daniell cell, but also represents the minimum voltage which must be impressed on the cell terminals from outside in order that the current may flow in such a way that electrical is transformed into chemical energy. This minimum voltage is known as the **reversible decomposition voltage** of the cell, and is equal to the reversible E.M.F. of the corresponding primary cell.

It must be noted that whereas, when a cell is furnishing current, its E.M.F. continually tends to fall, on the other hand, when current is being forced through, the decomposition voltage tends to rise. This difference is due to the opposite chemical effects which result. In the Daniell cell, the $Zn^{\cdot\cdot}$ ion concentration increases, and the $Cu^{\cdot\cdot}$ ion concentration decreases when giving current, whilst when current is being sent through the reverse is true. In the one case there is a decrease, in the other case an increase, of free energy.

We now see what are the conditions determining preferential reversible ionic discharge in a solution containing several different anions or cations. The various single potential differences corresponding to several possible cathodic reactions are (at 18°) :—

$$\mathcal{E}_1 = \text{E.P.}_1 + \frac{0{\cdot}058}{n_1} \log [C_1]$$

$$\mathcal{E}_2 = \text{E.P.}_2 + \frac{0{\cdot}058}{n_2} \log [C_2]$$

$$\mathcal{E}_3 = \text{E.P.}_3 + \frac{0{\cdot}058}{n_3} \log [C_3], \text{ etc.}$$

Now, a cathodic discharge will set in at an electrode as soon as its single potential difference has been *reduced below* the corresponding equilibrium value. Hence that cathodic reaction will set in first to which corresponds the *highest equilibrium potential*.

Suppose, for example, a solution to contain copper and nickel salts, together with free acid. Let the respective gram-ionic concentrations be $[Cu^{\cdot\cdot}] = 0{\cdot}015$, $[Ni^{\cdot\cdot}] = 0{\cdot}23$, $[H^{\cdot}] = 0{\cdot}72$. Then the possible cathodic reactions (excluding $Cu^{\cdot\cdot} \longrightarrow Cu^{\cdot} + \oplus$) are $Cu^{\cdot\cdot} \longrightarrow Cu + 2\oplus$, $Ni^{\cdot\cdot} \longrightarrow Ni + 2\oplus$, and $H^{\cdot} \longrightarrow \frac{1}{2}H_2 + \oplus$ and the corresponding single potentials

$$\begin{aligned}
\mathcal{E}_{Cu^{\cdot\cdot} \longrightarrow Cu} &= +0{\cdot}33 + 0{\cdot}029 \log 0{\cdot}015 = +0{\cdot}277 \text{ volt,} \\
\mathcal{E}_{Ni^{\cdot\cdot} \longrightarrow Ni} &= -0{\cdot}22 + 0{\cdot}029 \log 0{\cdot}23 = -0{\cdot}239 \text{ volt,} \\
\mathcal{E}_{H^{\cdot} \longrightarrow \frac{1}{2}H_2} &= 0{\cdot}0 + 0{\cdot}058 \log 0{\cdot}72 = -0{\cdot}008 \text{ volt.}
\end{aligned}$$

The highest single potential difference corresponds to the reaction $Cu^{\cdot\cdot} \longrightarrow Cu$, and (assuming the reactions to take place reversibly) discharge of $Cu^{\cdot\cdot}$ ions will be the first to occur.

The case is very similar with various possible anodic reactions. At this point we will consider two only, the solution of a metallic electrode and the discharge of an anion. As before, the equilibrium potential of the metal is given (at 18°) by

$$\mathcal{E} = \text{E.P.} + \frac{0{\cdot}058}{n} \log [C],$$

whilst the potential for the equilibrium between the anion in solution and its corresponding neutral substance is

$$\mathcal{E} = \text{E.P.} - \frac{0{\cdot}058}{n} \, log \, [\text{C}].$$

Current in either case will pass as soon as the potential of the electrode has become *more positive* than the corresponding equilibrium potential. That reaction therefore will set in first to which corresponds the *lowest* (*most negative*) *equilibrium potential.*

Suppose we have a nickel anode in NaI solution at 18°. The possible anode reactions are $\text{Ni} + 2 \oplus \longrightarrow \text{Ni}^{\cdot\cdot}$ and $\text{I}' + \oplus \longrightarrow \frac{1}{2}\text{I}_2$. In the one case nickel ionises directly; in the second case I′ ions are discharged and the liberated iodine acts on the nickel, forming nickel iodide. Whatever happens NiI_2 is formed, but in the second case as the result of a secondary reaction. The two electrode potentials are

$$\mathcal{E}_{\text{Ni}^{\cdot\cdot} \longrightarrow \text{Ni}} = -0{\cdot}22 + 0{\cdot}029 \, log \, [\text{C}_{\text{Ni}^{\cdot\cdot}}],$$
$$\mathcal{E}_{\frac{1}{2}\text{I}_2 \longrightarrow \text{I}'} = +0{\cdot}54 - 0{\cdot}058 \, log \, [\text{C}_{\text{I}'}].$$

If the $\text{Ni}^{\cdot\cdot}$ ion concentration at the start be $[\text{C}_{\text{Ni}^{\cdot\cdot}}] = 0{\cdot}001$, $log \, [\text{C}_{\text{Ni}^{\cdot\cdot}}] = -3$. We can suppose the concentration of the I′ ions to be 1 n. Then we get

$$\mathcal{E}_{\text{Ni}^{\cdot\cdot} \longrightarrow \text{Ni}} = -0{\cdot}307 \text{ volt},$$
$$\mathcal{E}_{\frac{1}{2}\text{I}_2 \longrightarrow \text{I}'} = +0{\cdot}54 \text{ volt}.$$

The direct ionisation of nickel occurs much more easily than the discharge of I′ ions (reversibility assumed).

Energy Efficiency.—If an electrolysis could be carried out reversibly, and with a 100 per cent. current efficiency, the amount of electrical energy needed to produce a certain quantity of substance electrolytically would be given by the product of the corresponding quantity of electricity and the theoretical decomposition voltage. But in practice this is never so. We have discussed the causes which lower the current efficiency. And, owing to *irreversibility of electrode processes*, and the voltage necessary to overcome the resistance of the electrolyte, the *working voltage* of an electrolytic cell always exceeds the theoretical decomposition voltage. The theoretical quantity of energy necessary to form one gram-equivalent of product is 96540 E joules. The necessary quantity in practice is the product of the working voltage into the quantity of electricity required. The percentage ratio $\dfrac{\text{theoretical quantity of energy}}{\text{quantity of energy actually used}}$ is termed the **energy efficiency** of the process, naturally a more important magnitude than the current efficiency, which deals with one factor of electrical energy only. Its calculation is very simple.

If, for example, the reversible decomposition voltage corresponding to a certain transformation is 1·7 volts and the working voltage 2·8 volts, whilst a 90 per cent. current efficiency is obtained, the energy efficiency is

$$\frac{1{\cdot}7}{2{\cdot}8} \times \frac{90}{100} \times 100 = 55 \text{ per cent.}$$

Measurement of Voltage.—Voltage is measured by voltmeters, which need no description here. They are simply high-resistance ammeters, which are shunt connected across the points between which the voltage drop is to be measured. The current passing through is proportional to the voltage, and the scale is graduated directly in volts. It is essential that the resistance of the instrument be high, compared with the resistance of the main circuit. A single voltmeter can be adapted for a wide range of measurement by introducing a series resistance C (Fig. 26) into the voltmeter circuit, and thus decreasing the current going through the circuit for a given difference of potential between A and B. If, for example, C has nine times the resistance of the voltmeter, then the resistance of the circuit is ten times what it would be in absence of C, the current is one-tenth as great, and the value of each scale-division in volts is increased tenfold.

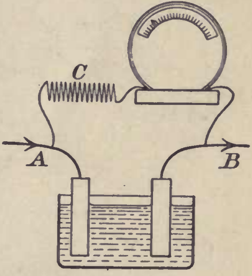

FIG. 26.
Voltage Measurement with Ballast Resistance.

The use of these ballast resistances ('multipliers') enables much higher voltages to be measured than would otherwise be possible with the same instrument.[1] When the voltmeter is designed to measure very high voltages, the multipliers are kept outside, but for low range instruments are placed inside the voltmeter and put into circuit by means of separate terminals.[2]

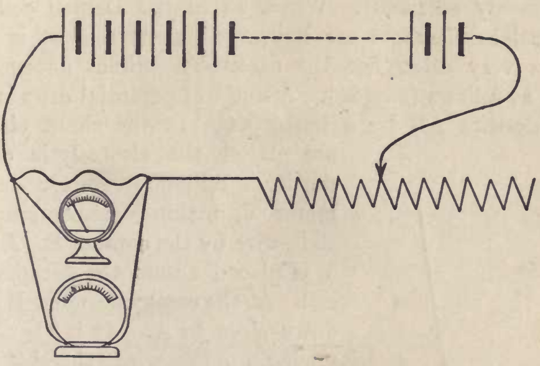

FIG. 27.—Voltmeter Calibration.

Voltmeters are most simply calibrated by direct comparison with

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[1] Cf. use of shunts for current measurement, p. 31.

[2] See p. 31 for the measurement of current with the aid of a high-resistance voltmeter.

a standard instrument. The two instruments are connected in parallel with the same two points in the main circuit, which contains a source of E.M.F. of greater magnitude than the maximum reading of the voltmeter, and an adjustable resistance. By varying this resistance, the potential drop between the points on which the voltmeters are laid is also altered. Simultaneous readings are taken. The apparatus is shown in Fig. 27.

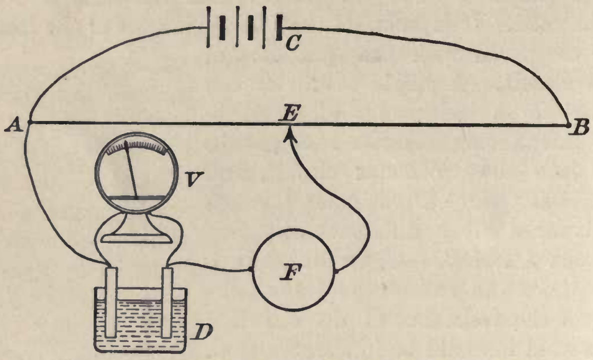

FIG. 28.—Measurement of Decomposition Voltage.

Measurement of Decomposition Voltage.—A knowledge of the reversible decomposition voltage is important for purposes of calculation of energy efficiency. When, as in the Daniell cell, the two single potential differences are known, no measurement is necessary, but that is very often not the case. The direct determination is carried out as follows (Fig. 28). A uniform potential drop is produced along a slide-wire AB by a battery C. In the shunt circuit ADE are placed the electrolytic cell and a sensitive milliamperemeter or galvanometer F, making connection with the slide-wire by the contact E. A voltmeter V is placed across the terminals of the cell. At the commencement E is brought down close to A. It is then gradually moved up the wire, thereby increasing the voltage applied to the ends of the shunt circuit. Readings of voltmeter and ammeter are simultaneously taken.

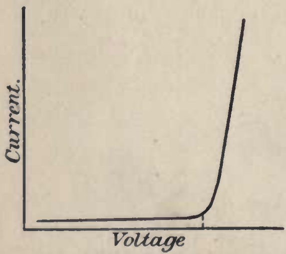

FIG. 29.—Decomposition Voltage Curve.

At first only a very small current goes through the circuit, but when the decomposition voltage has been reached, the current passing will suddenly increase, owing to decomposition commencing. The voltmeter reading at this point indicates the decomposition voltage.

It should strictly be corrected by an amount equal to the product of the resistance of the cell and the small current passing through. This correction is generally small. The type of curve obtained is shown in Fig. 29. An exactly similar one is got by plotting current against the electrode potential of a single electrode. When the potential difference passes the equilibrium value, the current will suddenly rise. Such a curve is a **current electrode-potential curve.**

Back Electromotive Force.—We have seen that the E.M.F. of a primary cell equals the reversible decomposition voltage of the same system, and the second method used for determining that magnitude depends on this fact. It consists in taking the **polarisation discharge curve** or in observing what is termed the **back E.M.F.** of the cell. Current is passed through the electrolysis vessel, and certain amounts of the products collect on the electrodes. The main circuit is then broken, and the cell simultaneously short-circuited through a *high-resistance* voltmeter. It now behaves as a primary cell, and will furnish current and give the corresponding voltage as long as traces of the precipitated products remain on the electrodes. The voltmeter reading under these conditions is equal to the decomposition voltage of the electrolyte. The voltmeter used must be of high resistance, otherwise the products will disappear too quickly to allow of satisfactory observations.

The voltmeter readings are generally plotted on a curve against time. A horizontal portion, indicating constancy of voltage, corresponds to the back E.M.F. and to the decomposition voltage of the electrolyte. Such a curve is shown in Fig. 30. The experiment is most conveniently made by putting the voltmeter in shunt across the terminals of the cell whilst the main current is passing. When the main circuit is opened, voltmeter and cell are then short-circuited.

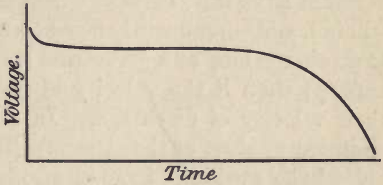

FIG. 30.—Polarisation Discharge Curve.

3. Factors affecting Electrolysis

So far we have only considered the polarisation of an electrolytic cell as due to the reversible decomposition voltage of the process taking place. But there are other effects which help to determine the working voltage. A certain amount of energy is lost in overcoming the electrolyte resistance. The current always causes concentration changes, due partly to the different rates of migration of the different ions, and partly to chemical changes at the electrodes. And these concentration changes always tend to act as a concentration cell, opposing the main impressed voltage and causing **concentration polarisation.** Still more important is the fact that the voltage required for passing current through an electrolyte is generally augmented by the incomplete reversibility of the electrode processes.

Reaction Velocity Effects.—This irreversibility is usually due to insufficient reaction velocity of some part of the electrode process. Suppose, for example, the process is the discharge of an ion which deposits its material part on the electrode. There are two successive stages involved. The ions give up their charge, liberating the neutral residues. Then the equilibrium in the electrolyte, disturbed by the ionic discharge, is adjusted through diffusion to the electrode of fresh ions or by dissociation of neutral molecules or complex ions. All our evidence shows that the ionic discharge takes place very quickly indeed.

But, on the other hand, the subsequent diffusion or dissociation may be far less rapid, and ions will be discharged from the electrolyte more quickly than they can be regenerated in their equilibrium concentration. Let the process be the discharge of a cation. If by reason of an insufficient reaction velocity the concentration of the ion at the electrode keeps permanently below its static equilibrium value (the concentration it would have if no current were passing), then the working value of $\mathcal{E}$ will fall, and consequently a *greater cathodic polarisation* will be necessary to discharge ions at a given rate (to work, that is, with a given current density) than if the velocity of resupply of the ions were as great as their velocity of discharge. In other cases an accumulation of precipitated product at the electrode (for example, a gas) may, so to speak, ‘ clog ’ the working of the electrode process. The mechanism of such effects we shall consider in Chapter X. Electrodes at which these irreversible processes commence at low current densities are said to be easily polarisable. Oxidation-reduction electrodes particularly often behave thus. We shall see later how sometimes the nature of the electrode process can be actually changed owing to some irreversible effect setting in.

The nature of the reaction resistance present can often be ascertained by marking the effect of stirring the electrolyte or of a temperature rise. When the slow reaction is of the nature of a diffusion, stirring will tend to decrease the necessary polarisation; if a chemical reaction or a dissociation, an increase of temperature may be expected to produce that effect. Increased temperature should also act favourably, only less so, if it is a diffusion phenomenon. This effect of temperature is of course precisely the same as its effect on reaction resistances met with in purely chemical reactions, such as the combination of hydrogen and oxygen to water at low temperatures. Polarisation must naturally always be avoided as far as possible. In a primary cell, it lowers the

E.M.F. that the cell would otherwise give. In electrolysis, it increases the voltage required.

Depolarisation.—Any agent through which the polarisation in a cell can be lessened is termed a **depolariser.** A depolariser can act in two ways. It can catalyse the slow reaction which is causing irreversibility, in which case the E.M.F. or voltage will more nearly approach the theoretical reversible value. Thus, when hydrogen is liberated electrochemically at a metal surface, the cathodic polarisation necessary is, in many cases, very considerable. But with a platinised platinum cathode, the electrode potential only very slightly differs from the reversible value. Similarly a low concentration of Cl' ion will catalyse the anodic solution of nickel in a nickel sulphate solution. With no chloride present, the nickel will practically cease dissolving when a certain low current density is exceeded.

Then a depolariser can also act by reducing the energy consumption at the electrode below the amount corresponding to the equilibrium electrode potential. This simply means altering the electrode process, and substituting for it one that can take place more easily. For example, in the Grove or Bunsen primary cell, the cathode system is a platinum or carbon electrode surrounded by strong nitric acid. In the absence of the strong acid, the cathode reaction consists in the discharge of $H^{\cdot}$ ions (at the anode zinc is dissolved) and the E.M.F. of the cell is about 0·7 volt. With the strong acid present the cathode reaction is depolarised. The $H^{\cdot}$ ions are no longer discharged, but the nitric acid is reduced to nitrous gases, and water is formed. The E.M.F. of this depolarised cell is about 1·0 volt.

Concentration Polarisation.—We have seen that, when a current passes through an electrolyte, it causes concentration changes at the electrodes, and that these changes always act in such a way as to oppose the E.M.F. driving current through the cell. Let us consider a simple case, two similar copper electrodes in a copper sulphate solution. Provided that no concentration differences are produced the single potentials of the two electrodes should be equal; in which case no polarisation would occur, and the voltage necessary to pass a given current through the cell would be simply that required to overcome the ohmic resistance of the $CuSO_4$ solution. But, as a matter of fact, copper is dissolved from the anode and deposited at the cathode, and the $CuSO_4$ concentrations in anolyte and catholyte respectively increase and diminish. This causes a raising of the anode potential and a lowering of the cathode potential as shown in Fig. 31, and the voltage absorbed by the cell is increased by the polarisation represented by the difference in height between the dotted lines.

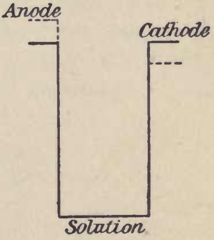

Fig. 31.

If the contents of the cell are thoroughly stirred or the concentrations in some other way equalised, this polarisation will more or less disappear, the more completely the more effective the mixing. On the contrary, if the current density be increased, the rate of stirring being maintained constant, the concentration differences between the layers immediately surrounding the electrodes and the great bulk of the electrolyte will become greater, and the potential differences and the polarisation of the cell will accordingly increase. We learn therefore that concentration polarisation increases with the current density, but is decreased by stirring or by circulating the electrolyte. In the case discussed, which is met with technically in copper refining, the concentration polarisation is reduced to very small amounts by an efficient circulation of the liquors.

Literature

Foerster. *Elektrochemie wässeriger Lösungen.*
Lorenz. *Elektrochemisches Praktikum.*

CHAPTER X

CATHODIC AND ANODIC PROCESSES IN DETAIL

A. Cathodic Processes

For our purpose, we can divide cathodic processes into four classes :

(*a*) hydrogen evolution,
(*b*) metal deposition,
(*c*) formation of anions (unimportant),
(*d*) electrolytic reduction processes.

1. Evolution of Hydrogen

The equilibrium potential of a hydrogen electrode in a solution containing $H^{\cdot}$ ions is expressed by the formula

$$\mathcal{E} = E.P._{H^{\cdot} \rightarrow \frac{1}{2}H_2} + 0{\cdot}0002\ T \log [C_{H^{\cdot}}]$$

We have taken as our zero of potential difference the single potential of the electrode $H_2 \mid {}^{N}/_{1}H^{\cdot}$, which means that we write $E.P._{H^{\cdot} \rightarrow \frac{1}{2}H_2} = 0{\cdot}0$ volt. Then the cathodic potential at which reversible $H^{\cdot}$ ion discharge to hydrogen at atmospheric pressure will commence is given by the formula $0{\cdot}0002\ T \log [C_{H^{\cdot}}]$. The greater [C], the sooner hydrogen evolution will set in. For an aqueous solution, in which the water dissociates giving $H^{\cdot}$ and OH' ions according to the equation $H_2O \rightleftarrows H^{\cdot} + OH'$, the concentrations of these ions are connected by the mass action equation

$$K \cdot [C_{H_2O}] = [C_{H^{\cdot}}] \cdot [C_{OH'}]$$

which can be written

$$K_w = [C_{H^{\cdot}}] \cdot [C_{OH'}]$$

since $[C_{H_2O}]$ may be regarded as a constant. K_w, the *dissociation constant* of water, has a value at 18° of $0{\cdot}56 \times 10^{-14}$. In a neutral solution,

$$[C_{H^{\cdot}}] = [C_{OH'}] = \sqrt{K_w} = 0{\cdot}8 \times 10^{-7}$$

Substituting this value in the expression for the potential difference of the hydrogen electrode, we get

$$\mathcal{E} = 0{\cdot}058 \log 0{\cdot}8 \times 10^{-7} = -0{\cdot}412 \text{ volt.}$$

This gives the potential at which reversible hydrogen evolution will commence in a neutral solution at 18°. If the solution is normal with respect to OH′ ions, $[C_{H^{\cdot}}] = 0{\cdot}56 \times 10^{-14}$ and we calculate $\mathcal{E} = -0{\cdot}827$ volt. So much for the reversible discharge of $H^{\cdot}$ ions.

Overvoltage.—But, as has already been mentioned, when hydrogen is electrolytically produced, a cathodic polarisation beyond the calculated reversible figure is almost invariably necessary, its amount depending on the nature of the electrode material. Table XVIII contains a number of these **overvoltages**—the overvoltage being the difference between the required cathodic potential and the equilibrium value. In column I are figures obtained by Caspari[1] for different electrodes when the formation of hydrogen gas bubbles could be first observed. Column II contains measurements of Coehn and Dannenberg,[2] who determined the cathode-potential current curve of the electrolyte by the method on page 112. Except with iron, $^{N}/_{1}$ H_2SO_4 was used in all cases.

TABLE XVIII

Cathode	I.	II.
Platinised Platinum	0·005 volt	0·000 volt
Iron (in NaOH)	0·08	0·03
Smooth Platinum	0·09	—
Silver	0·15	0·07
Nickel	0·21	0·14
Copper	0·23	0·19
Tin	0·53	—
Lead	0·64	0·36
Zinc	0·70	—
Mercury	0·78	0·44

Though the two figures for the same cathode material may differ considerably, the order is the same in both columns. Caspari's values are always higher than those of Coehn and Dannenberg. This is due to the fact that the overvoltage rises very quickly with increase of current density, and that while the numbers in column II were obtained with a very low current density, at a stage prior to visible gas evolution, this is not so with the figures in column I. We have already encountered this rapid rise in the magnitude of irreversible effects, caused by increased velocity of a process.

Of course, a greater current density means a greater concentration polarisation, but the effects noticed here far exceed any due to concen-

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[1] *Zeitsch. Phys. Chem.* **30**, 89 (*1899*).

[2] *Ibid.* **38**, 609 (*1901*).

tration changes. A comparison of the following figures with those in the table will show this. They were obtained[1] in 2n. H_2SO_4 at a cathodic current density of 0·1 amp./cm², and at 12°. (Iron and smooth platinum[2] in NaCl + $^N/_{100}$ NaOH at 22°.)

Hg	Pb (polished)	Pb (rough)	Sn	Cu	Ni	Pt (smooth)	Fe	Pt (platinised)
1·30	1·30	1·23	1·15	0·79	0·74	0·65	0·55	0·07

Graphite behaves very much like nickel,[3] as does brass also.[4] The following figures for Hg show the continuous effect of increasing current density.[5]

Current density	Overvoltage.
0·0004 amp./cm.²	1·04 volts
0·001	1·08
0·002	1·12
0·01	1·19
0·02	1·22
0·04	1·25
0·1	1·30

It is only with platinised platinum, at which hydrogen overvoltage scarcely comes into play, that the difference between the above figures and those in Table XVIII is of the order corresponding to an increase in concentration polarisation. With the other metals it is far greater.

Overvoltage does not usually assume its full value immediately after current begins passing. It may easily take hours before the maximum effect is reached. There are some exceptions—thus mercury and lead, two of the metals with the greatest hydrogen overvoltage, exert their full influence almost instantaneously. The overvoltage given by a metal depends much on the nature of its surface. The rougher the surface, the less will it be. The difference between platinised and polished platinum is a good example, whilst 0·28 volt more is required at smooth than at spongy lead.[6] This is doubtless largely an effect of current density, which is much less (under otherwise equal conditions) at a roughened or spongy surface. But the phenomena, including the variation of overvoltage with time, are often very complex, as the results of Nobis[7] on graphite and carbon cathodes show.

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[1] Tafel. *Zeitsch. Phys. Chem.* **50**, 641 (*1905*).

[2] Sacerdoti. *Zeitsch. Elektrochem.* **17**, 473 (*1911*).

[3] Nobis. *Dissertation* (Dresden, *1909*).

[4] Mott. *Trans. Amer. Electrochem. Soc.* **15**, 569 (*1909*).

[5] Tafel. *Loc. cit.*

[6] Strasser and Gahl. *Zeitsch. Elektrochem.* **7**, 11 (*1900*).

[7] *Loc. cit.*

A temperature increase, as with other irreversible effects, diminishes the overvoltage. Thus in alkaline NaCl solutions at 0·5 amp./cm.^{2}, Sacerdoti[1] found the overvoltage at a smooth platinum anode to be 1·4 volts at 22° and 0·95 volts at 99°. The possible causes of overvoltage are discussed on p. 133.

As we shall see, overvoltage can be technically very important. It does not merely mean an increased energy expenditure in the separation of hydrogen (or other gases, overvoltage not being peculiar to hydrogen), but, owing to the changes in the electrode potential which it causes, may actually alter the *nature* of the electrode process.

2. Cathodic Metal Deposition

Irreversible Effects.—The reversible process and concentration polarisation effects have already been discussed. Irreversible effects analogous to overvoltage do not often occur, but Foerster and his pupils have investigated a few cases. If copper or zinc be deposited from solutions of their potassium double cyanides, the cathodic polarisations needed increase very rapidly with increase in current density, far more rapidly than when using the simple salts. The accompanying Table XIX well shows this.[2]

TABLE XIX

Current density	Cathode potential in volts			
	N. $CuSO_4$	$^N/_{10}KCuCy_2$	N. $ZnSO_4$	$^N/_{10}K_2ZnCy_4$
0·0 (equilibrium potential)	+ 0·302	− 0·610	− 0·795	− 1·033
0·001 amp./cm.^{2}	+ 0·273	− 0·77	− 0·829	− 1·12
0·003 amp./cm.^{2}	+ 0·262	− 1·12	− 0·838	− 1·25

With the simple salts the difference in polarisation between the first and third lines only amounts to 0·04 − 0·05 volt; with the complex copper cyanide it is 0·51 volt, and with the complex zinc cyanide 0·22 volt. The considerable difference is due to the fact that in the cyanide solutions, the free metal ion concentration—*i.e.* $Cu^{\cdot}$ or $Zn^{\cdot\cdot}$ ions—is very low. Thus practically all the copper is present as $Cu(Cy)_2'$. When current passes, the store of free $Cu^{\cdot}$ ions is immediately exhausted, and must be regenerated by dissociation of the complex as follows:

$$Cu(Cy)_2' \longrightarrow 2\ Cy' + Cu^{\cdot}.$$

If this dissociation cannot keep pace with the removal of the $Cu^{\cdot}$

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[1] *Loc. cit.*

[2] Spitzer, *Zeitsch. Elektrochem.* **11**, 345 (*1905*); Coffetti and Foerster, *Ber.* **38**, 2934 (*1905*).

ions from the electrolyte, the $Cu^{\cdot}$ concentration will fall, and the electrode potential become more negative. That this happens is evidently the case.

With certain simple salts, notably those of nickel and iron, similar retarding influences act. The following Table XX[1] contains the cathodic potentials for the precipitation of iron and copper from slightly acid $FeSO_4$ and $CuSO_4$ solutions at 20°.

TABLE XX

Current density	$CuSO_4$	$FeSO_4$
$0{\cdot}00 \times 10^{-4}$ amp./cm.^{2}	+ 0·303 volt	— 0·465 volt
0·57		— 0·573
1·13	+ 0·292	— 0·594
2·27	+ 0·290	— 0·606
4·5	+ 0·289	— 0·616
11·3	+ 0·287	— 0·630
22·7	+ 0·281	— 0·644

The difference between the behaviour of the two salts is very marked. Nickel salts behave similarly to iron salts,[2] and Foerster believes the explanation to lie in the slow rates at which the reactions $Fe^{\cdot\cdot} \longrightarrow Fe + 2\oplus$ and $Ni^{\cdot\cdot} \longrightarrow Ni + 2\oplus$ proceed. In order to increase these velocities, the respective cathodic polarisations must be increased. The fact that this abnormal behaviour becomes less marked at higher temperatures strongly supports some such reaction resistance explanation.

Depolarisation of Metal Deposition.—This takes place when the metal precipitates in the form of an alloy. Its electrolytic solution pressure will then be less than in the pure state, and the cathodic potential drop necessary for ionic discharge will be lessened. The extent to which this depolarisation occurs will depend essentially on the type of the alloy. If the two metals form a solid solution in all proportions, the electrolytic solution pressure of the metal concerned can be taken as very roughly proportional to its concentration in the alloy. If this contains a high percentage of the second metal, the electrolytic solution pressure of the first metal will be correspondingly lowered, and *vice versa*. If the two metals only mix to a limited degree the depolarisation effected by the second metal will in all probability be small, as the saturation limit will soon be reached and the great bulk of the first metal will have to overcome its full electrolytic solution pressure during deposition. If the two metals form a compound which dissolves in excess of the second, we have the most favourable conditions. The electrolytic solution pressure of the first metal is very much lowered, and consequently also the potential drop required for its deposition.

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[1] Foerster and Mustad, *Abhand. Bunsen Ges.* **2,** 44 (*1909*).

[2] Schweitzer, *Zeitsch. Elektrochem.* **15,** 602 (*1909*).

The second metal which does the depolarising can either serve as cathode, or else can be deposited simultaneously with the first during electrolysis. A good example of the first-mentioned method is the electrochemical formation of alkali-metal amalgams. When a sodium chloride solution is electrolysed, using a mercury cathode, $Na^{\cdot}$ ions are discharged, the liberated metal dissolving in the mercury. This happens in spite of the exceedingly high electrolytic solution pressures of the alkali metals (that of sodium is $\mathcal{E}_h = -2{\cdot}72$ volts). The result is due to two factors.

The first is the high overvoltage of hydrogen at a mercury cathode, rendering the discharge of $H^{\cdot}$ ions more difficult. The second is the fact that sodium can combine with mercury, giving such compounds as Hg_6Na, etc., and that the electrolytic solution pressure of a solution of sodium in mercury is consequently far below that of sodium itself. This case is technically very important, and we shall meet it again later.[1] The results of Haber and Sack[2] show that direct precipitation of the $Na^{\cdot}$ ion can also take place under certain conditions when using cathodes of other materials, *e.g.* lead, tin, platinum. The use of an alkaline solution with its very low $H^{\cdot}$ ion concentration, and a high current density (with its high overvoltage) are favourable.

The depolarisation of the discharge of a metal by another simultaneously deposited can be illustrated by the electrolysis of an aqueous solution of a mixture of zinc and nickel salts.[3] Although zinc is more strongly electropositive than nickel and should therefore not deposit as easily, and although the nickel salt may be present in excess, the cathode deposit will nevertheless principally consist of zinc, so strongly has the nickel depolarised the discharge of the zinc ions. The slow rate of the process $Ni^{\cdot\cdot} \longrightarrow Ni + 2 \oplus$ (previously mentioned) cannot here alone explain the facts. Similar causes act and similar results are obtained in the electrolysis of mixtures of zinc and iron salts. The first fractions of the cathodic deposits contain a large excess of zinc.

Metals giving more than one Cation.—We must briefly consider the potential relations existing during the cathodic deposition of a metal which can furnish more than one kind of ion. Common examples are tin ($Sn^{\cdot\cdot\cdot\cdot}$ and $Sn^{\cdot\cdot}$), iron ($Fe^{\cdot\cdot\cdot}$ and $Fe^{\cdot\cdot}$), and copper ($Cu^{\cdot\cdot}$ and $Cu^{\cdot}$). If such a metal be put in a solution of one of its salts, chemical action will take place to a greater or less extent until equilibrium has been set up between the metal and the two kinds of ions. Thus, if iron be placed in a solution of $FeCl_3$, the $FeCl_3$ will be almost entirely reduced to $FeCl_2$, and the equilibrium arrived at will correspond to the equation

$$2Fe^{\cdot\cdot\cdot} + Fe \rightleftarrows 3Fe^{\cdot\cdot}.$$

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[1] P. 347.

[2] *Zeitsch. Elektrochem.* **8,** 245 (*1902*).

[3] Schoch and Hirsch, *Jour. Amer. Chem. Soc.* **29,** 314 (*1907*).

With copper the equilibrium lies over in favour of the $Cu^{\cdot\cdot}$ ions, with iron and tin in favour of the ions of lower valency. One of the ions may be to a great extent under the prevailing conditions converted into a complex ion. In that case the equilibrium moves over very much in favour of that valency. This happens with the copper system when the solution contains many Cl' ions. The tendency of the $Cu^{\cdot}$ ion to form complex anions such as $CuCl_3''$ is much greater than the corresponding tendency of the $Cu^{\cdot\cdot}$ ions. When therefore a solution of $CuCl_2$ in HCl is boiled with metallic copper, it is almost completely converted into the cuprous state. But very few $Cu^{\cdot}$ ions are present; the equilibrium

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

is still satisfied, the cuprous copper being present as H_2CuCl_3.

When such a metal is deposited from solution, the tendency is always for the corresponding equilibrium to set itself up, and for the two different ions to deposit in such proportions that the concentrations left in the solution always correspond to equilibrium conditions. From $CuSO_4$, the metal practically deposits as a di-valent metal, the $Cu^{\cdot}$ ion concentration in the equilibrium solution being very low, and the ratio $\frac{Cu^{\cdot\cdot}}{Cu^{\cdot}}$ deposited consequently high. From iron sulphate the metal behaves as if only $Fe^{\cdot\cdot}$ ions were deposited. But if copper be precipitated from a strong chloride solution, it behaves nearly quantitatively as if its ions were mono-valent. The lower the Cl' ion concentration, and hence the smaller the proportion of copper present as complex, the greater grows its apparent electro-valency, the larger becomes the proportion of $Cu^{\cdot\cdot}$ ions deposited. With gold from gold chloride solutions also, the metal behaves as if its valency were intermediate between one and three. We shall meet several of these cases later. The above considerations hold for equilibrium conditions, and therefore strictly for very low current densities only. With higher current densities one may get rather different results, if the ionic discharge proceeds more quickly than the chemical equilibrium can adjust itself.

The conditions for reversible cathodic precipitation of metals and hydrogen have been discussed in Chap. VIII, and it has been shown how to calculate the electrode reaction which sets in most easily on cathodic polarisation of a given solution. It is now seen that, in practice, a number of irreversible effects must also be considered before it can be stated whether the deposition of hydrogen or of such and such a metal will occur most easily. The overvoltage of the hydrogen evolution, the excess polarisation needed for the precipitation of certain metals, the dependence of both these factors on current density, any possible depolarisation of the discharge of an ion, must all be allowed for. Thus, though zinc is considerably more electropositive than iron, yet it can be cathodically precipitated from a solution containing much H_2SO_4 where iron, under otherwise similar conditions, does not deposit. This is due to the higher hydrogen overvoltage at a zinc surface, rendering $H^{\cdot}$ discharge more difficult, and to the resistances opposing the deposition of $Fe^{\cdot\cdot}$ ions. As these resistances to metal deposition only seldom occur, whereas hydrogen overvoltage invariably increases rapidly with increase of current density, it follows that high current densities favour the deposition of electropositive metals in presence of acid.

It is generally best to keep electrolytes from which metal is being deposited at least faintly acid; otherwise basic salts or hydroxides are liable to be precipitated in the solution. A high metal ion concentration is also of course advantageous. With very strongly electropositive metals, such as magnesium, even when using very concentrated faintly acid solutions, hydrogen is preferentially evolved, and precipitates of basic salts or hydroxides are produced near the cathode. With the alkali metals the same holds good, but the basic product is not insoluble. To get alkali metals, and not hydrogen, cathodically deposited from an aqueous solution, the conditions must be very favourable—powerful depolarisation of the metal precipitation and a big overvoltage for the $H^{\cdot}$ discharge.[1]

Physical Condition of Cathodic Deposits. — The physical condition of a deposited metal is of prime importance. The extractor or refiner wants it in coherent form, the plater must have it so that it can be burnished. In practice different metals can be deposited in very different conditions of aggregation, and at present one cannot satisfactorily co-ordinate all the differences observed with the conditions of electrolysis. Iron and nickel give very regular finely grained deposits from moderately strong sulphate solutions; copper gives a coherent product of a markedly crystalline character.[2] Other metals—*e.g.* lead and tin—are deposited (from $Pb(NO_3)_2$ or $SnCl_2$) as loose crystals, and platinum forms a loose amorphous powder. Many other metals — *e.g.* copper—can give such an amorphous precipitate, particularly from very dilute solutions.

The effect of concentration changes indeed is very marked and regular. The more concentrated the solution, the better and more coherent the deposit. The more dilute the solution, the smaller the crystals and the looser the deposit formed. Now, a high current density causes a low ionic concentration in the immediate neighbourhood of the electrode and therefore should give a worse deposit, and this conclusion is amply confirmed in practice. To get good cathodic deposits, the cathodic current density must generally in technical work

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[1] Pp. 318, 347.

[2] For the cause of the nodular or crystalline growths often observed at the edges of cathodes, see p. 150.

not exceed 0·02 amp./cm.^{2} at room temperature. At higher temperatures the conditions are different. We have seen that concentration polarisation can be largely avoided by working at higher temperatures (whereby the rate of diffusion of ions to the electrode is increased) or by agitating the electrolyte. The same treatment should therefore improve the character of the electrode deposit, and does so. At high temperatures, and with a rapid circulation of the electrolyte, or using a revolving cathode, good deposits can be obtained at a current density of 0·1 amp./cm.^{2} or more. In the electrolytic determination of metals by cathodic deposition, it is essential that the precipitate be perfectly coherent as well as pure. With a stationary electrolyte only a very low current density can be used; but if the cathode is rapidly rotated, this can be enormously increased and the time taken for the analysis correspondingly reduced. Revolving cathodes are occasionally used technically.[1]

A bad electro-deposit is often accompanied by hydrogen evolution[2] and the formation of a basic precipitate, and is sometimes stated to be due to these phenomena. It is better to regard all three effects as caused by the low metal ion concentration in the electrolyte. The formation of hydrogen is thereby facilitated, and the removal of $H^{\cdot}$ ions of course tends to precipitate basic substances. The evolution of hydrogen, some of the bubbles of which adhere to the electrode, is one of the causes of growths on the same. The whole effect of concentration on the nature of the cathodic deposit runs parallel to its effect on the nature of metal precipitated chemically in the wet way. In this case again a more finely crystalline or an amorphous deposit results from dilute solutions.[3]

The nature of the salt from which the metal is deposited has often considerable influence. But the only traceable regularity is that metals deposited from solutions in which they are chiefly present as complex anion generally come down in a dense smooth finely grained form. Examples are copper and silver from their alkaline cyanide solutions and tin from ammonium oxalate solution. Danneel[4] suggests that this characteristic form of metal is produced by the discharge of the complex anion, not of the simple cation. Thus from a $KAg(Cy)_2$ solution the process of cathodic discharge is

$$AgCy_2' \longrightarrow Ag + 2Cy' + \oplus,$$

and not

$$Ag^{\cdot} \longrightarrow Ag + \oplus.$$

Other independent evidence makes this explanation very probable.[5]

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[1] Pp. 270, 286, 287, 316, 317.

[2] For the effect of the hydrogen content on electrolytic iron deposits, see p. 300.

[3] Mylius and Fromm. *Ber.* **27**, 630 (*1894*).

[4] *Zeitsch. Elektrochem.* **9**, 763 (*1903*).

[5] See Haber, *Zeitsch. Elektrochem.* **10**, 433, 773 (*1904*).

One other point must be noticed, and that is the immense effect often produced on a metallic deposit by the addition of a trace of some organic substance, sometimes a colloid, sometimes not, to the electrolyte.[1] A very fine-grained smooth velvety deposit results. Instances are the addition of gelatine to a nickel-plating or copper bath, or of resorcinol to a zinc tank. The action of the *addition agent* is selective. Thus resorcinol does not improve the nature of lead or copper deposits. Further, if the quantity added increases beyond an exceedingly low limit, the deposit becomes very brittle, and is found to contain organic matter. Müller and Bahntje[2] suppose that the first product of ionic discharge is *colloidal metal*, and that the addition agent acts as a protective colloid, determining the size of metallic particle ultimately cathodically precipitated and affecting the direction in which the metal colloid wanders under the electric field. The same hypothesis would account for the marked differences brought about by small changes in acid and alkali concentration near the neutral point, presence of traces of colloidal hydroxide, etc.

Cathodic Production of Anions.—This does not concern us much. Two cases, however, present technical interest. If the cathodic solution of chlorine and of oxygen according to the equations

$$Cl_2 \longrightarrow 2Cl' + 2\oplus$$

and

$$O_2 + 2H_2O \longrightarrow 4OH' + 4\oplus$$

could be successfully brought about under technical conditions, it would be a matter of the first importance for the construction of *technical primary cells*.[3] But it has not been achieved up to the present.

3. Electrolytic Reduction

This is the last type of cathodic process to be discussed. The employment of electrolytic methods for oxidation (see later) and reduction reactions possesses several advantages. Thus as the reduction consists either of a change in the ionic charge, or of an alteration in the hydrogen or oxygen content of the substance effected by means of cathodically formed hydrogen, the final product contains no impurity needing removal, as happens with chemical reducing agents. If the reduction of nitrobenzene to aniline be considered, the electrolytic method furnishes directly a solution of an aniline salt with nothing else present but excess of acid and some unchanged nitrobenzene,

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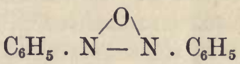
[1] For many qualitative data, see Kern, *Trans. Amer. Electrochem. Soc.* **15,** 441 (*1909*).

[2] *Zeitsch. Elektrochem.* **12,** 317 (*1906*).

[3] See pp. 209–219.

whilst the chemical method means using large quantities of iron or tin, the salts of which are found in the product.

A second advantage is that, whereas the formation of different oxidised or reduced products from the same starting material needs a different chemical oxidising or reducing agent every time, with electrolytic methods a whole series of different reactions may be effected by variation of electrode potential and electrode material. The series of reduced products of nitrobenzene, studied particularly by Haber and by Elbs, are a striking example. Nitrobenzene ($C_6H_5 . NO_2$) can give under different reducing conditions

nitrosobenzene	$C_6H_5 . NO$
β phenyl-hydroxylamine	$C_6H_5 . NH . OH$
azoxybenzene	 $C_6H_5 . \overset{\diagup O \diagdown}{N - N} . C_6H_5$
azobenzene	$C_6H_5 . N = N . C_6H_5$
hydrazobenzene	$C_6H_5 . NH . NH . C_6H_5$
aniline	$C_6H_5 . NH_2$.

Of these substances, no fewer than four—aniline, azoxybenzene, azobenzene, and hydrazobenzene—can be prepared electrolytically with excellent yields by suitable variation of temperature, cathode potential, and alkalinity or acidity of electrolyte.

Electrolytic reductions can be divided into two classes :

(*a*) reductions consisting in an alteration of the charge on an ion—such as $Fe^{\cdot\cdot\cdot} \longrightarrow Fe^{\cdot\cdot} + \oplus$ and $MnO_4' \longrightarrow MnO_4'' + \oplus$;

(*b*) reductions in which the hydrogen content of the reduced material is increased or its oxygen content diminished.[1] Examples are—

$$NO_3' + 10H^{\cdot} \longrightarrow NH_4^{\cdot} + 3H_2O + 8\oplus$$
$$C_6H_5 . NO_2 + 6H^{\cdot} \longrightarrow C_6H_5NH_2 + 2H_2O + 6\oplus.$$

Reversible reactions of the first kind have been fully discussed in Chap. VIII. Reduction—*i.e.* discharge of positive electricity—will commence as soon as the electrode potential is lowered beneath the equilibrium value for the solution. But in practice, at all but the lowest current densities, polarisation effects are bound to enter. This is due to exhaustion of the more highly oxidised ion, and to accumulation of the reduced ion in the immediate neighbourhood of the electrode, and to the slow rate of the diffusion processes which restore equilibrium. In the case of $Fe^{\cdot\cdot\cdot} \longrightarrow Fe^{\cdot\cdot} + \oplus$, $Fe^{\cdot\cdot\cdot}$ ions must diffuse to the electrode and $Fe^{\cdot\cdot}$ ions diffuse away. As these diffusions cannot keep pace with the electrolytic process, the polarisation at constant current increases.

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[1] For the theory of this type of electrolytic reduction, see particularly Haber, *Zeitsch. Phys. Chem.* **32**, 193 (*1900*); Haber and R. Russ. *Zeitsch. Phys. Chem.* **47**, 257 (*1904*).

Nor do reductions of the second type usually take place reversibly. Here we must conceive of cathodic reduction as consisting of two superimposed processes, (*a*) discharge of $H^{\cdot}$ ions to atomic hydrogen; (*b*) reduction of the depolariser by the atomic hydrogen. (Gaseous molecular hydrogen cannot reduce.) This depolarisation of $H^{\cdot}$ ion discharge by the material undergoing reduction prevents the hydrogen concentration in the electrode from reaching the value necessary for gas evolution against atmospheric pressure. To the low concentration of hydrogen corresponds a low electrolytic solution pressure, and the cathodic potential needed for the whole process is consequently less negative than would be required for the discharge of gaseous hydrogen. Now the velocity of the whole reaction depends essentially on the velocity of the second process. When this can keep pace with the velocity of the first process, the reduction will proceed reversibly. But when the depolarisation by the substance to be reduced is slow, then the concentration of hydrogen in the electrode rises, its electrolytic solution pressure increases, and the cathodic potential necessary for the reaction becomes more negative.

These differences manifest themselves in various forms of the cathode-potential current curve. In Fig. 32 EGD represents the cathode-potential current curve for reversible $H^{\cdot}$ ion discharge, which begins at the potential corresponding to G. If a depolariser be added which can react very quickly, the cathodic-potential current curve will now be EFA. The working cathode potential is less negative, and the curve still bends sharply at the point where decomposition sets in. If the depolariser does not act quickly, then the curves are of the type EFB or EFC. At higher current densities particularly, the cathode potential needed is more negative than it would be with a reversibly acting depolariser. In some cases the curves B or C may cut the curve D. When that happens, the potential needed for $H^{\cdot}$ discharge is reached, and part of the current will produce hydrogen gas. Not only will the voltage necessary for the reduction be increased, but the current efficiency will fall. The velocity of depolarisation is therefore all-important in electrolytic reduction. There is no essential difference in this respect between depolarising electrolytes (as HNO_3) and non-electrolytes (as nitrobenzene).

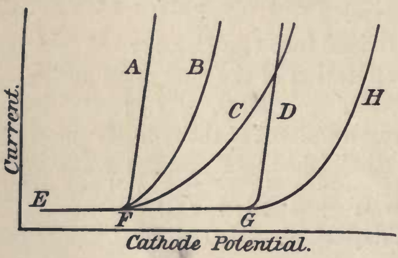

FIG. 32.

The effect of increase of current density on an electrolytic reduction is always to increase the cathodic polarisation. Not only are more $H^{\cdot}$

ions discharged in a given time, but the layer of depolariser around the electrode becomes largely depleted. Both causes increase the concentration of gas in the electrode, and hence its electrolytic solution pressure. Where the reduction is incomplete, the fraction of current used in evolving hydrogen will also rise. An increase in concentration of the depolariser will of course bring about more efficient depolarisation and a less negative cathode potential. A rise in temperature, by increasing the rates of diffusion of the depolariser and of its reaction with hydrogen, will act similarly.

Catalytic Action of Cathode.—The effect of the cathode material on the course of reduction is twofold. Firstly, different cathodes catalyse the reaction between depolariser and hydrogen at very different rates. The result is that the same reduction process can take place with a far less negative cathode potential at some cathodes than at others; or conversely, at the same cathode potential, the permissible current density can vary widely. Nitrobenzene in acid solution is far more easily reduced to aniline at a zinc than at a platinum cathode. In alkaline solution, the reaction goes better at platinum or copper than at iron, zinc, tin or lead. Chlorates are generally not capable of electrolytic reduction, but with an iron cathode they go readily. Then the physical condition of the metal surface is also significant. Nitrates give ammonia at an ordinary smooth copper cathode, whilst at a spongy copper electrode nitrites result. The influence of the electrode material is well shown in the accompanying diagram[1] of cathode-potential current curves for the reduction of a slightly alkaline n. KNO_3 solution (Fig. 33). There is a great difference between the potentials required in using platinised platinum and mercury cathodes, the reaction between depolariser and hydrogen being catalysed far more powerfully at the former electrode.

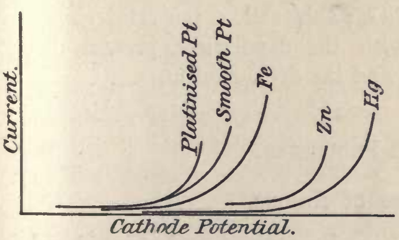

FIG. 33.

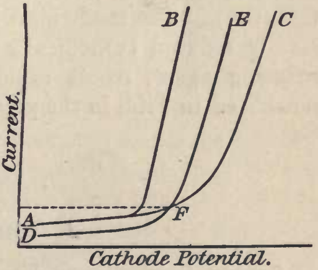

FIG. 34.

Overvoltage Action of Cathode.—The nature of the cathode can also affect electrolytic reduction by increasing the polarisation needed for $H^{\cdot}$ ion discharge. In Fig. 34 let AB be the cathode-potential

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[1] Müller. *Zeitsch. Anorg. Chem.* **26**, 1 (*1901*).

current curve for reversible hydrogen discharge, and the curve DE the curve for the reduction process. It is obvious that if the electrode used allows reversible $H^{\cdot}$ ion discharge, then no reduced product will be formed—all the current will give hydrogen. But if the hydrogen overvoltage be at all considerable, then the $H^{\cdot}$ ion discharge curve will have the form AC, and at current densities above that corresponding to F reduction, still accompanied by hydrogen evolution, will begin. Similarly in Fig. 32, the curve C is represented as cutting the reversible $H^{\cdot}$ ion discharge curve D. If, however, hydrogen overvoltage comes into consideration, the hydrogen curve will be represented by H, and even at high current densities the yield of reduced material will be nearly 100 per cent.

The use of such cathodes enables us to carry out reductions requiring a very large cathodic polarisation. Tafel has been the chief worker on the reduction of these very difficultly reducible substances, such as pyridine and various alkaloids of the uric acid group. The best electrodes are of course those at which the hydrogen overvoltage is highest, *e.g.* Hg, Pb and Zn.[1] One point should be noticed. Although, with *complete* reduction, temperature rise always acts favourably, with incomplete reduction of difficultly reducible substances, made possible by hydrogen overvoltage, the reverse may hold. A temperature rise diminishes overvoltage and therefore facilitates hydrogen discharge. If this effect overbalances the effect of increased rate of diffusion of depolariser to electrode, the yield of reduced material will fall.

Catalysts in Electrolyte.—Finally, the velocity of reduction can often be essentially increased by the addition of some catalyst to the electrolyte. Titanium and vanadium salts are often active. Thus quinone ($C_6H_4O_2$) can be readily reduced in acid solution to hydroquinone ($C_6H_4(OH)_2$) in presence of titanium chloride, whereas in absence of this salt the reduction stops at quinhydrone, $C_6H_4O_2$, $C_6H_4(OH)_2$. The mechanism of catalysis is here clear. The $TiCl_4$ is readily reduced cathodically to $TiCl_3$; this salt, a powerful chemical reducing agent, reacts rapidly with the depolariser present, being reoxidised to $TiCl_4$ in the process, and the cycle continues.

B. ANODIC PROCESSES.

4. Discharge of Anions.

Oxygen Overvoltage.—The first anodic process to be considered is the discharge of OH' ions to oxygen gas—

$$2OH' \longrightarrow H_2O + \tfrac{1}{2}O_2 + 2\ominus.$$

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[1] In such cases the electrolyte must be free from all traces of salts of metals which have a low hydrogen overvoltage and are also liable to be cathodically precipitated. Otherwise no reduction may take place, only hydrogen evolution.

This process is invariably accompanied by irreversible effects, and it has not been found possible to directly measure the value of E.P. Indeed the mechanism of the anodic formation of oxygen is probably different from that expressed by the above equation. For example, Grube[1] has shown that the evolution of oxygen in 2n . H_2SO_4 at a platinised platinum electrode undoubtedly takes place through the intermediate formation of PtO_3. But it has been calculated with certainty that the reversible potential of an oxygen electrode in equilibrium with oxygen at atmospheric pressure is 1·23 volts more positive than the potential of the hydrogen electrode in the same solution. In a normal $H^\cdot$ solution, the electrode potential will be +1·23 volt. Similarly, knowing the OH' concentration in such a solution[2] to be $0{\cdot}56 \times 10^{-14}$, the potential in a normal OH' solution, or E.P. for

$$\tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O \longrightarrow OH' + \oplus,$$

can be calculated to be

$$+1{\cdot}23 + 0{\cdot}058 \log 0{\cdot}56 \times 10^{-14} = +0{\cdot}404 \text{ volt}$$

(all figures for room temperature).

In practice, the calculated equilibrium oxygen potential must always be more or less exceeded before oxygen is discharged.[3] This question of oxygen overvoltage was first studied by Coehn and Osaka.[4] Working by the anode decomposition potential method, and using therefore exceedingly low current densities, they obtained the following values :—

TABLE XXI

Electrode	Overvoltage
Spongy nickel	0·05 volt
Nickel	0·12
Cobalt	0·13
Iron	0·24
Platinised platinum	0·24
Lead peroxide	0·28
Smooth platinum	0·44

Nobis,[5] using a rather higher current density, found the overvoltage at graphite to be about 0·4 volt. Oxygen overvoltage, like that of hydrogen, increases rapidly with the current density. It also does not reach its maximum value at once, but after hours, and in some cases (*e.g.* platinised platinum) days. The following Table XXII contains

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[1] *Zeitsch. Elektrochem.* **16**, 621 (*1910*).

[2] P. 117.

[3] A very high overvoltage favours the production of the strongly oxidising ozone which is often formed under those conditions.

[4] *Zeitsch. Anorg. Chem.* **34**, 86 (*1903*).

[5] *Dissertation* (Dresden, 1909).

figures calculated from the results of Foerster and Piguet,[1] working with 2n . KOH at 15° and with a current density of 0·033 amp./cm.^{2}

TABLE XXII

Electrode	At start	After two hours.
Nickel	0·38 volt	0·56 volt
Iron	0·50	0·59
Platinised platinum	0·44	0·86
Smooth platinum	0·84	1·46

Finally, the overvoltage diminishes very considerably with rise of temperature.

It is clear that, when hydrogen and oxygen are liberated by the electrolysis of dilute acid and alkali, very different voltages may be needed under different circumstances, depending on electrolyte, temperature, electrode materials, time after commencement of electrolysis, rate of circulation of electrolyte, etc. With a low current density, *e.g.* 0·01 amp./cm.^{2}, a platinised platinum cathode, a nickel anode, and good circulation, the voltage needed soon after the commencement of electrolysis will consist of the reversible decomposition voltage 1·23 volts, the cathode overvoltage (say 0·03 volt), the anode overvoltage (say 0·25 volt), and the voltage for overcoming the resistance of the electrolyte (perhaps 0·05 volt), a total of 1·56 volts. Whilst with a mercury cathode, a polished platinum anode, and a high current density (0·1 amp./cm.^{2}) the voltage after some hours will amount to 1·23 volts, *plus* cathode overvoltage 1·30 volts, *plus* anode overvoltage about 2 volts, *plus* the electrolyte voltage about 0·5 volt, *plus* any amount due to concentration polarisation. This makes a minimum of 5 volts.[2]

Halogen Ion Discharge.—Besides oxygen, the discharge of Cl' and Br' ions to the free halogens usually necessitates a certain overvoltage. This question has been studied by Müller,[3] by Boericke,[4] and by Foerster and Yamasaki.[5] They found that, at platinised platinum electrodes, all the three halogens—Cl_2, Br_2, and I_2—are precipitated very nearly reversibly, provided that the electrodes remain free from oxygen. But at smooth platinum electrodes this was only true with iodine. Bromine required an overvoltage of about 0·33 volt, chlorine 0·7 volt, the current density in both cases being 0·017 amp./cm.^{2}. These were the final values reached after continued electrolysis, for, like hydrogen and oxygen, chlorine overvoltage is at first low, and gradually rises to a maximum constant value. Increased temperature

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[1] *Zeitsch. Elektrochem.* **10,** 714 (*1904*).

[2] For the technical production of hydrogen and oxygen by electrolysis, see p. 386.

[3] *Zeitsch. Elektrochem.* **6,** 573 (*1900*); **8,** 426 (*1902*).

[4] *Zeitsch. Elektrochem.* **11,** 57 (*1905*).

[5] *Zeitsch. Elektrochem.* **16,** 321 (*1910*).

effects a big diminution. Thus Sacerdoti,[1] working with platinum electrodes at 0·06 amp./cm.^{2}, found the overvoltage to decrease from 0·7 volt to 0·2 volt on raising the temperature from 21° to 100°.

Theories of Overvoltage.—The cause of these complex overvoltage phenomena has long been the subject of investigation and discussion, and is still not finally settled. Haber[2] postulates the adsorption or occlusion of a layer of gas at the electrode—electrolyte surface. This film of poor conductivity increases the potential gradient to be overcome by ions passing from electrolyte to electrode, and as its thickness depends on the nature of the electrode material, the differences observed with different electrodes are explained.

According to Nernst,[3] overvoltage is essentially due to the low rate at which an electrode saturated with gas gets into equilibrium with the atmosphere. For bubble formation, a certain minimum gas concentration in or at the surface of the electrode is required. If the electrode be of a material with a very low solvent power for the gas, before the minimum concentration is reached it will have become saturated with gas at atmospheric pressure. The further quantity of gas needed to produce bubbles corresponds to a supersaturation of the electrode and to an increase in the electrolytic solution pressure. Overvoltage is then an increase in the electrode polarisation, due to an increase in electrolytic solution pressure, caused in turn by the slow rate at which the electrode, charged with gas, gets into equilibrium with the atmosphere. Lately Möller[4] has modified these conceptions as the result of a research in which he showed that overvoltage and surface tension at the electrode-electrolyte surface run parallel. He takes the view that the immediate cause of the former is the energy necessary to produce, between electrode and electrolyte, a gas film of sufficient thickness to give bubbles.

Foerster[5] has experimented in a different direction. He showed that oxygen evolution at a platinised platinum anode undoubtedly has, as an intermediate stage, the formation in the metal of a solid solution of an unstable oxide[6] of platinum, which subsequently decomposes. In the pure state this oxide would give a very high anodic potential. Its solid solutions in platinum have anodic potentials the more positive the greater the oxide concentration. The longer electrolysis continues, the greater this concentration becomes, and therefore the higher the anode potential. The solid solution finally decomposes as quickly as it is formed by OH′ ion discharge, and the electrode assumes a

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[1] *Zeitsch. Elektrochem.* **17,** 473 (*1911*).

[2] *Zeitsch. Elektrochem.* **8,** 539 (*1902*). Also Haber and R. Russ, *Zeitsch. Phys. Chem.* **47,** 257 (*1904*).

[3] *Theoretische Chemie* (4th edition), p. 714 (*1903*).

[4] *Zeitsch. Phys. Chem.* **65,** 226 (*1909*).

[5] *Zeitsch. Phys. Chem.* **69,** 236 (*1909*); *Zeitsch. Elektrochem.* **16,** 353 (*1910*).

[6] Identified by Grube with PtO_3.

constant potential value. This accounts for the frequent rise of overvoltage after the commencement of electrolysis. Its dependence on current density can also be explained. As the final concentration is determined by the amounts of oxide formed and decomposed in the same time being equal, it is clear that a higher current density, and therefore a greater rate of formation of the oxide, must mean a higher final concentration, and hence a higher anode potential.

Foerster supposes these relations to hold generally for oxygen overvoltage, an intermediate unstable superoxide being always formed. If this decomposes very quickly, as with nickel, where the production of NiO_2 is assumed, then the final concentration of the oxide solid solution and the overvoltage will be low. Experimental evidence is difficult to obtain, but it exists with nickel, as with platinum.[1] Further, anodic oxygen, discharged at graphite, produces a certain amount of an insoluble substance of strong oxidising properties, which readily evolves oxygen and is probably a higher oxide of carbon.[2] Applied to $H^{\cdot}$ discharge, one must imagine produced a solid solution of hydrogen in the metal, and gaseous hydrogen indirectly evolved through this. In the case of chlorine, Luther and Brislee[3] and Pfleiderer[4] had before suggested that there is some unknown anodic product intermediate between Cl' ion and Cl_2 gas, whose slow rate of decomposition determines the overvoltage.

To sum up, the discharge of $H^{\cdot}$, OH', or halogen ions very probably first results in the formation of some compound or solution between electrode material and precipitated substance, and the concentration of the gas thus dissolved in some form in the electrode material determines the anode potential. This gas concentration itself depends on a number of factors—viz. the rate of decomposition of the same solid solution, current density, time, and the surface tension relations between electrode, electrolyte, and gas.

Depolarisation of Halogens.—The overvoltage increases the polarisation necessary for the discharge of the halogen ions. But the discharge of Br' and I' ions is also to some extent depolarised in strong solutions, owing to the tendency to form complexes such as Br_3' and I_3'; and all the halogens will be depolarised to a greater or less extent by any OH' ions present, whether furnished by water or alkali.[5]

Of the discharge of other anions—SO_4'', NO_3', etc.—little or nothing is with certainty known, not even whether the anodic oxygen evolved during the electrolysis of a salt containing such ions must always

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[1] See also the interesting results of Joost, *Dissertation* (Dresden, 1910).

[2] Joost, *loc. cit.* Also Nobis, *Dissertation* (Dresden, 1909).

[3] *Zeitsch. Phys. Chem.* **45**, 216 (*1903*).

[4] *Zeitsch. Phys. Chem.* **68**, 49 (*1902*).

[5] Pp. 319–320.

be ascribed to the primary discharge of OH' ions, and not perhaps to the discharge of the anion present, followed by interaction with water and secondary oxygen evolution. For example :—

(*a*) $$SO_4'' \longrightarrow SO_4 + 2 \ominus$$

(*b*) $$SO_4 + H_2O \longrightarrow H_2SO_4 + \tfrac{1}{2}O_2.$$

The chemical result is the same, and as the phenomena observed can be explained satisfactorily on the assumption of OH' ion discharge, we will not further consider *pros* and *cons*.

5. Solution of Metals

The next type of anodic process is the behaviour of metallic anodes. We can, conveniently for our purpose, divide anodic processes in which metals take part into three classes :—

(*a*) the metal completely and easily enters solution;

(*b*) owing to reaction resistances, the solution of the metal is partly, sometimes wholly, stopped;

(*c*) the metal does not dissolve, and some other anodic reaction takes place.

We will first discuss the case of a pure metal which completely dissolves. If it can only furnish one kind of ion the process is a very simple one. Reversible solution, when possible, will commence when the anode potential exceeds the equilibrium value for the electrolyte. But in general the anode potential will be higher than the reversible value, owing to concentration polarisation. Even with a well-circulated electrolyte the metallic ion concentration in the layer immediately surrounding a dissolving anode is bound to be greater than in the bulk of the electrolyte, and the anodic potential necessary for solution is thereby raised.

Influence of Physical Condition of Metal.—The electrolytic potential of a metal depends to some extent on its mode of preparation and its previous thermal and mechanical treatment. Generally speaking, if it has been cast and rapidly cooled, it is not in a stable state at room temperature, and will tend more strongly to enter the ionic condition than the stable form does. Mechanical working will tend to remove this instability, and an anode of wrought metal will have a nobler potential than one of cast metal.

Finally, an electro-deposited metal will have the noblest single-potential value, as it is usually deposited in the stable condition, though there are certainly marked exceptions. It follows that a cast anode dissolves most easily, and least so an electro deposited one. On the other hand, an electro-deposited one dissolves most *evenly*. A cast or wrought anode, particularly the latter, has local differences in structure, with corresponding slight differences in electrolytic potential. The more easily dissolved parts of the anode will enter solution first, and often the undissolved particles will fall off and escape solution altogether.[1] This is one of the causes which produce anode 'slimes.'

Metals giving more than one Cation.—When a metal can furnish two or more kinds of ions in aqueous solution, the conditions correspond to the cathodic relations discussed on pp. 122–123. The anode will always tend to dissolve so that the different ions are produced in the electrolyte in equilibrium amounts—thus, with copper, a great excess of $Cu^{\cdot\cdot}$ ions; with iron, $Fe^{\cdot\cdot}$ ions. With a very low current density this will actually happen; but if it be high, reaction resistances may cause one ion to be furnished in unduly preponderating amount. When, moreover, the formation of one ion is powerfully depolarised by some constituent of the electrolyte and is thus continuously removed from the solution, the metal will apparently dissolve as if its own valency were that of the ion in question. The tendency for $Cu^{\cdot}$ ions to form complexes with Cl' and CN' ions being much greater than that of $Cu^{\cdot\cdot}$ ions,[2] a copper anode in a cyanide or chloride solution dissolves as a monovalent metal, the copper practically entirely going into the complex form.

The possibility of the formation of more than one kind of ion is another cause of the production of anode 'slimes.' The concentrated layer of electrolyte near the dissolving anode may be in equilibrium with the electrode, but when it mixes with the bulk of the solution of different concentration, one ion will be present in excess. If this be the one of lower valency, it will break up as follows: $2Cu^{\cdot} \longrightarrow Cu^{\cdot\cdot} + Cu$ (taking copper as an example), and metallic powder will be precipitated near the anode.[3]

Alloys.—Very important practically is the question of the anodic solution of *alloys*, which we meet in electrolytic metal refining. The anodic behaviour of alloys is governed by the same principles which determine their cathodic deposition, or the depolarisation of the discharge of a metal ion by the material of the cathode.[4] The equilibrium potential of an electrode determines how it will dissolve, and the potential, in turn, depends on how the different constituents of the electrode are combined together. Consider the alloy (a binary one for simplicity) as electrode in some solution which does not react on it chemically. Then, if the alloy contains any appreciable quantity of its more electropositive constituent as a pure independent phase, uncombined with the other constituent either as compound or as solid solution, the potential of the alloy will be the potential of this metal. If the alloy consists of a solid solution of the two metals, it will have a potential somewhere between those of its pure constituents. If the alloy consists

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[1] In an anode which has been worked in some way, the surface layer dissolves less readily than the parts underneath.

[2] See p. 123.

[3] Cf. pp. 248, 272.

[4] See p. 121.

of pure compound without excess of either constituent, its potential will *probably* lie between those of the two metals, but can, however, exceed the potential of either of them. If a mixture of solid solution and compound, then the potential is that of the more electropositive of these.

Figs. 35 and 36 illustrate these cases. The zero of potential is always taken as the potential of the more electropositive constituent of the alloy when in the same electrolyte. In curve I[1] we have the potentials of tin-copper mixtures (bronzes) of different compositions. Up to 66 per cent. Cu (atomic) the potential is practically that of pure tin.

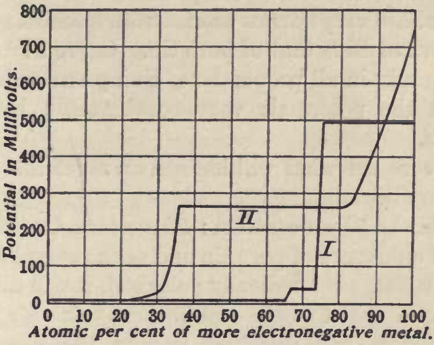

FIG. 35. I.—Sn-Cu in N. H_2SO_4. II.—Cd-Cu in N. H_2SO_4.

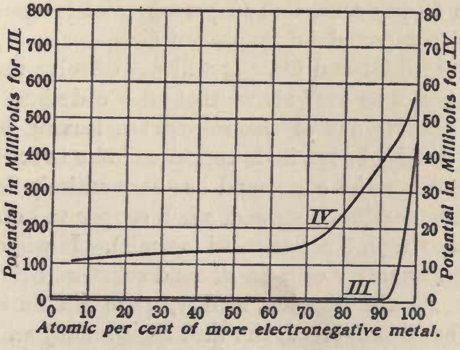

FIG. 36. III.—Sn-Bi in N. H_2SO_4. IV.—Cu-Ag in N. $CuSO_4$.

Then there is a sharp rise of 0·04 volt to the potential of the compound, whose composition, Cu_2Sn, is given by the value of the corresponding abscissa.

A second rise up to a potential difference of nearly 0·5 volt corresponds to a second compound, Cu_3Sn, which has practically the same potential,

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[1] Puschin, *Zeitsch. Anorg. Chem.* **56**, 1 (*1907*).

against the electrolyte as copper itself. In the cadmium-copper curve[1] (II), we observe a horizontal line denoting the presence of a compound, which, as the line commences at 33 per cent. Cu (atomic), has evidently the composition Cd_2Cu. The two sloping curves denote the potentials of solid solutions of Cd and Cd_2Cu and of Cd_2Cu and Cu; whilst the horizontal line up to 20 per cent. Cu means that alloys with less copper than this amount will give the potential of pure Cd. Curve III[2] shows that Sn-Bi mixtures contain no compounds, and only form one set of solid solutions within very narrow concentration limits. Their potential up to 90 per cent. of Bi is that of pure tin. Curve IV[3] finally indicates that Cu and Ag mix in all proportions, giving one series of solid solutions, of which the potentials vary continuously between those of the pure metals.

Let us now consider what will happen on reversible anodic solution of some of these alloys.

(*a*) If the alloy be 50 per cent. Sn : 50 per cent. Cu (atomic per cent.), it will consist of a mixture of pure tin and of the compound Cu_2Sn (with perhaps some Cu_3Sn). If anodically polarised, it will dissolve when the potential has been raised to the equilibrium value for pure tin in the same solution. Tin will dissolve, leaving the compound behind. When all the free tin has entered solution, the anode potential must be increased. If the compound left behind be Cu_2Sn it may be possible to dissolve out the tin, leaving behind the copper. But if Cu_3Sn be also present, it is evident from the diagram that solution of copper will take place just as easily and the compound will dissolve as a whole.

(*b*) Alloy is 60 per cent. Cu : 40 per cent. Cd (atomic per cent.), a mixture of the compound Cd_2Cu and of either pure copper or else a solid solution of Cd_2Cu and Cu. It will not dissolve until the anodic potential is raised 0·25 volt above that of a cadmium anode. Then cadmium will dissolve out of the compound, leaving behind copper. (If the current density be too high, copper will also to some extent enter the solution.) When the compound has been entirely decomposed the potential must be further increased, when copper will dissolve.

(*c*) Sn-Bi alloy with 3 per cent. Bi (atomic). It will consist of pure tin with a small quantity of a Sn-Bi solid solution, containing a large excess of Bi. It will dissolve readily, pure tin entering solution. When all this has disappeared, the tin-bismuth alloy will dissolve as a whole, necessitating increased polarisation.

(*d*) A copper-silver alloy of any composition, except perhaps very extreme values. It will completely enter solution, needing a higher anode potential the bigger the silver content.

We see that complete separation of the constituents of an alloy in

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[1] Puschin, *loc. cit.*

[2] Puschin, *loc. cit.*

[3] Herschkowitsch, *Zeitsch. Phys. Chem.* **27**, 123 (*1898*).

this way is not often possible. Pure material may dissolve, but a solid solution or a compound will generally be left behind. Further, in technical work there are other considerations. Firstly, the necessity of using fairly high current densities. This means that the anode potential must somewhat exceed its equilibrium value, and that therefore constituents may dissolve which otherwise would not do so. Still more important is the fact that a coating of undissolved metal may form on the electrode, hinder the solution of the right constituent, and itself dissolve. In this connection the structure of the alloy will be of importance. If the undissolved crystals readily fall away from the anode, these disturbances will be eliminated. Other points to be noticed are that the crude anodes used technically have generally only a few per cents. of impurities, commonly consisting of small quantities of a large number of metals, not of one metal only. Both these circumstances favour efficient electrolytic refining. A solid solution composed of many constituents will dissolve less readily than one containing two or three only.

Passivity.—We must now discuss the behaviour of metallic anodes which dissolve *partly or not at all* when current passes. Sometimes this behaviour is caused by another anode reaction—*e.g.* the discharge of an anion, setting in at a lower reversible anodic potential. But generally this is not so. The non-solution or partial solution of a metallic anode is commonly bound up with the phenomena of **passivity.** If a piece of chromium or iron with a fresh active metallic surface be dipped into strong HNO_3, no action takes place. When subsequently washed and dipped into cold dilute H_2SO_4 or a $CuSO_4$ solution, no hydrogen is evolved or copper precipitated, as would have happened in the absence of the treatment with HNO_3. In a solution of one of its salts it has the same potential as an indifferent electrode, such as platinum. No change in weight or difference in appearance is perceptible. These metals behave in fact like *noble metals*, far more electronegative in character than ordinary iron and chromium. They are said to have become *passive*, the passivity being produced by the action of the strong nitric acid.

This chemical passivity has its analogy in electrochemical passivity, a metal being termed passive when it behaves electromotively as a nobler metal than it really is—thus, when it requires an anodic polarisation exceeding the equilibrium value before it will enter solution, the excess polarisation often sufficing to cause another process to commence. Examples are abundant. Platinum under most conditions, gold in KCy or in $AuCl_3$, chromium in alkaline solutions, nickel in Na_2SO_4 solution, iron in dilute H_2SO_4, all more or less show the phenomena.

The cause in every case is the low velocity of the corresponding electrode reaction. In order that this may proceed at a convenient, or even at a measurable, rate, the anodic polarisation must be increased beyond the equilibrium value. Passivity can manifest itself in several ways. Sometimes the metal dissolves, not as it would at the equilibrium potential, but as a more strongly *oxidising* ion, corresponding to the higher anodic polarisation. The best known example is chromium.[1] Normally it should dissolve as the ion $Cr^{\cdot\cdot}$, analogous to $Fe^{\cdot\cdot}$. But if anodically polarised in an alkaline solution, it does not dissolve till a potential $\mathcal{E}_h = +0{\cdot}62$ volt is reached, and then as hexa-valent ions $Cr^{\cdot\cdot\cdot\cdot\cdot\cdot}$. These immediately react with the alkali,

$$Cr^{\cdot\cdot\cdot\cdot\cdot\cdot} + 8OH' \longrightarrow CrO_4'' + 4H_2O,$$

the final result being an alkaline chromate. But generally, as the anodic current density (and anodic potential) is raised, the fraction of the current carried by metal ions entering the electrolyte decreases, anions are discharged, and finally the metal may entirely cease to dissolve, the current being completely employed in discharging anions. Thus at a gold electrode in $AuCl_3$, chlorine gas is evolved, and at a nickel anode in caustic alkali, or at an iron anode in an alkaline sulphate, oxygen. The higher the current density, the greater the passivity, as measured by the fraction of the current carried by the anions leaving the electrolyte.

The nature of the anion exerts much influence on passivity phenomena. Generally, the ions of acids which are also strong oxidising agents favour passivity—for example ClO_3' and NO_3'. Cl' and Br' ions tend to remove it.[2] The action of other ions is intermediate. Of cations, the $H^{\cdot}$ ion always acts against passivity, whilst others have little or no effect. An increase of temperature always tends to destroy passivity. As its cause lies in slow reaction velocities, this fact is natural. Cathodic polarisation acts similarly. Passive iron which has been cathodically polarised is rendered active. The passive state of a metal is not a permanent one. Iron which has been passivated by anodic polarisation will, after some time, dissolve in dilute acids. The single potential of chromium which has been similarly treated becomes more and more negative on standing, the metal gradually losing its passivity and acquired noble nature. On the other hand a fresh (and therefore active) surface of iron exposed to dry air, though unaltered in appearance, becomes to a certain extent passive, as shown by its potential against an electrolyte.

Theories of Passivity.—The cause of passivity is not yet certainly known. It is now generally accepted that a reaction resistance of some kind to the reversible anodic process is concerned, but

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[1] Hittorf, *Zeitsch. Elektrochem.* **4**, 482 (*1898*); **6**, 6 (*1899*); **7**, 168 (*1900*).

[2] For the case of gold in $AuCl_3$, see p. 271.

its precise nature remains in dispute. It may vary in different cases. The following explanations have been suggested :—

(1) *Slow rate of ionisation of the anode metal : e.g.* of the reaction

$$Ni + 2\oplus \longrightarrow Ni^{\cdot\cdot} \text{ (Le Blanc).}$$

(2) *Slow rate of combination of discharged anion and material of anode*, with action consequently taking place between the former and water.

E.g.

$$SO_4'' \longrightarrow SO_4 + 2\ominus$$

$$SO_4 + Ni \longrightarrow NiSO_4 \text{ (slow reaction).}$$

$$SO_4 + H_2O \longrightarrow H\,SO_4 + \tfrac{1}{2}O_2.$$

(3) Discharge of anions which react with water giving oxygen. Then a *slow combination of the atomic oxygen and the anode material to an oxide* (subsequently dissolved by the electrolyte) and consequent accumulation of an oxygen layer on the electrode surface.

E.g.

$$SO_4'' \longrightarrow SO_4 + 2\ominus.$$

$$SO_4 + H_2O \longrightarrow H_2SO_4 + O.$$

$$Ni + O \longrightarrow NiO \text{ (slow reaction).}$$

$$NiO + H_2SO_4 \longrightarrow NiSO_4 + H_2O \text{ (Fredenhagen : Muthmann and Frauenberger).}$$

(4) Formation of an oxide or other insoluble compound on the anode. *Its removal by decomposition or by diffusion is slow*, and as it coats the electrode and hinders ions entering the solution, the potential rises and anions are discharged. (Faraday ; Haber and pupils). The insoluble coating may be sometimes formed by discharge of anions, and sometimes by metal ions entering the solution, reacting there with anions present, and forming a precipitate on the electrode.

(5) Sackur assumes every metal anode to contain a certain amount of dissolved hydrogen formed by chemical reaction with the $H^{\cdot}$ ions in the electrolyte, its concentration (pressure) corresponding to the equilibrium expressed by the equation (for a bi-valent metal)

$$Me + 2\,H^{\cdot} \rightleftarrows H_2 + Me^{\cdot\cdot}.$$

The primary anodic process consists in the discharge of anions. The resulting halogen or oxygen combines with the hydrogen dissolved in the electrode, giving water or a halogen acid. To maintain equilibrium, the above reaction must then proceed from left to right, with formation of fresh hydrogen and dissolving of fresh metal. The anodic solution of metals is consequently a chemical process. Passivity results from a *slow rate of combination of hydrogen with the gas discharged from the electrolyte*, a layer of the latter, usually oxygen, accumulating on the electrode. The immediate cause is therefore identical with (3).

E.g.

$$Ni + 2H^{\cdot} \rightleftarrows Ni^{\cdot\cdot} + H_2$$

$$SO_4'' \longrightarrow SO_4 + 2\ominus.$$

$$SO_4 + H_2O \longrightarrow H_2SO_4 + O.$$

$$H_2 + O \longrightarrow H_2O \text{ (slow reaction).}$$

It follows that those metals should most readily become passive which do not catalyse the combination of hydrogen and oxygen to water. Sackur, in fact, showed that there is some kind of parallelism between these two properties. Thus Ni, Fe, and Cr all catalyse the velocity of this reaction very slightly only.

(6) Foerster, from experiments on iron, assumes with Le Blanc *the slow reaction to be ionisation of the metal: e.g.* $Ni + 2\oplus \longrightarrow Ni^{\cdot\cdot}$. He has shown[1] the converse process (metal deposition) to be retarded, and it follows directly that the ionisation should then also suffer retardation. He goes further and assumes that the *pure* metal in these cases is passive, and only becomes active when charged with hydrogen. On these lines he accounts satisfactorily for the effects of cathodic polarisation, content of hydrogen, standing in air, oxidising agents, degree of fineness of division, etc.

We have no space here to consider the experimental evidence for and against these different theories.[2] The actual mechanism of passivity possibly varies in different cases. Where an insoluble film of salt or oxide can actually be seen on the anode, that explanation is probably the correct one. But even then we can suppose with Foerster that such films are often the effect, rather than the cause, of passivity. The views of Foerster[3] or of Sackur[4] perhaps most nearly approach the actual truth. Sackur of course assumes the primary anodic process to consist of anionic discharge, never of cations entering the solution, the latter being the view taken throughout this book.

Aluminium Rectifier.—One remarkable case of passivity undoubtedly due to a film of insoluble solid is furnished by aluminium. If an aluminium electrode be made anode in certain electrolytes, current passes for an instant, but immediately drops to zero. The passage of more current now demands a very high anodic polarisation, depending on the temperature and nature of the electrolyte. With a strongly acid solution it may amount to 27 volts. With cooled electrodes in very dilute $AmHB_2O_4$ it may reach 600 volts. When the

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[1] See p. 121.

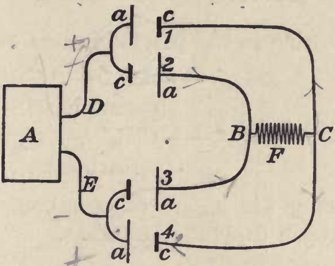
[2] For an excellent critical review of the subject, see Grave, *Jahrb. Radio.* **8,** 91 (*1911*).

[3] *Abhand. Bunsen Ges.* **2,** 20 (*1909*).

[4] *Zeitsch. Elektrochem.* **10,** 841, 929 (*1904*); **12,** 637 (*1906*); **14,** 607 (*1908*).

current does pass the process is of course a violent one, arcing and boiling taking place. The cause of this behaviour is the formation on the surface of the electrode of a thin compact film of basic salt or hydroxide, impervious to $Al^{\cdots}$ or SO_4'' ions, and to many other anions. $H^{\cdot}$ ions can pass through, and hence such a coated electrode *will act as a cathode.* Cl', Br', and NO_3' ions can also pass through, and therefore the electrode can function as anode in solutions containing these ions.

The work of G. Schultze[1] renders it very probable that a gas-layer underneath the layer of basic salt or hydroxide plays a part in the phenomenon. But that the layer of solid also is effective was shown by Taylor and Inglis,[2] who found that a platinum plate coated with



A, Source of alternating current.
a, Aluminium electrodes.
c, carbon electrodes.
F, external circuit.

FIG. 37.—Aluminium Electrolytic Rectifier.

$Al(OH)_3$ acted similarly. The phenomenon is not peculiar to Al; Bi, Ta, and Cb in particular exhibit it in very dilute alkaline solutions. It has been proposed to use such a cell as a high voltage safety fuse, and also to apply it to the problem of converting alternating into direct current. For this purpose the arrangement is shown in Fig. 37. The four cells, containing each an aluminium and a carbon electrode, are so connected with a source of alternating current that electricity of one sign only is continually fed into the arm B, and electricity of the opposite sign into the arm C. If the external circuit be now joined to B and C, direct current will flow through it. In the arrangement as shown, positive electricity *only* can pass from A through cells 2 and 3 into B, negative electricity *only* through cells 1 and 4 into C. In the external circuit F there will be a positive current flowing from B to C. The energy efficiency of the arrangement, however, only averages 60 per cent.

One other important case of anodic passivity, that of hydrogen, will be met with later.[3]

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[1] *Zeitsch. Elektrochem.* **14,** 333 (*1908*).
[2] *Philos. Mag.* [6], **5,** 301 (*1903*).
[3] Pp. 213, 217, 219.

6. Electrolytic Oxidation

This is the last class of anodic processes to be considered. Much already said about electrolytic reduction applies here, and we need go into no very great detail. Anodic oxidation processes can be divided into three classes :—

(*a*) Processes involving a decrease in the number of negative charges or an increase in the number of positive charges on an ion.

E.g.

$$Cu^{\cdot} + \oplus \longrightarrow Cu^{\cdot\cdot}$$

$$Fe^{\cdot\cdot} + \oplus \longrightarrow Fe^{\cdot\cdot\cdot}$$

$$MnO_4'' + \oplus \longrightarrow MnO_4'.$$

(*b*) Processes resulting in the polymerisation of anions.

E.g.

$$2SO_4'' \longrightarrow S_2O_8'' + 2\ominus$$

(persulphate).

$$2CO_3'' \longrightarrow C_2O_6'' + 2\ominus$$

(percarbonate).

(*c*) Processes during which the oxygen content of a substance increases or its hydrogen content diminishes.

E.g.

$$NH_3 + 7OH' \longrightarrow NO_2' + 5H_2O + 6\ominus$$

$$H.COOH + 2OH' \longrightarrow CO_2 + 2H_2O + 2\ominus.$$

We know that *reversible* oxidation, if possible, commences in every case when the anodic potential has been raised above the equilibrium value for the given system. Oxidations of the first type, apart from concentration polarisation due to depletion of the less oxidising ion near the anode, proceed nearly reversibly. The same general statement holds of processes of the second kind. But in class (*c*), reaction resistances are very often met with. We can suppose OH′ ions to be first discharged to oxygen, and the oxygen to oxidise the reducing agent present. It is this depolarisation which is subject to the reaction resistances, considerable with most organic depolarisers. Their presence necessitates an increased driving force if the electrode reaction is to proceed at anything above a very low rate (current density). Now, as the *reversible potentials* at which many of these oxidations begin are very near the potential required for the discharge of free oxygen at the electrode—generally far nearer than the corresponding potentials in electrolytic reduction are to the potential of hydrogen discharge—it often happens under such conditions that this potential is reached, oxygen is evolved, and the yield of oxidised product falls below 100 per cent. When once this has happened the anodic polarisation slowly increases, owing to the gradually rising oxygen overvoltage.[1]

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[1] P. 132.

Finally, such high oxidising potentials are often reached that the depolariser, if an organic substance, is oxidised much more vigorously than is intended, and a low yield of the product sought after results. For this reason electrolytic oxidation is far less used than might be supposed, both in the laboratory and technically.

Changes of current density, temperature, and concentration act as in cathodic reduction. A high concentration of depolariser opposes concentration polarisation and keeps down the anode potential, whilst a high current density has the opposite effect. A rise in temperature increases the velocity of diffusion of the depolariser to the electrode, and is therefore favourable (if the oxidation is complete). The influence of the OH' concentration is twofold. Firstly, it determines the potential at which oxygen evolution can begin. This is necessarily much higher in acid solution, and the oxidation of difficultly oxidisable substances is consequently best carried out in an acid electrolyte. Secondly, it may actually alter the nature of the substance *submitted to oxidation.* If this be an acid, and the anolyte be made alkaline, we shall be dealing with the anion of the acid; but if the anolyte be acidified with a strong mineral acid, the depolarising acid, if not a strong acid, will largely be present as undissociated molecules; and the results of oxidising anion and free undissociated acid can sometimes be quite different.

Overvoltage Effect of Electrode.—The nature of the electrode material is very important. As in cathodic reduction, it can act in two ways, one in virtue of its oxygen overvoltage, the other depending on its catalytic influence on the reaction between oxygen and depolariser. We have seen that the oxygen overvoltage at nickel and iron anodes is somewhat less than at a platinised platinum anode, and considerably less than that necessary at smooth platinum. Dealing therefore with a substance that is only oxidised with difficulty at a very high anodic potential, it is best to use a smooth platinum anode and a high current density which invariably increases the overvoltage of oxygen discharge. But if, on the contrary, an oxidation takes place with a current efficiency of less than 100 per cent. (*i.e.* with the accompaniment of oxygen evolution), and if the materials present are readily still further oxidised, such a metal as nickel or iron should be used as anode. It must be remembered that, as the full oxygen overvoltage does not set in immediately, a reaction may progress after a lapse of time differently from the way it did at the start.

The influence of an increase of temperature on an electrolytic oxidation when oxygen is being simultaneously evolved can vary. It acts favourably by increasing the velocity of diffusion of the depolariser. But it also lowers the oxygen overvoltage, and thus facilitates the discharge of oxygen. According as one or the other of these two effects predominates, it will be better to work at a high or a low temperature.

Catalytic Effect of Electrode.—This may affect the working electrode potential, just as in electrolytic reduction. A good example is the oxidation of iodic acid (HIO_3) to periodic acid (HIO_4).[1] With a current density of 0·0375 amp./cm.^{2}, the reaction takes place with a 100 per cent. current efficiency at an anode of PbO_2, and with a 1 per cent. current efficiency at a smooth platinum anode. The reason is that, using PbO_2, the depolarisation is so rapid that the anode potential is kept some 0·2 volt below the value necessary for oxygen evolution, whilst with platinum the reaction is catalysed very slightly, and the potential consequently reaches a figure at which oxygen is liberated. PbO_2 is often found to have a similar action in other cases. For example, the electrolytic oxidation of $Cr^{\cdots}$ ions to CrO_4'' ions also takes place far more readily at PbO_2 than at Pt anodes.[2] It is highly probable, as Haber suggests,[3] that not only at PbO_2 but also at electrodes of platinum, nickel, etc., it is a superficial coating of oxide, continually regenerated by the current, which does the oxidising, and not oxygen at all.[4]

Catalysts in Electrolyte.—Not only the material of the electrode, but also additions to the electrolyte, can act as catalysts in anodic oxidations. Some of these *oxygen carriers* are very important. Cerous sulphate, $Ce_2(SO_4)_3$, is an example. This salt can be readily anodically oxidised to ceric sulphate, $Ce(SO_4)_2$, a powerful oxidising agent which reacts rapidly with many organic substances, converting them smoothly and quantitatively into single oxidation products. If therefore a suitable organic substance be added as depolariser to the anolyte, together with some $Ce_2(SO_4)_3$, on passsing a current, the latter will be oxidised to $Ce(SO_4)_2$, which will then react with the organic depolariser, regenerating cerous sulphate. This will be reoxidised, the result of the whole operation being the quantitative oxidation of the organic substance.[5] If carried out without the addition of the oxygen carrier, the oxidation would probably have proceeded much less smoothly in every way, owing to reaction resistances.[6] The mode of action of the catalyst in this case is perfectly clear. But sometimes this is not so. Thus the oxidation of $Cr^{\cdots}$ ions to CrO_4'' ions is strongly catalysed by small quantities of various salts[7]—*e.g.* Na_2HPO_4, KF, etc.; the presence of chlorides or fluorides facilitates the formation of $H_2S_2O_8$

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[1] Müller and Friedberger, *Ber.* **35**, 2655 (*1902*); Müller, *Zeitsch. Elektrochem.* **10**, 61 (*1904*).

[2] Müller and Soller, *Zeitsch. Elektrochem.* **11**, 863 (*1905*).

[3] *Die Elektrolytischen Prozesse der Organischen Chemie* (Moser), p. 59 (*1910*).

[4] Cf. the considerations on pp. 133–134.

[5] Cf. p. 130.

[6] See also p. 145.

[7] Schmiedt, *Dissertation* (Charlottenburg, 1909).

from H_2SO_4;[1] and with a little $Cu(HO)_2$ present, ammonia can be oxidised at an iron anode almost quantitatively to NH_4NO_2,[2] nitrogen being the chief product without this addition.

Literature.

Foerster. *Elektrochemie wässeriger Lösungen.*

Haber-Moser. *Die Elektrolytischen Prozesse der Organischen Chemie.*

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[1] Elbs and Schönherr, *Zeitsch. Elektrochem.* **2,** 250 (*1896*); Müller, *Zeitsch. Elektrochem.* **10,** 776 (*1904*).

[2] W. Traube and Biltz, *Ber.* **37,** 3130 (*1904*).

CHAPTER XI

THE ELECTROLYSIS BATH

General.—A technical electrolysis bath may take up to six volts between anode and cathode when working, seldom more.[1] As current is usually supplied by direct current machines at least 150–200 volts, a number of electrolysis tanks are generally connected in series, the same current being passed through each. Thus, a 1,000 K.W. 500-volt generator furnishes 2000 amperes. If cells could be conveniently designed to carry this current, each with its leads absorbing five volts, the arrangement would simply consist of one hundred baths in series with one another and with the dynamo. The disadvantage of this is that a mishap in *one* of the cells means a stoppage of the whole plant unless special means are taken to avoid it (movable shunt leads, etc.).

The remedy is to use a dynamo of lower voltage, but higher amperage, and to arrange the cells in two or more shorter series, in parallel with one another. This, however, means more expensive generating plant. The amount of current a single unit will take depends on the nature of the electrolysis, on considerations of convenience of size, on the efficiency of circulation required, on the working temperature, on the first cost, repairs, labour charges, etc. If the current density used is high, the current carried by a cell of convenient standard size will of course be greater. If the working temperature is to be kept low, a unit with relatively great cooling surface—that is, one of small size—will be advantageous, and *vice versâ*. If exceptionally good circulation of the electrolyte is needed, then again the units should be small, necessitating frequent changes in the direction of flow of the solution.

Arrangement of Electrodes.—With a bath carrying a large current, the use of *one* anode and *one* cathode only would mean the employment of a tank and electrodes of inconvenient size and shape. Hence, unless the conditions of electrolysis preclude it, it is customary to have a large number of smaller anodes connected in parallel, alter-

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[1] A perchlorate bath may take seven volts, etc. See p. 402.

nating with a large number of smaller cathodes similarly connected. In this way the necessary electrode surface is obtained, and the electrolysis vat can be constructed in a convenient rectangular form (Fig. 38). It sometimes[1] happens that, instead of connecting many low voltage tanks in series, it is convenient for the total fall of potential to occur in the one tank. In that case the electrodes are so arranged that one side of each acts as anode and the other side as cathode to the cathode and anode sides respectively of its two neighbours (Fig. 39).

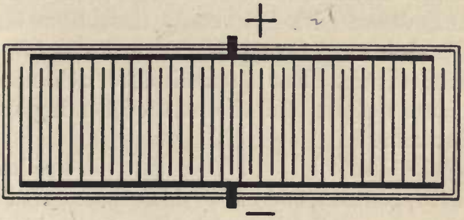

Fig. 38.—Paralleled Electrodes.

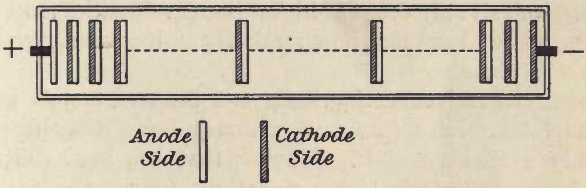

Fig. 39.—Bi-Polar Electrodes.

A complete electrolysis process, absorbing the voltage of an ordinary vat, will then take place between every pair of plates. Such electrodes are termed *bi-polar* electrodes.

Bath Voltage.—The voltage drop across an electrolytic bath is determined by—

(*a*) the reversible decomposition potentials at the two electrodes,

(*b*) irreversible effects at the two electrodes,

(*c*) the product I × R, where R is the liquid resistance of the bath,

(*d*) the voltage drop at the diaphragms (if any) used to separate anolyte and catholyte, and

(*e*) the voltage drop in the leads and terminals, depending on the resistance of their material, and on the efficiency of the electrical contacts made.

Current density and temperature are of importance in determining

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[1] See pp. 258, 327–333, 340, 387, 392.

these magnitudes. (*a*) is independent of current density, and usually decreases with rise of temperature. So does (*b*) (the result of concentration polarisation, passivity, overvoltage, etc.), whilst a heavy current density increases it. (*c*) and (*d*) both vary directly as the current, and are less at high temperatures. (*e*) will increase with the current density, whilst small rises of temperature will have but little effect (larger ones will appreciably *increase* it). Generally then, from the point of view of voltage, a bath is most favourably worked at a low current density and a high temperature. But in technical work the necessity of rapidly obtaining a large output and the cost of heating usually outweigh these considerations.

Not only the electrolyte between two electrodes, but also the electrolyte above, beneath, and at the sides, takes part in the conducting of a current, as the path followed by the latter is not straight, but curved. Thus the resistance of a cell is always *less* than the calculated value, assuming that only the liquid between the electrodes conducts. Hence a current does not enter and leave an electrode with a uniform current density at all points. On the contrary, this is perceptibly greater at all edges and corners, and causes the growths often observed at such edges in the deposition of metals. For the same reason it is inadvisable to use too small electrodes, as then an appreciable fraction of the electrolysis may occur at higher current densities than the calculated one, and we have seen how markedly an increased current density can affect the results.

As material for connecting leads and busbars, copper is generally used, its conductivity (per unit volume) being the highest of all commonly available metals. Copper that has been electrolytically refined has a particularly high conductivity (twelve times that of lead, seven times that of iron, four times that of zinc). Of late aluminium has been coming into use. Although per unit volume its conductivity is not much more than half that of copper, yet, on account of its extreme lightness, its conductivity per unit weight exceeds that of copper. And its price is at present rather the lower of the two. It is stated that in an atmosphere containing chlorine it is considerably less attacked than copper.[1] Voltage losses can also occur in the leads owing to defective contacts. In copper refining they have occasionally amounted to 20 per cent. of the total voltage across the tank.[2] Where electrodes are permanently fixed in position they can be securely attached to their leads, but when they are constantly being removed and replaced, as in copper refining, any elaborate system of connection is impossible. They are often then simply suspended from busbars. In that case a clean plane metal surface is of prime importance.

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[1] *Electrochem. Ind.* **7**, 313 (*1909*).

[2] P. 256. Compare also p. 424.

Cathodes.—Of cathodes used in technical operations where hydrogen, and not a metal, is produced, little need be said. The most important materials are iron and graphite. Platinum is only occasionally used,[1] on account of its high price; copper gauze is said to be the cathode in the Hargreaves-Bird electrolytic alkali cell;[2] lead is used in the electrolysis of dilute H_2SO_4 for obtaining hydrogen and oxygen;[3] mercury is the cathode in the various 'mercury' alkali-chlorine cells.[4] But usually, when the catholyte is alkaline, iron is used, and when acid, graphite. The most important property of a cathode is the amount of its hydrogen overvoltage. Figures are given on pp. 118–119. It is fairly low for iron and platinum, which is fortunate, considering the extended use of the former in alkali-chlorine cells. Copper, nickel, and graphite give values nearly equal, but a little higher than iron. Lead and mercury have very high overvoltages, in the latter case advantageous when acting as cathode in 'mercury' alkali-chlorine cells. Platinised platinum of course would usually be an ideal material, but, apart from its cost, it has a surface that is easily mechanically destroyed.

Anodes.—Technical insoluble anodes should satisfy two conditions. They should not be attacked or disintegrated when under use, and the oxygen or chlorine overvoltage should be low. They should also, of course, conduct electricity well. Of those used or suggested we may mention platinum, smooth and platinised; hard artificial carbon; graphite; Fe_3O_4; carborundum; ferro-silicon; iron; PbO_2; MnO_2. Except the last four, they are particularly intended for use with chlorine. (Ferro-silicon and carborundum are of minor importance.)

Platinum Anodes.—Pure platinum is by no means always unattacked by anodic chlorine. Under certain conditions it can to some extent lose its passivity, as was shown by Haber and Grinberg[5] and by Bran.[6] But alloyed with 10 per cent. Ir it is far more resistive.[7] The accompanying Tables XXIII and XXIV show this.

TABLE XXIII. *Platinum—Iridium*

Electrolyte	Current Density. amp./cm.^2	Temp.	Amp.-hours used.	Loss of weight per d.m.^2 of electrode.
Conc. KCl	0·1	20°	240	0·0 mg.
or NaCl	0·167	80°	(*a*) 200 (*b*) 200	(*a*) 3·5 mg. (*b*) 0·4 mg.

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[1] Pp. 328, 332.
[2] P. 376.
[3] P. 387.
[4] P. 347.
[5] *Zeitsch. Anorg. Chem.* **16**, 446 (*1898*).
[6] *Zeitsch. Elektrochem.* **8**, 197 (*1902*).
[7] Denso, *Zeitsch. Elektrochem.* **8**, 149 (*1902*).

TABLE XXIV. *Platinum*

Electrolyte	Temp.	Current density amp. /c.m.^{2}	Per cent. current used in dissolving Pt
30 per cent. HCl	17·4°	2	0·0
36 per cent.	11°	1	0·3
32·5 per cent.	25°	$\frac{1}{35}$	10·79
25·8 per cent.	25°	$\frac{1}{35}$	7·48
20 per cent.	23·4°	$\frac{1}{35}$	1·02
16·2 per cent.	24·5°	$\frac{1}{35}$	0·06
11·2 per cent.	24·2°	$\frac{1}{35}$	0·081
32 per cent.	50°	1	4·16
32 per cent.	65°	1	5·2

Platinum is expensive, and when used, the maximum possible surface must be employed—*e.g.* a gauze construction. Such anodes are fragile mechanically, and must be carefully mounted.[1] In order to decrease the chlorine overvoltage, platinised electrodes would be preferable. Here, again, the flimsy nature of the surface prevents their use. The use of grey platinum—*i.e.* platinum which has been carefully heated up for a few hundred degrees—would seem to avoid this drawback.[2]

Carbon and Graphite Anodes.—At one time hard artificial carbon anodes were much used in chloride electrolysis. They are prepared by compressing together lampblack and tar, heating to a temperature of about 1400°, and slowly cooling. When of good quality, they are intensely hard and give a sharp metallic ring when struck. Used as anodes they behave satisfactorily as long as oxygen evolution is excluded. But when this commences they usually rapidly burn away and disintegrate, fouling the electrolyte with carbonaceous matter and often with inorganic constituents. Lepsius states[3] that the anodes formerly used in the Griesheim-Elektron alkali-chlorine cell lasted about a year, an exceptionally long life for the conditions of electrolysis in that cell. Graphite anodes[4] are now generally used in the electrolysis of chlorides.[5] They conduct better than those of artificial carbon, are less readily attacked, do not disintegrate to the same extent, and are very easily machined on account of their softness. Their resistance indeed to the action of anodic chlorine is extraordinary. If oxygen evolution be excluded, very little action can be detected after a year or more.[6] Lately[7] the technique of making artificial carbon

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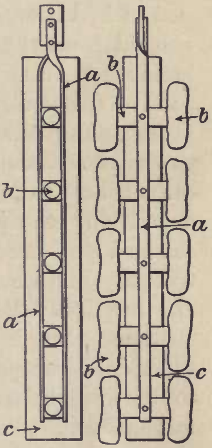
[1] See p. 353. [2] See p. 339. [3] *Electrochem. Ind.* **7**, 189 (*1909*).
[4] See p. 495. [5] *Electrochem. Ind.* **1**, 26 (*1902*).
[6] *Electrochem. Ind.* **5**, 209 (*1907*).
[7] Joost, *Dissertation* (Dresden, 1910). This publication also contains results of experiments which show that the evolution of oxygen from alkaline solution at carbon electrodes is considerably facilitated, and the corrosion of the electrodes much diminished, if the latter are previously soaked in a strong solution of a cobalt salt. The oxygen evolution takes place through the successive formation and decomposition of a higher oxide of cobalt. Cf. pp. 133–134, 241–242.

electrodes appears to have been much improved, and anodes can now be obtained which are very nearly as chemically resistive against oxygen as those of graphite. These anodes are much softer than the older ones, and, although still really amorphous carbon, resemble graphite in several respects.

In cases where carbon or graphite anodes are actually attacked, they are so constructed that, instead of having to scrap the whole electrode, that part only which is attacked need be replaced. With graphite this is very simply effected by screwing the new part into a permanent seat in the main portion of the anode. Fig. 40 shows a more complicated construction, such as is used by the Electrolytic Alkali Co., of Middlewich. The carbon blocks are cemented into the copper frame by molten lead. The metallic parts are subsequently covered with some such material as asbestos or tar, and finally with Portland cement. The porosity of a carbon anode is of importance in determining the extent to which it will be attacked.[1]



a, copper.
b, carbon.
c, Portland cement.

FIG. 40.—Electrolytic Alkali Co. Anode.

The use of Siemens carborundum electrodes in chloride electrolysis has achieved no importance, though comparative experiments carried out with graphite anodes gave favourable results.[2] Where graphite had lost 17 per cent. of its weight, carborundum was unaffected in twice the time. A considerable drawback is its low conductivity. Fe_3O_4, on the other hand, is now used for the anodes in the Griesheim alkali-chlorine cell.[3] It is both cheap and resistive, and for that particular type of cell is the best electrode available.

Chlorine Overvoltage.—Billiter[4] found this to be very low at graphite. For smooth platinum and magnetite, Sacerdoti[5] found almost the same figures—in both cases (at a current density of 4 amp./cm.^{2}) an overvoltage of about 0·7 volt at 18° and 0·35 volt at 100°. Billiter (*loc. cit.*) found far larger values, those for magnetite moreover being much greater than those for platinum. At the same current density and at 17° he obtained, for platinum 1·0 volt, for

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[1] See p. 345. Also for studies of various kinds of carbon and graphite electrodes, see Foerster, *Zeitsch. Angew. Chem.* **14**, 647 (*1901*); *Zeitsch. Elektrochem.* **8**, 143 (*1902*); *Chem. Ind.* **26**, 86 (*1903*); Sprösser, *Zeitsch. Elektrochem.* **7**, (*1901*); Joost, *loc. cit.*

[2] *Zeitsch. Elektrochem.* **13**, 2, 3, 12 (*1907*).

[3] See p. 363.

[4] *Die Elektrochemischen Verfahren, etc.*, vol. ii., p. 140 (*1911*).

[5] *Zeitsch. Elektrochem.* **17**, 473 (*1911*).

magnetite 1·9 volts; while at 70° he found 0·8 and 1·4 volts respectively.

Anodes to withstand Oxygen.—For anodes at which oxygen is being evolved hard carbon and graphite are useless. They are vigorously attacked, more rapidly in acid than in alkali, carbon more than graphite. Platinum is usually ruled out as too expensive, though otherwise suitable. For alkaline solutions, iron and nickel are suitable on account of their passivity. Iron is used in the electrolytic preparation of hydrogen and oxygen,[1] and also employed in the precipitation of gold from the dilute cyanide liquors[2] used in its extraction from 'tailings.' In acid or neutral solution also, iron is to a great extent passive (particularly at high current densities) if chlorides, etc., are absent. But nevertheless some dissolves, and if absolutely necessary to avoid contamination of the electrolyte with metallic impurities it cannot be used. This condition must be fulfilled in the electrolytic deposition of zinc from acid $ZnSO_4$ liquors obtained by leaching calcined zinc ores.[3] Electrodes of graphite, Fe_3O_4, hard lead, etc., are useless. But success has been obtained with Ferchland's anodes of electrolytically-deposited PbO_2.[4] No trace of lead appears to enter solution, though the surface of the anode is slowly broken up. Chlorides must presumably be absent. Electrodes of MnO_2 are stated to be even better, and promise to last several years. They are also mechanically stronger, and can be prepared in more convenient shapes.

Oxygen Overvoltage.—The table on p. 132 shows that the amounts of oxygen overvoltage at nickel and at iron are low and nearly equal to one another, whereas at platinum it is much higher. In acid solution we find the overvoltage at platinum to be far lower, and that of PbO_2 to be very nearly equal to it. Thus Müller and Soller[5] found the overvoltage at smooth platinum in n . H_2SO_4 at 20° with a current density of 0·0228 amp./cm.^{2} to vary between 0·37 and 0·42 volt, whilst PbO_2 under the same conditions gave 0·42 volt; and Müller[6] found the overvoltage at Pt to be by 0·03–0·08 volt the greater. MnO_2 apparently has a still lower oxygen overvoltage. Working in 0·5 n . H_2SO_4, when PbO_2 gave an overvoltage of 0·35 volt, Schmiedt[7] found MnO_2 to give 0·23 volt.

Diaphragms.[8]—We finally come to the question of diaphragms, one that frequently determines the success or otherwise of electrolytic processes. A good diaphragm must first of all be of suitable mechanical strength, and as far as possible unattacked chemically by any solutions or gases with which it comes into contact, so that renewal expenses and disturbances in working are reduced to a minimum. Then,

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[1] See pp. 387–388. [2] P. 278. [3] P. 284. [4] E.P. 24,806 (*1906*).
[5] *Zeitsch. Elektrochem.* **11**, 863 (*1905*). [6] *Zeitsch. Elektrochem.* **10**, 61 (*1904*).
[7] *Dissertation* (Charlottenburg, 1909). [8] See also pp. 356, 369–370.

whilst capable of effectually stopping diffusion and convection, it must not for obvious reasons have too high an electrical resistance. Generally this last condition is comparatively easily satisfied, and most diaphragm troubles are concerned with chemical attack or mechanical weakness.

Alkali-resisting Diaphragms.—For diaphragms to withstand alkaline liquors, asbestos is generally a good starting material. The pores of ordinary asbestos sheet easily become choked up, but asbestos which has been treated with acid and baked acts very well. A good example is the diaphragm prepared by Bernfeld (Leipzig). Asbestos also possesses sufficient mechanical strength to enable it to be securely fastened into position, if necessary under pressure, without fear of breakage. Asbestos diaphragms have been used extensively in alkaline chloride electrolysis, and we might particularly refer to those employed in the Townsend and Billiter cells.[1] Another material from which alkali-resisting diaphragms can be prepared is Portland cement. These again are used in the electrolytic alkali industry.[2]

Acid-resisting Diaphragms.—These are made with more difficulty. Most clays and porcelains contain too much basic material to be satisfactory. For weak acid solutions, Betts[3] recommends that powdered sulphur be sifted over asbestos millboard, the whole heated just above the melting-point of sulphur, and then allowed to stand in an acid solution for a few weeks before use. For electrolytes containing much sulphuric acid and chromic acid, Le Blanc,[4] together with the firm Villeroy and Bock (Mettlach), devised diaphragms consisting (in the finished state) of 25 per cent. Al_2O_3 and 75 per cent. SiO_2. Such a material is naturally useless in alkaline electrolytes, but it was unaffected by the chromic acid mixture in the course of a year. Its chief disadvantage is its brittleness, though the difficulties of preparing pieces of large size were to a great extent overcome.

For diaphragms in acid electrolytes the material recommended by Buchner[5] would also appear to be suitable. It is composed of a mixture of kaolin and the artificial corundum resulting as a by-product in the Goldschmidt Thermite process. Not only is it very resistive to acids even at high temperatures, but its coefficient of expansion with heat is very low. It consequently does not readily crack on cooling, and plates, etc., of large size can be made. Many other materials have been suggested and tried at different times for diaphragm construction, but it is hardly necessary to enumerate them, much less discuss them. They include paper, leather, silk, felt and parchment, treated in various ways; unglazed porcelain and artificial clays, composed of different basic and acid constituents in almost every possible proportion; soap,

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[1] Pp. 375, 380.

[2] See p. 363.

[3] *Electrochem. Ind.* **6**, 272 (*1908*).

[4] *Zeitsch. Elektrochem.* **7**, 290 (*1900*).

[5] *Zeitsch. Angew. Chem.* **17**, 985 (*1904*).

powdered magnesia, gypsum, etc., etc. Some we shall meet with again.

Testing of Diaphragms.—Chemical questions apart, we are concerned with the efficiency of the diaphragm in preventing the mixing of the liquids on its two sides, and with the extra resistance introduced into the electrolyte because of its use. These properties should be investigated for every diaphragm, and the way of doing so has been clearly pointed out by Guye and Tardy.[1] Besides the dimensions of a diaphragm, something should be known of the volume of its pores, of its action in preventing the passage of a liquid through it, of its action in preventing diffusion of a dissolved substance from one side to the other, and finally of its electrical resistance. The **volume of the pores** is readily determined by weighing the diaphragm dry, and, after soaking it in water, reweighing. The fraction of the total volume of the diaphragm due to the pores may vary widely—between 20 per cent. and 70 per cent.

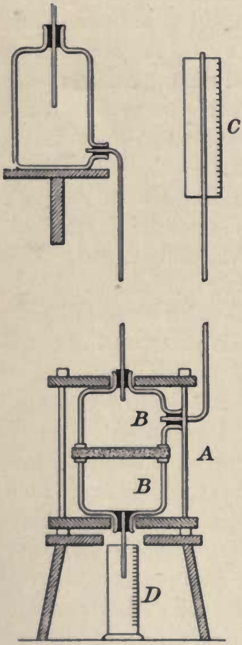

Fig. 41.—Measurement of Permeability of Diaphragm.

The **permeability** of the diaphragm, measuring the ease with which a liquid passes through it, can be determined by the apparatus in Fig. 41. The diaphragm A is clamped in a horizontal position between the two vessels BB. The upper one of these is filled with a liquid (water is suitable), and the liquid head above the surface of the diaphragm measured on the scale C. Water percolates through, and is collected in the vessel D. The quantity v which has passed will vary directly as the area of the diaphragm a, as its permeability K, as the head of liquid h, and as the density of the same δ. It will vary inversely as the viscosity of the liquid η, and we get

$$v = \mathrm{K} \cdot \frac{h \cdot \delta \cdot a}{\eta}$$

The measurement of the **diffusion coefficient** is carried out with a similar apparatus, in which the diaphragm is now placed vertically, and the head of the electrolyte is the same on both sides. The concentrations of solute on the two sides of the diaphragm are different, and the quantity which passes through in a certain time is measured. It is best to stir the liquid on both sides of the diaphragm, to keep the more

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[1] *Jour. Chim. Phys.* **2**, 79 (*1904*).

concentrated solution saturated, and to run pure water continually through the other side. The concentration difference between the two sides is thus kept constant. If now the same salt be always used (to avoid differences of diffusion coefficients), and if the experiment be continued always for the same length of time, the quantity which passes through will be

$$m = \mathrm{K}'.\frac{a}{d},$$

where a is the area and d the thickness of the diaphragm, whilst $\frac{1}{\mathrm{K}'}$ gives the relative resistance to diffusion of the diaphragm material.

The measurement of **electrical resistance** is simply carried out by determining the resistance between two electrodes kept at a fixed distance apart in an electrolyte when both stand on the same side of the diaphragm, and then when they are on opposite sides. Subtraction gives us the apparent resistance of the diaphragm, which varies very considerably in different cases. The acid-resisting diaphragms of Le Blanc—5 mm. in thickness—absorbed 0·15–0·2 volt with a current density of 0·02 amp./cm.^{2}, which is a somewhat low figure.

CHAPTER XII

MOLTEN ELECTROLYTES

THE electrolysis of fused salts is of considerable importance technically. In this chapter we shall deal with their general behaviour as electrolytes, noting particularly how it differs from that of aqueous solutions. The chief worker in this field during the last fifteen years has been Lorenz, and most of the results quoted below are the work of him and his pupils.

Conductivity.—Molten salts are good conductors of electricity, and their conductivity is electrolytic. At anode and cathode are liberated the products we should expect to result. Thus $PbCl_2$ gives lead and chlorine, $NaNO_3$ gives sodium together with oxygen and nitrous gases. Table XXV contains the specific conductivities of a number of fused salts a few degrees above their melting-points.

TABLE XXV

Salt	θ	κ (reciprocal ohms per centimetre cube)
$NaNO_3$	318°	1·022
KNO_3	343°	0·645
$CaCl_2$ (m.p. 774°)	800°	1·90
K_2CO_3	900°	1·95
$ZnCl_2$ (nearly pure)	300°	0·00186
$ZnCl_2$ (impure)	258°	0·224
$PbCl_2$	528°	1·596
NaCl (m.p. 800°)	850°	3·50

If we compare the table[1] of conductivities of aqueous solutions at 18° we see that the figures for molten salts are usually considerably greater, though of the same order. As with aqueous solutions, the conductivity increases considerably with rise of temperature, indeed for moderate temperatures almost linearly. At higher temperatures the increase of conductivity falls behind the rise of temperature.

[1] P. 64.

Tables XXVI and XXVII give results obtained by Lorenz and Kalmus[1] and by Arndt and Gessler.[2]

TABLE XXVI

$K_2Cr_2O_7$ (L. and K.)		*$NaNO_3$ (L. and K.)*	
θ	κ	θ	κ
397°	0·1959	308°	0·965
407°	0·2198	318°	1·022
417°	0·2381	328°	1·065
437°	0·2745	338°	1·108
457°	0·3109	348°	1·151
477°	0·3473	358°	1·195
497°	0·3837	368°	1·239
507°	0·4019	378°	1·283

TABLE XXVII.

AgBr (A. and G.)		*$CaCl_2$ (A. and G.)*	
θ	κ	θ	κ
450°	2·93	800°	1·90
500°	3·02	850°	2·12
550°	3·10	900°	2·32
600°	3·18	950°	2·50
700°	3·34	1000°	2·66
800°	3·50	1050°	2·76
900°	3·68		

The measurement of the conductivity of fused salts usually offers no particular difficulties. The arrangement used is essentially that described on p. 60. *Unplatinised* platinum electrodes must be employed, as platinum-black at high temperatures quickly changes its structure. With particularly good conducting salts, the electrodes must be separated by a capillary tube, in order to increase the resistance to a convenient amount.

Current Efficiency.—The next question is—Is Faraday's Law valid for the electrolysis of molten salts? That it is has been rigorously proved by Lorenz and Helfenstein[3] and by T. W. Richards and Stull.[4] But it happens that the causes which lower current efficiencies at room temperature are far more active at high temperatures. Velocity of chemical reaction and velocity of diffusion are both much greater. Hence, unless the anodic and cathodic products are carefully kept separated from one another and from the action of the electrolyte and the air, the yields obtained will be less than those calculated from Faraday's Law. Thus Lorenz and Helfenstein, in the electrolysis of

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[1] *Zeitsch. Phys. Chem.* **59,** 17 (*1907*).

[2] *Zeitsch. Elektrochem.* **14,** 662 (*1908*).

[3] *Zeitsch. Anorg. Chem.* **23,** 255 (*1900*).

[4] *Zeitsch. Phys. Chem.* **42,** 621 (*1903*).

lead chloride, where the disturbing effects are comparatively small, obtained the following figures for the cathodic current efficiency at 520° :—

(*a*) anode protected from electrolyte, 97·95 per cent. ;
(*b*) cathode protected from electrolyte, 99·46 per cent. ;
(*c*) both electrodes protected from electrolyte, 99·98 per cent.

The chief sources of loss of cathodic metal in the electrolysis of molten salts are volatility, diffusion of anode products to cathode, formation of metal 'fog,'[1] and action of atmospheric oxygen. With

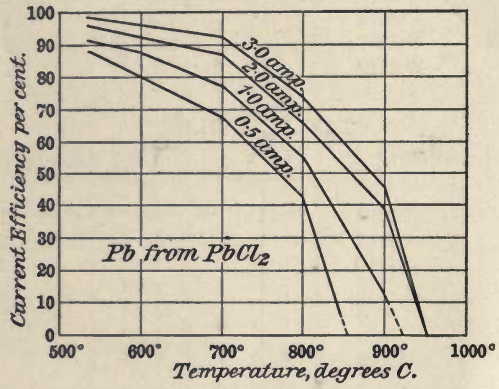

FIG. 42.

increase in temperature, the yield must therefore fall rapidly. This is well shown in Fig. 42, where the different curves hold for different current densities. The effect of increased current density on current efficiency simply depends on the fact that, whilst the *absolute* losses of cathodic product do increase to a certain degree owing to increased diffusion from the anode, yet the quantity produced in unit time increases still more quickly, and the current efficiency must rise.[2] At very low current densities, the quantity of product formed in a given time may not exceed the amount absorbed by the different sources of loss, and the current efficiency may consequently fall to zero. The increase of current density is only limited by considerations of voltage and development of Joule heat near the electrodes, and by the entrance of an 'anode effect,'[3] resulting in a great rise in voltage. Occasionally losses may occur owing to the formation of a subsalt between the precipitated metal and the melt. This can happen under certain conditions in the electrolysis of $CaCl_2$: red crystals of CaCl are produced. Or, again, the

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[1] See below.

[2] Cf. the effect of *current concentration* (p. 30).

[3] See below.

melt may actually dissolve the metal, forming a true solution. This occurs during the electrolysis of molten NaOH. Such cases are, however, rare.

Metal Fog.—But there is one cathodic source of loss quite peculiar to molten salts—the '**metal fog**' first noticed by Lorenz. If a metal such as zinc or lead be melted under one of its own fused salts (*e.g.* $ZnCl_2$ or $PbCl_2$), the molten salt will remain unaffected if the temperature be kept low. But if it is raised, dark clouds rise up from the metal and apparently dissolve in the melt, and this continues until a state of equilibrium is reached. With lead in $PbCl_2$, a yellow melt results, and at higher temperatures a brown one. Zinc gives a bluish-coloured fog, silver a black one. When the temperature falls, the clouds settle down slowly, and finally re-enter the metal. If the excess of massive metal be removed and air kept excluded, then the coloured melt appears stable. But if oxygen be admitted, or a trace of an oxidising agent added, the colour disappears.

On the other hand, it can be produced in the absence of the massive metal by the addition of a small quantity of a reducing agent. Essentially the same phenomena must occur during the electrolysis of molten salts, and will adversely affect the yield, as the metal present in that form is far more readily attacked chemically than the massive metal. It is true that only a small quantity of metal ($< 0·1$ per cent.) is present in such melts, even in those which have a very dark appearance.[1]

The exact nature of these metal fogs is a matter of conjecture. It is most probable that they are analogous to colloidal solutions—are in fact colloidal suspensions of very finely divided drops of fused metal. In this connection it is interesting to notice the effect on the metal fog formation of additions of certain neutral salts to the original melt. It largely prevents fog formation, just as the addition of electrolytes to an aqueous colloidal solution may precipitate the colloid. The mode of action in the two cases can hardly be the same, however. Lorenz supposes[2] that when fused metal and fused salt come into contact, a certain amount of *complex cation* is produced, thus perhaps $Pb^{\cdot\cdot} + Pb \leftrightarrows Pb_2^{\cdot\cdot}$ (like the $Hg_2^{\cdot\cdot}$ ion). The metal fog would then represent metal dissociated off from this complex and in equilibrium with it. The effect of the added salts he explains by saying that they remove the cation of the first salt from the melt as *complex anion*[3]—thus perhaps

$$Pb^{\cdot\cdot} + 2Cl' + KCl \longrightarrow K^{\cdot} + PbCl_3'.$$

The concentration of complex cation, and hence the metal fog, must therefore become less.

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[1] Lorenz, v. Hevesy, and Wolff, *Zeitsch. Phys. Chem.* **76**, 732 (*1911*).

[2] *Loc. cit.*

[3] See p. 57.

The effect of this addition of neutral electrolytes can be studied by measuring its effect on the cathodic current efficiency during electrolysis. As the fog formation is one of the chief sources of loss in the preparation of metal, the two effects will run more or less parallel. The influence of the addition of different salts on the course of electrolysis of molten $PbCl_2$ is shown in Fig. 43.[1] In other cases, where the electrolysis losses under normal conditions are greater, the effects produced are even more marked. But not every addition to the electrolyte increases the current efficiency. Thus, if $FeCl_3$ be added to $PbCl_2$, the yield diminishes considerably, even if the addition be very small.

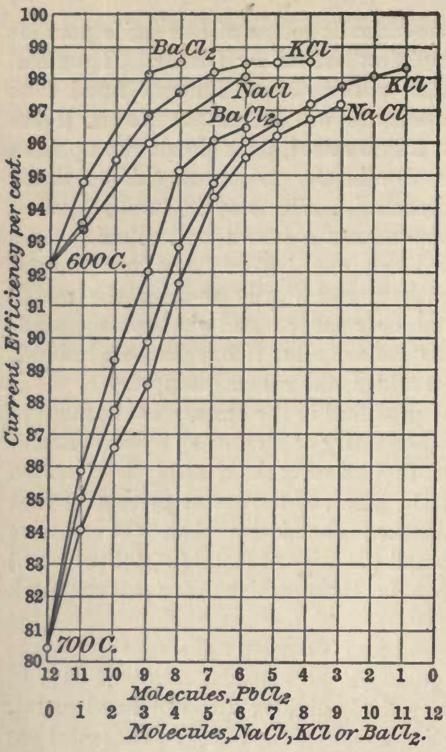

FIG. 43.

Appelberg obtained the following figures[2]:

$PbCl_2$ at 600°

Per cent. $FeCl_3$ added	Current efficiency
0·0	96·3
0·005	95·6
0·03	87·6
0·1	76·8
0·4	70·5
0·8	51·7
1·6	22·3
3·2	19·8

The effect here can doubtless be explained by the $FeCl_3$ being reduced at the cathode, either electrochemically or by the action of the metal fog. The $FeCl_2$ is reoxidised at the anode, and the losses thus become continuous. Traces of iron entering a fused melt from

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[1] Lorenz, *Zeitsch. Elektrochem.* **13,** 582 (*1907*).

[2] *Zeitsch. Anorg. Chem.* **36,** 36 (*1903*).

the material of the containing vessel may thus exert considerable influence on the electrolysis.

Voltage Relations.—When discussing the E.M.F.'s of cells with aqueous electrolytes, we saw that the values depended on the concentrations of the solutions. With pure fused salts, questions of concentration do not enter. The reversible E.M.F. of a primary cell depends simply on the nature of electrodes and electrolyte and on the temperature. So does the corresponding decomposition voltage. And these are of course equal. For example, the decomposition voltage of fused $PbCl_2$ at 570° is 1·25 volts, whilst the E.M.F. of the cell $Pb | PbCl_2 | Cl_2$ at the same temperature is 1·24 volts. But with fused mixtures of salts it can be shown that the E.M.F.'s depend on the concentration of the salt corresponding to the metal used as electrode. Thus Gordon[1] measured cells made up as follows:

$$\begin{array}{c|c|c|c} & \mathrm{AgNO_3}\text{ in a} & \mathrm{AgNO_3}\text{ in a} & \\ \mathrm{Ag} & \text{mixture of} & \text{mixture of} & \mathrm{Ag}, \\ & \mathrm{KNO_3 + NaNO_3} & \mathrm{KNO_3 + NaNO_3} & \end{array}$$

the $AgNO_3$ concentration in the melts surrounding the two electrodes being different. He found that the E.M.F.'s of such cells could be expressed by the well-known formula for concentration cells,[2]

$$E = \frac{0{\cdot}0002T}{n} \log \frac{[C_1]}{[C_2]},$$

where n is of course one in this case and $[C_1]$ and $[C_2]$ are the molecular concentrations of the $AgNO_3$ (in aqueous cells $[C_1]$ and $[C_2]$ represent the gram-ionic concentrations).

We know that the reversible E.M.F. of a primary cell is a measure of the useful work which the corresponding chemical reaction can furnish. This varies with temperature, and as a large range of working temperatures is possible with fused salts, the corresponding E.M.F.'s or decomposition voltages can show considerable variation. With cells of the type metal | salt | halogen, or with electrolytic processes corresponding to the reaction salt ⟶ metal + halogen or non-metal (the kind of process with which we shall principally have to deal), the E.M.F. or decomposition voltage diminishes as the temperature rises, corresponding to the tendency of the compound to dissociate more and more with rise of temperature, the free energy liberated during the combination of its constituents consequently becoming less. As examples we may take the cells $Ag | AgCl | Cl_2$ and $Pb | PbBr_2 | Br_2$.[3]

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[1] *Zeitsch. Phys. Chem.* **28**, 302 (*1899*).

[2] See p. 104.

[3] Czepinski, *Zeitsch. Anorg. Chem.* **19**, 208 (*1899*).

TABLE XXVIII

$Ag \mid AgCl \mid Cl_2$		$Pb \mid PbBr_2 \mid Br_2$	
θ	E.M.F.	θ	E.M.F.
480°	0·903 volt	310°	1·132 volt
520°	0·891	411°	1·095
560°	0·882	502°	1·022
600°	0·871	580°	0·960
620°	0·865	680°	0·873
660°	0·854	740°	0·808

From the point of view of voltage alone, it would be advantageous to use high temperatures in technical fused-salts work, but this gain would be more than neutralised by the increased wear and tear of the apparatus and by the heat expenditure necessary to compensate for radiation losses. Decreased current efficiencies would also result.

Anode Effect.—Irreversible voltage effects, etc., are far less important with molten salts than with aqueous solutions. Such effects ultimately depend on the low velocity of some stage of the electrode process, and, in view of the known effect of temperature on reaction velocity, it is natural that at high temperatures they should be in general very slight. But nevertheless, when the current density becomes excessive, they may make their appearance; and particularly what is known as the **anode effect** is observed at carbon anodes in fused metallic halides. The electrode becomes covered with a film of gas—Cl_2, F_2, Br_2 or I_2—through which the current can only pass as an arc discharge. The voltage rises very considerably and the anode appears to glow, as a consequence of the number of tiny arcs which are passing. The anodic current densities above which this happens will vary with the nature of the electrolysis and the temperature; they average about 4–5 amp./cm.^{2} with hard carbon and 7–8 amp./cm.^{2} with graphite.

The phenomenon has been observed with chlorides of Pb, Cd, Ag, Ca, Mg, Al; with bromides of Ag and Pb; with PbI_2; and with Na_3AlF_6 (cryolite) and AlF_3.[1] It is most pronounced with fluorides, least so with iodides. It is sometimes accompanied by loss in weight of the anodes, owing to formation of halides of carbon, the more the higher the temperature and the heavier the current density. The cause of this behaviour is that the gas is liberated at the electrode more quickly than it can stream away, and that the current can then only pass as an arc discharge between electrolyte and anode. It should be mentioned that by stirring, or by raising the anode from the melt for a moment, or by reversing the current—in other words, by removing

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[1] See, amongst other references, Hulin, *Zeitsch. Angew. Chem.* **11,** 159 (*1898*); Lorenz and Czepinski, *Zeitsch. Anorg. Chem.* **19,** 246 (*1899*); Muthmann, Hofer and Weiss, *Lieb. Ann.* **320,** 237 (*1901*); Wöhler, *Zeitsch. Elektrochem.* **11,** 612 (*1905*); Arndt and Willner, *Ber.* **40,** 3,025 (*1907*); A. Oettel, *Dissertation* (Dresden, *1908*); Kailan, *Zeitsch. Anorg. Chem.* **68,** 141 (*1910*); particularly Frary and Badger, *Trans. Amer. Electrochem. Soc.* **16,** 185 (*1909*).

the gas layer—the effect can be made to disappear. Kailan found that an increase of temperature at constant current density acted similarly.

The only other appreciable irreversible effect is the *concentration polarisation* which occurs at high current densities. Apart from any formation of gas layer on the electrode, the voltage of a working cell increases with current density, just as with aqueous electrolytes. In the latter case the cause is exhaustion of ions near the electrode, and if we assume the presence of ions in molten salts, we can suppose the same cause to be active there.

The reversible E.M.F. of a cell can be determined by either decomposition voltage or polarisation discharge method. In the latter case, the curve obtained falls far more rapidly than a similar curve got with an aqueous electrolyte, owing to the high temperature and the rapid rate of diffusion of products away from the electrodes.

Owing to the differences in decomposition potential shown by different fused salts, a separation of the several metallic constituents from a mixture is possible in the molten state, just as in aqueous solution. The relations of course may be rendered rather complex by the varying tendencies of the metals to alloy amongst themselves, and thus to depolarise one another's discharge. With a mixture of the chlorides of silver, lead, and zinc, Lorenz[1] obtained results shown in Fig. 44. The abscissæ represent the quantity of electricity passed since the commencement of electrolysis, and the ordinates the composition of the cathode product taken from the cell at the corresponding intervals of time. The silver is preferentially deposited, then the lead, finally the zinc.

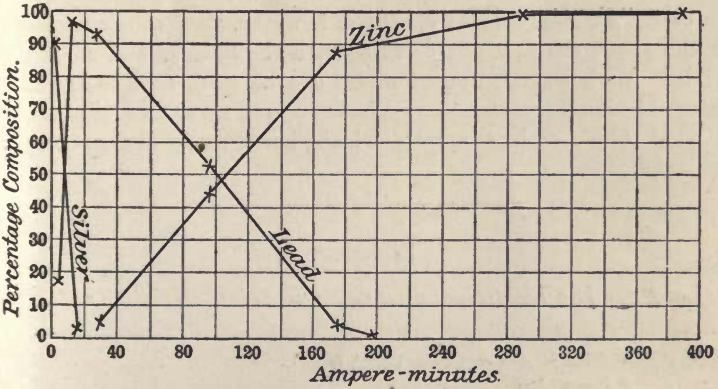

FIG. 44.

Constitution of Fused Electrolytes.—An interesting point which we cannot discuss here is how far the theory of electrolytic ionic

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[1] *Zeitsch. Anorg. Chem.* **10,** 78 (*1895*).

dissociation is applicable to fused electrolytes. We can only say that all the evidence renders it probable that *ions* as we know them in aqueous solution are here also. But as to what extent that is so, and as to what laws govern their equilibrium with the rest of the melt, nothing definite can be stated. It is certain that the molecular condition of a fused salt is very complex. Thus, fused lead chloride, besides simple molecules $PbCl_2$ and simple ions $Pb^{\cdot\cdot}$ and Cl', contains without doubt complex neutral molecules $(PbCl_2)_n$, and also very probably complex anions, such as $PbCl_3'$ or Pb_2Cl_5'. This last statement is rendered likely by the results of migration experiments of Lorenz and Ruckstuhl[1] on mixtures of $PbCl_2$ and KCl. n_{Pb} was found to be negative when excess of KCl was present, and this indicates the presence of lead as anion.[2]

Apparatus.—As far as possible a fused-salt bath is worked so that its temperature is kept up by the Joule heat supplied by the current. No external heating is used, and the walls become lined with a solidified layer of the electrolyte. The longer life of the plant thus secured compensates for the use of the more expensive electric heating. The walls of the vessel are made of iron, or of some suitable refractory, depending on the nature of the electrolyte. The cathode employed often consists of the precipitated metal itself. In other cases (*e.g.* with $MgCl_2$ or NaOH) iron can be used, whilst graphite is suitable in halide melts if the current density be not too high, in which case it disintegrates.[3] As anode material, when a halogen is being evolved, graphite is by far the best. At high current densities, however, such as are responsible for the anode effect, it can combine with the halogen and rapidly lose weight. With NaOH, iron or nickel can be used, and, in the manufacture of aluminium, where oxygen is evolved from a cryolite-alumina bath at 950°, carbon anodes which burn away continuously are employed.

Literature

Lorenz. *Die Elektrolyse geschmolzener Salze.* Vols. II and III.

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[1] *Zeitsch. Anorg. Chem.* **52**, 41 (*1907*).

[2] See p. 162; also p. 57.

[3] Kemmerer, *Trans. Amer. Electrochem. Soc.* **9**, 117 (*1906*).

CHAPTER XIII

GENERAL PRINCIPLES OF ELECTROTHERMICS

1. Electric Heating

So far we have dealt only with electrolytic processes. But an exceedingly important branch of applied electrochemistry is that of **electrothermics,** the chemical effect resulting from a heat effect, itself produced by electrical means. On p. 4 we briefly noticed some of the advantages of electric heating, and must now consider the matter in more detail.

We can distinguish three types of electric heating. In the first, the current passes through some resistant material, and the heat thus produced is imparted to the reacting substances (Fig. 45). These may surround the resistor where the heat is produced, or may actually themselves entirely or in part form the resistor. Examples are the carborundum and cyanamide furnaces. Secondly (Fig. 46), the heat may be produced by means of a low voltage *arc discharge*,[1] in which case it is transmitted to the reacting substances by radiation. The Stassano steel and the de Laval zinc furnaces work on this principle. In many technical furnaces, including some of the most important, the arc is the chief heating agent, but a certain amount of resistance heating also occurs. The ferro-silicon furnace is an example. Thirdly, we have induction heating, only possible with alternating currents. Here the furnace consists essentially of a step-down transformer,

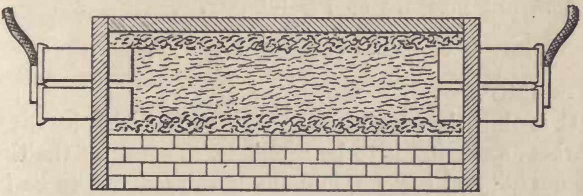

FIG. 45.—Resistance Furnace.

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[1] Strictly a special case of resistance heating.

with a short-circuited secondary in which enormous currents, and consequently powerful heating effects, are produced. The well-known Kjellin steel furnace is an example. As induction heating differs considerably from other forms of electrical heating, we will defer its consideration to Chap. XXIV, dealing with the electro-metallurgy of iron and steel.

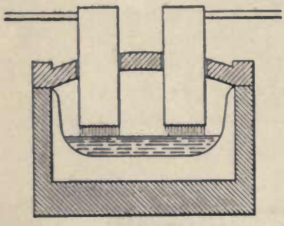

FIG. 46.—Arc Furnace.

Let us now compare electrical and fuel heating, assuming at first that the fuel or products of combustion come into direct contact with the charge.

Temperature Range.—The first point is the available range of temperature, and there electrical heating has a great advantage. The temperature attainable by the combustion of a fuel depends essentially on its heat of combustion and on the specific heats of the products. Consider the combustion of pure carbon by means of the theoretical quantity of oxygen to CO_2. When 12 kilos of carbon are burnt, 44 kilos of CO_2 result, and the heat liberated, if both starting materials and final product are at room temperature, is 97,200 Cals. If all this heat were imparted to the CO_2, we should have, putting the mean molecular specific heat of the latter between room temperature and $\theta°$ C. at constant pressure as $7{\cdot}5 + 0{\cdot}0037\,\theta$,

$$97{,}200 = (7{\cdot}5 + 0{\cdot}0037\,\theta)\,\theta,$$

whence $\theta = 4210°$.

4200° C. is thus the highest temperature attainable by the combustion of carbon, assuming it to be complete, to consume the theoretical minimum quantity of oxygen, and the heat produced to be imparted solely to the CO_2 resulting.

But in practice these conditions are never fulfilled. Firstly, the combustion is not complete. CO_2 dissociates as the temperature is raised into CO and oxygen, and appreciably above 2000° C. Thus at 2000° and atmospheric pressure 6 per cent. is dissociated, at 2800°, 16 per cent. Consequently, *if* carbon on burning actually gave products at such high temperatures, the heat liberated would not be that furnished by its complete combustion to CO_2, but rather that produced by its combustion partly to CO_2 and partly to CO. Further, the heat actually liberated is not entirely imparted to the gaseous products, but in part is lost by conduction through the furnace hearth and walls. Lastly, and of most importance, the fuel is not burnt by oxygen, but by air, and apart from any excess of air which may be used, the heat generated heats up four volumes of nitrogen for every one volume of CO_2 formed, the maximum possible temperature being thus correspondingly depressed. Under these circumstances it is not surprising that the maximum temperature attainable with ordinary fuels is about 1800° C.

In electric heating, the quantity of heat produced per second in a given system is equal to $\frac{I^2R}{4\cdot19}$ Cals., where I is the current flowing in amperes, and R the resistance in ohms of the system. The temperature is determined by the heat capacity of the system and by the conduction and radiation losses, etc. etc. If the latter could be entirely avoided, it should be possible to increase the temperature indefinitely by merely increasing the current passing.

But in practice a limit is set by these losses, and particularly by the volatility of the resistor or of the electrodes between which the arc is passing. At this boiling or volatilisation point, as the case may be, the heat produced will be largely absorbed as latent heat of vaporisation or volatilisation respectively, and the temperature will rise no further. This limit is generally far higher than is the case with fuels. With an arc between carbon electrodes, for example, it is about 3500° C. Hence, when operations are to be carried out demanding exceedingly high temperatures, electrical heating can be employed where fuel heating would be useless. Thus it becomes possible to treat highly refractory ores and to carry out endothermic reactions (which take place best at high temperatures[1]), to eliminate rapidly impurities which are only removed slowly at lower temperatures, as in steel refining, and further, to procure good castings of very difficultly fusible metals and alloys.

Then there are other important advantages. By a simple regulation of the power consumed in a furnace, effected by altering the applied voltage or the position of the electrodes, the temperature can be varied within wide limits and also kept very constant. Further, the heat generated is localised and produced exactly where wanted. In all electric furnaces the reacting substances and the source of heat are very close together: often the charge actually envelops the region where the heat is produced. It is obvious that the utilisation of the heat must be far more perfect than with fuel, in which case the heat is developed in a more diffused manner, and where there are considerable losses owing to the hot waste gases.

The fact that in many forms of furnace the heat is generated in the centre of the charge has another important advantage, in that the walls of the furnace are thereby protected from its direct action, and expenses of repairs are consequently lessened. It is a mistake to suppose, as is often done, that electric furnaces require linings of most exceptional refractory properties. If we except carbon itself, no refractory could stand the *direct* action of the electric arc, and with this therefore excluded, it becomes possible to use the ordinary technical materials.

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[1] P. 23.

Finally, the furnace product is free from those impurities which are necessarily present when fuel is mixed with the charge or when fuel gases have played on its surface.

Several of the above statements also hold good for a comparison between fuel heating with the heat transmitted through the walls of a retort or muffle, and electrical heating. In the latter case the utilisation of heat is far better, and the retort or muffle is not exposed to the action of hot flue gases.

Comparative Cost.—Electrical heating has only one essential disadvantage as compared with fuel heating, but that is often insuperable. It is generally considerably more expensive. For our present purpose, we will define, with J. W. Richards, the *efficiency* of a furnace as the ratio of the heat usefully employed in heating or causing chemical or physical changes to the total heat used. The efficiency of electric furnaces varies considerably according to the process in question and the design and size of the furnace. Generally speaking, the larger the latter is, the smaller are the radiation losses in comparison to its load, and the higher the efficiency. Indeed, results, which on a small scale appear to be hopeless, may prove to be quite satisfactory with a large commercial unit. One can perhaps set the average efficiency (*so defined*) of a well-designed technical furnace at about 70 per cent. *It depends largely on the temperature*, being greater the lower this is. Thus Snyder[1] describes a 35 K.W. electric resistance furnace used for the distillation of turpentine from wood, in which the maximum temperature is 190° and the efficiency about 96 per cent. The efficiency of a fuel-heated furnace shows similar but greater variations. If fuel and charge are mixed, the efficiency will be comparatively good, though lower than that of an electric furnace. Let us assume 50 per cent. But if a high temperature is needed, involving the use of a powerful blast, then the efficiency falls off. Whilst if the question is one of external heating of muffles or crucibles, the utilisation of heat is small, and at high temperatures—1500° C. and over—very small. It may easily fall to 5 per cent. or less. For purposes of comparison with electrical heating, this rapid decrease of the efficiency of fuel heating with rise of temperature must be strongly emphasised.

Now the heat equivalent of a H.P. year is

$$\frac{8760 \times 3600 \times 746}{4{\cdot}19 \times 1000} = 5{,}610{,}000 \overset{\text{Kg Cals}}{\text{Cals.}},$$

of which we assume 70 per cent., or 3,930,000 Cals., are utilised by the electric furnace. As a mean value for the calorific power (units of heat generated by combustion of one unit mass) of solid fuel we can take 7,800 Cals. per kilo. or 7,800,000 Cals. per ton. The fraction of this total

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[1] *Trans. Amer. Electrochem. Soc.* **13**, 371 (*1908*); **19**, 191 (*1911*).

usefully utilised varies between 3 per cent. and 50 per cent. One ton of fuel therefore furnishes 230,000–3,900,000 Cals. for the carrying out of the process. Hence, other conditions apart, with some processes it will be more economical to employ electrical heating only when a H.P. year can be got for less than the price of a ton of fuel; whilst in other cases, electrical heating is more economical when a H.P. year costs less than 13–14 tons of fuel. Obviously the first condition corresponds to a country where fuel is dear and power cheap; whilst for the second extreme case mentioned, it should be advantageous to use electric heating even where fuel is very cheap. In many processes it would probably pay to carry out the first part of the heating, during which the temperature is low and the thermal efficiency high, by means of fuel firing; and then employ the more expensive electric heating for the final high temperature stages when the efficiency of fuel heating is correspondingly low.

Conclusions.—We thus arrive at the following conclusions:

(*a*) electrical heating is essential for very high temperature work;

(*b*) it is often more economical for temperatures which, though high, *can* nevertheless be attained by fuel firing;

(*c*) it is to be recommended if any specially pure product is needed;

(*d*) for most purposes where temperatures lower than 1400° C. are required, its use is only economical in certain exceptional regions where power is cheap and fuel expensive.[1]

2. General Principles of Electric Furnace Design

Electric furnaces may work continuously or discontinuously. Arc heating can be used in both cases, but resistance heating by itself is practically only applied to discontinuous processes. To enter at all precisely into electric furnace design would be impossible; here we can only mention a few sufficiently obvious general principles. Thus an electric furnace should be as simple in construction as possible. This, of course, is an excellent rule for the design of all large-scale chemical plant, but particularly so for apparatus exposed to high temperatures, or through which an electric current passes. Every extra complication means more care in handling, and increases the possibility of a breakdown. An electric furnace should be so constructed that all parts of it, particularly those likely to need frequent repair, are readily accessible. To minimise these necessary repairs, the arc (assuming an arc furnace) must not be allowed to play directly on any part of the hearth, walls, or roof. If possible it should be

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[1] One or other of the distinctive characteristics of electric heating may lead to its introduction in certain cases; for example, in the turpentine furnace mentioned above, the ease with which a *constant* and *regular low temperature* can be produced. A higher temperature would destroy the turpentine.

entirely surrounded by the charge. But the charge should never be in contact with the electrodes at the point where the latter pass through the furnace lining. If this occurs, it is difficult with high current densities to avoid fusing the refractory and destroying the furnace wall. The electrodes themselves must be protected against overheating and oxidation by water-jacketing or other means.

To reduce radiation losses, the ratio

$$\frac{\text{outside exposed surface of furnace}}{\text{volume of furnace}}$$

must be small, and the walls, or some thickness of them, made of a good heat insulator. Further, the lining should have a high electrical resistance at its working temperature, as the heat produced by any current passing along the lining between two electrodes (often a considerable amount) is mostly lost. To secure a proper utilisation of the heat supplied the charge must be sufficiently great, and suitably placed with respect to that part of the furnace where the heat is being generated. A paper by Collins[1] on the design of intermittent resistance furnaces deals particularly with these last points. Finally, for continuously working furnaces, the charging and tapping arrangements must be convenient, and if valuable gaseous products are evolved, as in the pig-iron, ferro-silicon, and carbide furnaces, they should be collected and utilised. It is only recently that steps have been taken to recover these gases.[2]

We have stated that when possible the charge itself or else the cooled product should form the *effective* furnace lining, in which case the ordinary materials—firebrick, silica, calcined magnesite or dolomite, etc.—can be used for the furnace walls. But this is not always practicable. In ferro-silicon furnaces the hearth is filled with the corrosive liquid product; in steel furnaces walls and bed undergo the action of liquid slag and steel, and the roof is exposed to slag vapours and more or less to direct radiation from the arc (not of course in induction furnaces). In such cases it may be necessary to use particularly resistive linings, according to the temperature and the chemical properties of the substances present. But not always so. A dolomite hearth and a silica or magnesite roof are found to serve excellently in most steel furnaces. Of more resistive refractories, several are themselves products of the electric furnace. Alundum,[3] carborundum,[4] and siloxicon[5] are examples. This last substance, though oxidised at 1500°, is stable up to 3000° in absence of air, and is not attacked by molten metals as carborundum is. Another good refractory is crystallised and ground magnesia, made by fusion in the electric furnace. Finally,

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[1] *Trans. Amer. Electrochem. Soc.* **9**, 31 (*1906*).

[2] *Trans. Farad. Soc.* **5**, 254 (*1909*).

[3] P. 495. [4] P. 488. [5] P. 492.

for the highest furnace temperatures attainable, carbon is the only possible material. Air must naturally be excluded. Carbon is also the only possible lining for the hearth of a ferro-silicon furnace. Everything else is attacked and dissolved.

Whilst the lining of a furnace must be sufficiently refractive, the materials of which the walls are constructed should be poor conductors of heat and electricity. It does not always happen that these properties are found combined in the same substance with adequate refractoriness. Thus carborundum and carbon conduct heat and electricity well. The best practice is to make the refractory lining of *as small a thickness as is practicable,* and to back it with bricks which are primarily poor conductors of heat and electricity. It has indeed been found practically that the thickness of refractory necessary to prevent melting of the more fusible low-conductivity bricks behind it is usually exceedingly small. It is generally possible to apply it in the form of a wash, thus minimising both the current losses between electrodes embedded in the walls, and also its effect on the heat lost by conduction outwards through the walls.

The quantity of heat passing in unit time through a plate of a given substance is expressed by the formula—

$$Q = \frac{a}{l} \cdot k . \theta,$$

where a is the area of the plate, l its thickness, θ the difference in temperature between the two sides, and k the specific conductivity of the substance. This formula cannot be directly applied to technical furnaces, because a varies between the limits of the inside and outside surfaces of the furnace, and to use the mean of these values by no means always gives a good approximation. Hering[1] has worked out, for the more simple shapes of furnace, simple and accurate expressions by which $\frac{a}{l}$ in the above equation can be replaced. His paper brings out the extreme importance for effective and economical insulation of (1) making the load per single unit as heavy as possible, when the relative loss is reduced, and (2) for a furnace of given load, of making its inside area as small as possible.

Our only accurate knowledge of the heat conductivities of furnace materials at high temperatures we owe to Wologdine,[2] who carried out measurements on bricks of many materials up to temperatures of 1,000°, and discovered several interesting relations between temperature of firing, conductivity, permeability to gases, etc. Some of his results are given in the following Table XXIX. The conductivities

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[1] *Trans. Amer. Electrochem. Soc.* **14**, 215 (*1908*).

[2] *Electrochem. Ind.* **7**, 383 (*1909*).

are expressed in $\frac{\text{calories} \times \text{c.m.}}{\text{second} \times \text{c.m.}^2 \times 1^\circ \text{ C.}}$, and are mean values for the range 0° to 1000°.

TABLE XXIX

Material	Conductivity	Relative Conductivity
Graphite brick	0·025	100
Carborundum brick	0·0231	92·4
Magnesia brick	0·0071	28·4
Chromite brick	0·0057	22·8
Firebrick	0·0042	16·7
Gas retort brick	0·0038	15·2
Bauxite brick	0·0033	13·2
Silica brick	0·0020	7·8
Kieselguhr brick	0·0018	7·1

As far as the size of furnaces is concerned we appear to be in a period of rapid transition. Taussig[1] points out that the practical limit with uncovered arc furnaces is reached at about 3000 K.W. per hearth, above this the difficulties of charging and working and the fume nuisance becoming too great. But with closed furnaces, such as those of Helfenstein[2] (Fig. 47), great developments may be anticipated. Of considerable advantage will be the possibility of collecting and utilising the furnace gases, often of very high calorific power. These remarks apply particularly to carbide furnaces. But the new Héroult steel furnaces of the United States Steel Corporation represent another big advance, and we may also expect interesting results during the development of the electrothermal pig-iron industry, still in its infancy.

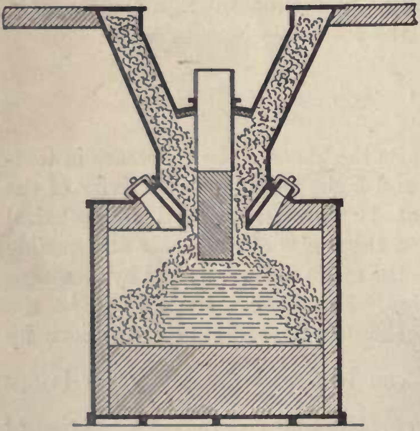

FIG. 47.—Closed Helfenstein Furnace.

It is noticeable that all the furnaces concerned in these developments are of the arc type—far more suitable than those of the resistance type for large commercial units by reason of their ease of regulation, the flexible way in which load and rate of production can be varied, and the possibility of continuous working.

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[1] *Trans. Farad. Soc.* **5**, 254 (*1909*).

[2] See also *Zeitsch. Elektrochem.* **17**, 642 (*1911*).

3. Electrical Aspects of Electric Furnace Design

The Electrodes.—Of electrode materials we need consider only two—carbon and graphite. We have seen[1] that for electrolysis, graphite has very considerable advantages over carbon, owing to its greater chemical resistivity. But in furnace processes the case is somewhat altered. At the high temperatures employed, electrodes of either material usually disintegrate or oxidise comparatively quickly, and their cost is often very important, amounting to even 20 per cent. or more of the total charges. Under these circumstances, though the rate of oxidation of graphite is undoubtedly less than that of carbon, and its electrical conductivity greater, its high price generally renders its use inadmissible, and carbon electrodes are employed. The manufacture of large carbon electrodes for furnace work has been described by Louis.[2] The raw material—anthracite, retort carbon, coal tar—must be as free as possible from ash, including sulphur and phosphorus, in order to avoid subsequent contamination of the furnace product. It is first distilled in closed vessels, and powdered to a grain not exceeding 0·5–1 mm. Then 10–15 per cent. of finely divided dry pitch is added, and the whole thoroughly incorporated at 70°–90°. After compressing into moulds, the mixture is very carefully heated to a temperature not exceeding 1200° for 8–10 hours. A very slow cooling succeeds, without which the electrode is fragile, and liable to break.

The maximum permissible current density is put as 3–4 amps./cm.^{2}, but in practice this is often exceeded, values of 10 amps./cm.^{2} being not uncommon. Of course under these circumstances the electrode becomes exceedingly hot, and oxidises rapidly if air be present. The permissible value really depends somewhat on the cross-section of the electrode, being greater the smaller the latter is. The reason is that the smaller electrodes can be made of a far more regular structure and freer from flaws. It is indeed often advantageous to use a bundle of electrodes of small cross-section instead of one large electrode for carrying heavy currents. With graphite electrodes, a current density of 20 amps./cm.^{2} can be easily maintained.

Heat Losses in Electrodes.—But electrodes, besides their function of conducting the current into the furnace, also act in another way. A certain amount of heat is produced in them by the passage of the current, and some of this will be conducted outside the furnace. Moreover, an electrode, being a good conductor of electricity, is also a good conductor of heat. One end is at the temperature of the interior of the furnace, the other end is usually cooled by water. So the electrode will also conduct heat *from the reaction zone of the furnace* to outside, and thus in two ways will cause heat losses. The sum of these two losses

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[1] P. 152.

[2] *Jour. Four Elect.* **19**, 247 (*1910*).

is known as the **electrode loss**, and, when all the electrodes in a furnace are reckoned, may assume considerable dimensions. In a small furnace, indeed, it may form a large percentage of the total energy consumption.

This subject has been much discussed in America during the last few years[1] and the chief conclusions arrived at are stated below. The minimising of the electrode losses depends essentially on a correct proportioning of the electrodes. This is plain when we see that an increase in *length* of an electrode increases the electrical losses, but decreases the amount of heat conducted out from the interior of the furnace, whilst an increase in its *cross-section* has the opposite effect. Moreover, as a result of their different electrical and heat conductivities, the correct proportions of an electrode for one material will not be the correct proportions for another material. And for the same electrode material, the proportions will depend on the difference of temperature between the two ends of the electrode, and on the current. Suppose the heat produced in an electrode by the current to be I^2R. If we assume that the resistance of the electrode is independent of temperature, that the heat is thus uniformly produced along its length, and that none leaves the electrode along its length but only at the ends (both obviously very approximate assumptions), then this heat will tend to flow out equally at both ends. Imagine also that an amount of furnace heat, Q, enters the hot end of the electrode. Then the net amount of heat entering the hot end of the electrode is $Q - \frac{1}{2}I^2R$, whilst the total amount of heat leaving the cold end—*i.e.* the electrode loss—is $Q + \frac{1}{2}I^2R$. Assuming the furnace temperature to be fixed, the minimum electrode loss will coincide with *no* interchange of heat between furnace and the hot end of the electrode. The condition is therefore that $Q = \frac{1}{2}I^2R$, giving an electrode loss of I^2R. This condition is fulfilled when the temperatures of the furnace and the hot end of the electrode are identical. If not so, the electrode will either convey heat out of the interior of the furnace or else will pour it in, the loss at the cold end being in either case correspondingly greater.

On the above basis Hering has deduced certain simple formulæ, from which the best proportions for electrodes in any given case can be readily calculated. He makes one or two assumptions—either the conductivities entering the calculation are independent of temperature, or they can be represented by certain mean values, in which case the electrode temperature gradient is regarded as uniform. He has succeeded in showing that these arbitrary and obviously only very approximately true assumptions bring no great errors into the final results. Suppose the total electrode loss per second be X, the heat flowing

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[1] See many papers by Hering and by Hansen in *Metall. Chem. Engin.* (*Electrochem. Ind.*) and *Trans. Amer. Electrochem. Soc.* *1909–1911.* Particularly *Electrochem. Ind.* **7,** 442 (*1909*); *Metall. Chem. Engin.* **8,** 276, 471 (*1910*); *Trans. Amer. Electrochem. Soc.* **17,** 171 (*1910*).

into the electrode Q, the heat produced in the electrode by the current W, all values expressed in joules, which allow of simple treatment. Then

$$X = Q + \frac{W}{2}.$$

And $Q = k . \theta . \frac{a}{l}$, where a and l are the section and length[1] of the electrode, either in inches or cm., k the thermal conductivity in joules and the chosen unit of length, and θ the temperature difference between the two ends. Also

$$\frac{W}{2} = \frac{I^2}{2} \cdot r \cdot \frac{l}{a},$$

where r is the specific resistance in ohms per unit cube. We get then

$$X = k \cdot \theta \cdot \frac{a}{l} + \frac{I^2}{2} \cdot r \cdot \frac{l}{a}.$$

This is a minimum when the two right-hand terms are equal, and we have

$$X_{\text{minimum}} = I\sqrt{2rk\theta}.$$

The minimum loss depends on the product of the heat conductivity and electrical resistance of the material, on the current, and on the temperature difference between the ends of the electrodes. Also on the correct proportioning of the electrodes. For the most favourable proportions we have the equation

$$\frac{a}{l} = I\sqrt{\frac{r}{2k\theta}}.$$

It thus appears that as far as the losses are concerned the absolute dimensions of the electrode are of no account—only the *ratio* of cross-section to length, determined in any given case by the current, the temperature difference between the ends of the electrode, and the ratio of electrical resistivity and thermal conductivity of the material.

In designing electrodes one therefore proceeds as follows: From [illegible] number of kilowatts the furnace is to consume the voltage and current relations are calculated, the voltage being made as large and the current as small as other conditions render practicable. In that way the heat generated in the electrode is minimised. Then, knowing the furnace temperature and the values of r and k, the most favourable ratio of $\frac{a}{l}$ is calculated by the last formula. Finally l is made as short as is practicable.

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[1] The *length* is taken as that part of the electrode below the water-jacket.

The application of these formulæ is illustrated by the following two simple examples. The values of rk and $\frac{r}{k}$ are taken from one of Hering's papers, and refer to inch units.

(1) A 300 K.W. furnace takes 60 volts and 5000 amps. Current is led both in and out of the furnace by two paralleled carbon electrodes. What are the best proportions for these, and what are then the electrode losses of the furnace? The temperature difference between the ends of the electrodes is 2000°.

For carbon,
$$rk = (18500 + 1{\cdot}90\theta)10^{-7}$$
$$\frac{r}{k} = 0{\cdot}00080 \text{ above } 1100^\circ$$
For $\theta = 2000^\circ$, rk becomes $22{\cdot}3 \times 10^{-4}$.
As 2500 amps. are carried by each electrode we have
$$\frac{a}{l} = 2500\sqrt{\frac{0{\cdot}0008}{4000}} = 1{\cdot}12.$$

A normal current density in a carbon electrode is 25 amps./inch². The cross-section of each electrode must accordingly be 100 sq. in. Whence we get that the length is $\frac{100}{1{\cdot}12} = 90$ inches. This would probably be inconveniently long. It might, however, be possible to double the current density, in which case the length of the electrode would be reduced to 45 inches. The power loss in each electrode is
$$2500\sqrt{22{\cdot}3 \times 10^{-4} \times 4000} \text{ watts}$$
$$= 7{\cdot}5 \text{ K.W. per electrode}$$
$$= 30 \text{ K.W. for the furnace.}$$
As the load of the latter is 300 K.W. the electrode losses amount to 10 per cent.

(2) A small 40 K.W. furnace works with graphite electrodes at 40 volts and 1000 amps., θ being 1500°. According to Hering, for graphite
$$rk = (12800 - 3{\cdot}56\theta)10^{-7}$$
$$\frac{r}{k} = (5500 + 5{\cdot}86\theta)10^{-8} \text{ above } 800^\circ$$
For $\theta = 1500^\circ$ $rk = 74{\cdot}6 \times 10^{-5}$
$$\frac{r}{k} = 142{\cdot}9 \times 10^{-6}$$
Whence
$$\frac{a}{l} = 1000\sqrt{\frac{142{\cdot}9}{10^6 . 2 . 1500}} = 0{\cdot}22.$$

Working at 100 $\frac{\text{amps.}}{\text{inch}^2}$, the cross-section of the electrode is 10 sq. inches, and its length $\frac{10}{0{\cdot}22} = 45$ inches.

The loss per electrode becomes
$$1000\sqrt{2 . 1500 . 74{\cdot}6 . 10^{-5}} \text{ watts}$$
$$= 1{\cdot}5 \text{ K.W.,}$$
the total loss being 3 K.W. As the furnace load is 40 K.W., the electrode losses amount to 7·5 per cent.

Of course it may easily happen that the best conditions with respect to electrode losses do not coincide with the other conditions for the highest efficiency or convenience of working. For example, a correctly designed carbon electrode always tends to be short and stumpy with furnaces of small capacity. And what is necessary is a maximum efficiency for the furnace as a whole, not for any particular part. For further details on this subject, including experimental determinations and many numerical 'electrode constants,' the reader is referred to the original papers.

The specifically electrical or mechanical features of the electric furnace do not here demand a full treatment. Provided there is no chance of a disturbing electrolysis, alternating or direct current can be indifferently used. In calcium carbide manufacture, for example, the output per unit of energy is the same in the two cases. Whether then alternating or direct[1] current is adopted, and, if alternating current, whether single- or poly-phase, depends on such factors as the size of the furnace in question, the relative costs of generators, transformers, cables, electrodes, etc. It would be impossible to discuss these matters adequately here.

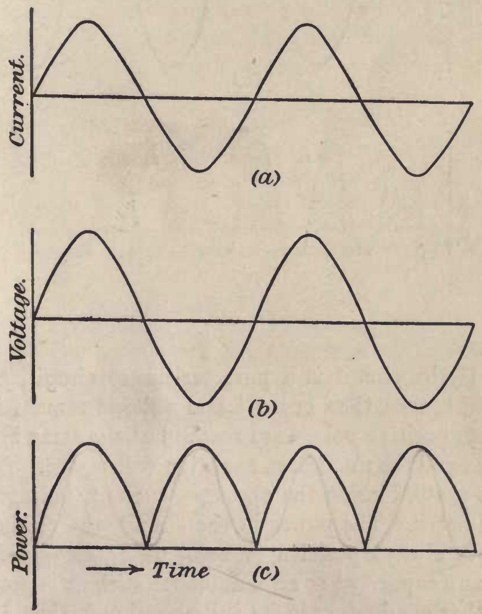

FIG. 48.

Power Factor.—One important point, however, arises when an alternating current is used—that of the *power factor* of the furnace; and as

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[1] The use of direct current in practice is exceedingly rare.

this question frequently appears to present difficulty to chemists we will briefly discuss it. The power in a given circuit at any moment is the product of the instantaneous current and the instantaneous voltage. Using an alternating current, at one instant the current flows in one direction, during the next instant in the opposite direction, whilst the voltage applied to the circuit simultaneously changes in sign and magnitude. If the circuit is a pure resistance circuit, containing no *capacity* or *inductance*, then current and voltage remain in phase—*i.e.* their maximum positive values are reached at the same instant, as also the zero values and the maximum negative values, etc. See Fig. 48, in which time is plotted along the abscissæ, current, voltage, and power along the ordinates. The power in the circuit, the product of voltage and current, is always positive or zero, never negative. But if the circuit contains a capacity[1] or an inductance such as is produced by the presence of other conductors in its neighbourhood, then a *phase difference* arises between voltage and current. Their maxima and minima no longer correspond (Fig. 49*a* and *b*), and consequently the product, at

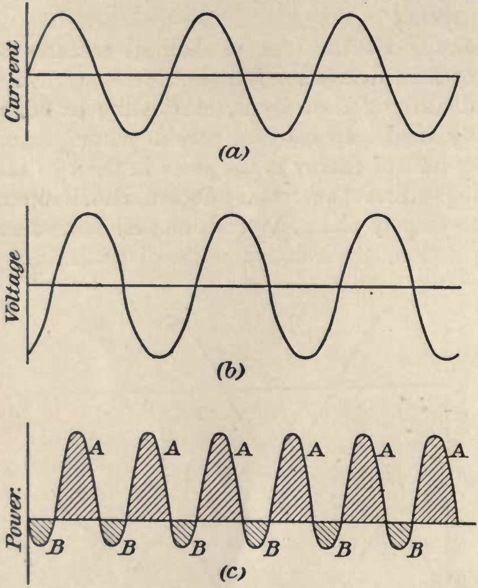

FIG. 49.

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[1] The presence of capacities is important in ozonisers (Chap. XXVIII), but plays no appreciable rôle in electrothermal furnaces. (See, however, footnote on p. 457.) It may be mentioned here that capacities and inductances, though both separately lowering the power factor of a circuit, mutually destroy one another's effect if in the same circuit. Cf. pp. 511, 526.

any instant, of current and voltage is no longer always positive or zero (Fig. 49*c*). There is a *surging of power*. Energy at one instant passes from the generator into the circuit, at the next instant in the opposite direction; and only the *difference* between these two quantities of energy is consumed in the circuit—*i.e.* the sum of areas A minus sum of areas B (Fig. 49*c*). This does not mean that power is lost (it passes back into the generator); it only means that the power consumption is not equal to the product of the voltage and amperage of the circuit, but is less than this, and that a larger generator must be used, and cables and leads must be provided which will carry larger currents than would be necessary if the **power factor**,[1] defined as $\frac{\text{watts in circuit}}{\text{volts in circuit} \times \text{amperes in circuit}}$ were unity.[2] A low power factor means therefore higher costs for electrical appliances. Suppose we wish a circuit to consume 630 K.W. and its power factor is 0·7. The value of the product volts × amps. must be $\frac{1\cdot0}{0\cdot7} \times 630000 = 900000$. Suppose 120 volts to be available, the necessary current will be 7500 amps., whereas with a power factor 1·0, only 5250 amps. would have been needed.

We cannot here fully discuss the phenomena of inductance,[3] and must simply quote some of the more important formulæ and expressions. Instead of having, as in a pure resistance circuit, the relation $E = IR$, we have

$$E = I\sqrt{R^2 + 4\pi^2 n^2 L^2}.$$

Here n is the number of complete cycles or periods the alternating current makes per second, the **periodicity** ($2\pi n$ is termed the **frequency**); L is the **inductance or coefficient of self-induction** of the circuit, a measure of the ease with which an *opposing* E.M.F. is produced when the external alternating voltage is applied, and is essentially a magnetic property. If L is zero, then we have again $E = IR$. At constant voltage, I becomes small if L is very great. Its effect is

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[1] Usually written $\cos\theta$.

[2] As the voltage and amperage of an alternating current circuit are varying from instant to instant, it is obvious that the figures used in this expression must be average values, which give the same mean result over a stretch of time as would the instantaneous figures if suitably summed. They are here in fact the *r.m.s.* (root mean square) values, got by taking the square root of the average value for the square of the alternating current or voltage. This particular mean value is taken because the useful effect produced by an alternating current at any moment is usually measured by the *square of the current or voltage* (*e.g.* in electrical heating I^2R, or $\frac{E^2}{R}$). And these *r.m.s.* values are those read off on alternating current (*e.g.* hot wire) measuring instruments.

[3] See, however, also p. 451.

practically equal to the introduction of a new resistance into the circuit, a resistance however which does not absorb power. The expressions $2\pi n\mathrm{L}$ and $\sqrt{\mathrm{R}^2 + 4\pi^2 n^2 \mathrm{L}^2}$ are termed the *reactance* and *impedance* of the circuit respectively. Further we have

$$\begin{aligned}\cos\theta &= \frac{\text{watts}}{\text{volts} \times \text{amps.}}\\ &= \frac{\mathrm{I}^2\mathrm{R}}{\mathrm{E} \times \mathrm{I}}\\ &= \frac{\mathrm{IR}}{\mathrm{E}}\\ &= \frac{\mathrm{IR}}{\mathrm{I}\sqrt{\mathrm{R}^2 + 4\pi^2 n^2 \mathrm{L}^2}}\\ &= \frac{\mathrm{R}}{\sqrt{\mathrm{R}^2 + 4\pi^2 n^2 \mathrm{L}^2}}.\end{aligned}$$

We see that *the power factor is greater the higher the resistance of the circuit, the lower the self-inductance, and the smaller the frequency of the alternating flux.*

In designing and installing technical furnaces, inductance effects must naturally be avoided. There should be no large masses of metal in the neighbourhood, as these cause actual power losses, not merely a lowering of cos θ; and the nature of the leads and the way they are connected to the furnace should be carefully thought out.[1] The power factors of technical furnaces vary between 0·5–0·95.

Literature.

Stansfield. *The Electric Furnace.*

Rodenhauser and Schoenawa. *Elektrische Öfen in der Eisenindustrie.*

Borchers. *Electric Furnaces.*

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[1] For further on this point and on other details of furnace construction, see Conrad, *Electrochem. Ind.* **6**, 397 (*1908*).

CHAPTER XIV

ELECTRICAL DISCHARGES IN GASES

1. Gas Ions

By suitably varying the conditions under which electricity discharges through air, either ozone or nitric oxide can result. Both reactions are important technically, and in this chapter we shall discuss generally the different types of electrical discharge in air, their production, and associated phenomena.

The conduction of electricity through gases is now universally regarded as due to the presence of *charged gaseous ions*, a theory propounded by Sir J. J. Thomson. Even in the normal state every gas contains a very small number of these ions, which may be either positively or negatively charged. A positive gas ion is a positively charged atom, usually associated with one or more neutral gas molecules. Negative ions can similarly consist of negatively charged atoms associated with neutral molecules.

But they can also, on the other hand, be subatomic in nature, and identical with those discrete particles of negative electricity out of which we presume atoms of 'matter' to be constituted. These subatomic negative particles are called **electrons.** Owing then to the presence of these ions, a gas has a very slight electrical conductivity even in the normal condition, and if a potential difference be maintained between two insulated metal plates set up in air, a small current will traverse the intervening air space. Suppose now that the voltage difference between these plates be raised. The greater it becomes, the steeper the potential gradient along the path which the ions take, and consequently the more rapid the rate at which they are urged along. Collisions between ions and neutral molecules are constantly occurring, and with a sufficiently high potential gradient, the velocity of the ions, and hence their kinetic energy, may increase to such an extent that, by their collision with the neutral particles, the latter are split up themselves into two or more ions, which at once begin to conduct. When this happens the current will rise rapidly, the temperature also, This process of *ionisation by impact* is accompanied by luminescence of the gas.

As the voltage difference between the two electrodes is steadily raised, the potential gradient necessary for ionisation by collision is not reached simultaneously in all parts of the path. Consequently, ionisation and luminescence do not commence in all parts of the gap between the electrodes at once, but perhaps at first in one region only, with a correspondingly smaller increase in current. This first change will be followed by subsequent ones. The current voltage relations in a gaseous electrical discharge are in fact very complex, as the following curves show. These *characteristic curves* are obtained by plotting voltage against a steadily increasing current. The simplest cases are those where direct current is used and the influence of one electrode eliminated. This can be effected by allowing the discharge to pass from a small pointed electrode to a large earthed plate.[1] The phenomena observed are essentially due to the charged point, and vary somewhat with its sign. If it be positively charged, we obtain a discontinuous[2] curve as in Fig. 50; if negatively charged, as in Fig. 51.

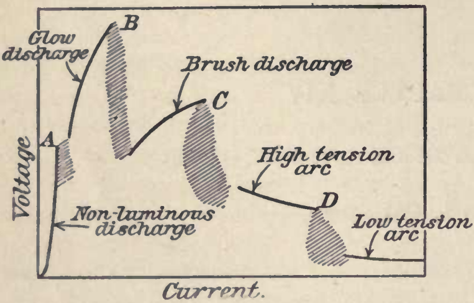

FIG. 50.

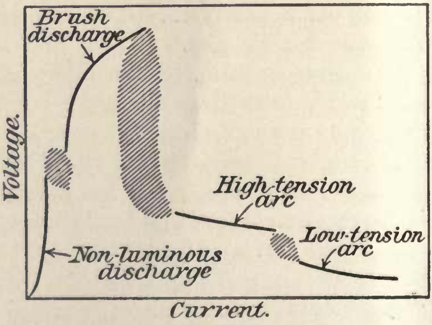

FIG. 51.

Suppose the current passing through air from a positively charged point to earth be gradually increased. The voltage will first rise very rapidly to A. At this point there will be a slight discontinuity, the voltage will rise rather less rapidly, and the discharge will become luminous. At B the voltage gradient is great enough to cause considerable impact ionisation. The conductivity very rapidly rises, the voltage falls, and a new type of

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[1] Toepler, *Drud. Ann.* 7, 477 (1902).

[2] Shaded parts denote discontinuity of discharge.

discharge, the *brush discharge*, sets in, the current being greater and the gas more luminous than in the previous *glow discharge.* This transition is accompanied by sparking. At C there is more discontinuity, and the character of the discharge alters radically. It has now become a *high-tension arc*, the whole of the current path is strongly luminous, the ratio $\frac{\text{current}}{\text{voltage}}$ is much higher than before, and the characteristic has become *negative*, the voltage *decreasing* whilst the current increases. This means that owing to very powerful impact ionisation, caused by the large number of charged particles present, the resistance of the gap *decreases* more quickly than the current *increases*, and hence an increase of current is accompanied by a decrease of voltage. As the current becomes greater and the temperature rises, even this form of discharge becomes unstable. Charged particles and vapours are given out by the hot electrodes, there is another discontinuity, and the final form of discharge, the *low-tension arc*, is reached. The characteristic is here again negative at first.

The results obtained with a *negatively* charged point are similar. High voltages are involved. The points A and B correspond to thousands or tens of thousands of volts for a discharge distance measured in centimetres; whilst the currents are small, only amounting to a few amperes even in the low-tension arcs. If now, instead of one point and one plate electrode, we consider two similar electrodes—*e.g.* rods—we get a curve[1] such as in Fig. 52. This is merely drawn diagrammatically, as the influence of the various experimental conditions—nature and size of electrodes, nature of gas, length of discharge, etc.—is enormous. An alternating discharge gives a similar characteristic.[2]

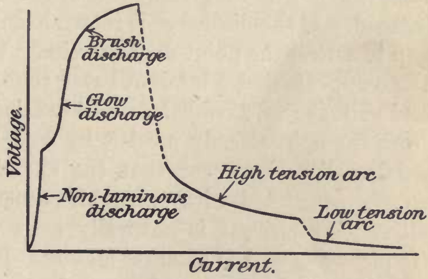

FIG. 52.

2. Different Types of Discharge

We will now consider the different types of discharge in more detail. The non-luminous discharge need not detain us. Very small currents pass and it produces no chemical effects. At a certain voltage, depending on the pressure, electrode distance, etc., there is discontinuity, and the discharge becomes luminous.

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[1] Brion, *Zeitsch. Elektrochem.* **14**, 245 (*1908*).

[2] Cramp and Hoyle, *Electrochem. Ind.* **7**, 74 (*1909*).

Silent Discharge.—The appearance and exact nature of this luminous discharge varies considerably. It depends on whether the discharge is a direct-current point discharge (and, if so, on its sign) or whether it is an alternating current discharge. It depends on the current and on the shape of the electrodes. For our purpose we can group together all these different kinds of discharge (glow, brush, strip) by the facts that their characteristic is almost always positive, the voltage increasing with increasing current, and that the ratio $\frac{\text{voltage}}{\text{current}}$ is always high. When passing through air they generate ozone, and the commonly used generic term, '*silent discharge,*' is often applied to them (frequently a misnomer). Electrically considered they are stable.[1] The truth of this statement is readily seen. As an increase of current necessitates increased voltage, such a change cannot commence spontaneously if the voltage is kept constant.

When luminous discharge begins from a positively charged point, there appears first a thin reddish glowing layer on the electrode. With increasing current, small 'twigs' of light appear, and finally a strongly luminous brush discharge. If continuously used, the point gradually loses its power of giving this brush discharge, and sparking occurs instead. If the discharge is intermittent (thus, if there is a tiny spark-gap in series) the point does not tire. With a negatively charged point there appears first a luminous star round the electrode, and as current and voltage rise, a reddish conical brush (the positive column), separated from the light already present by a dark space, starts out towards the anode. We shall see[2] that the chemical action of the discharge is closely connected with these phenomena. The appearance with an alternating current is naturally more complex, and depends on the frequency as well as on other factors. In all cases the voltage necessary at ordinary gas pressures for any given effect increases with the diameter of the electrodes, their distance apart, and the pressure.

High-tension Arc.—The next form of discharge is the high-tension arc. This is the name it now generally receives, and refers more particularly to heavy current discharges. Produced on a small scale, in a gas at low pressure, it is the well-known *glow current* (with its Faraday dark space, positive column, etc.). It is this discharge which is the most active in producing nitric oxide when burning in air, and is essentially the one used in the various successful technical processes. We have seen that it results in a steady increase of the current in an ordinary brush discharge. At a certain point, depending on conditions, the brush discharge breaks down, sparking occurs, and the high-tension arc begins to pass. The first noticeable point about this arc is its

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[1] Except at their extreme upper limits, where both voltage and current (comparatively) are high.

[2] P. 523.

negative characteristic; that is, as the current allowed through increases, the voltage falls. The reason is that the increased current means an increased temperature and a greater velocity of the particles in the arc. Further, the hot electrodes (with direct current the cathodes) begin to emit electrons in large numbers. The rate of production of ions by impact consequently increases, and hence the resistance falls. It, moreover, falls more quickly than the current increases, and therefore the product IR = E, where R is the apparent resistance, decreases as I increases.

Suppose now the arc to be fed by a source of constant voltage. If any small increase of current occurs the arc voltage drops, and, the external voltage remaining constant, a still larger current passes. The tendency is therefore for the current flowing to increase enormously; that is, the discharge becomes unstable, sparking takes place, and a final form of discharge, the *low-tension or lighting arc*, begins to pass. If, on the contrary, a slight decrease in current occurs, the temperature will fall and the resistance rise, and, as there is no reserve of voltage on which to draw, the current will decrease indefinitely, and the arc will go out. To render the arc stable, means must therefore be adopted to lower the voltage across it simultaneously with any increase in current, and *vice versa*. This is effected by placing in series a resistance (with direct current) or an inductance (with alternating current) of high value. An increased current then automatically increases the voltage drop across the resistance or inductance, and therefore decreases the same across the arc. A decreased current increases the voltage available for the arc. A slight alteration in current produces therefore a corresponding alteration in voltage.

The greater the resistance or impedance, the more powerfully will any change of current be checked, and the more stable the arc will be. The series resistance used with direct current means of course considerable consumption of electrical energy outside the arc. With an alternating current an impedance of very low resistance may be used, and the losses thus minimised. Using such an impedance it is occasionally possible with high-tension alternating current arcs to increase the current so much that the characteristic changes sign and becomes positive. An increase in current is then accompanied by an increase in voltage.

Another difference between direct and alternating current arcs is the fact that, although a very high initial voltage is necessary to *start* a direct-current arc at atmospheric pressure, when once it has passed, assuming it stable, a much lower voltage suffices to keep it discharging. The current in an alternating arc, on the contrary, sinks to zero every half-period, the temperature falls, the ionisation decreases, the resistance rises, and consequently a higher voltage is needed to restart the arc as the current again increases. An alternating-current arc requires therefore a higher external voltage than does a direct-current arc, and this must be controlled by powerful choking coils.[1] If the electrodes do not cool overmuch at the end of each half-period, this excess voltage may be largely avoided. A third point to be reckoned with in alternating-current arcs is the power factor. In most technical arc circuits this is low, 0·6–0·8, chiefly because of the big series inductances used.

In appearance the high-tension arc, if burning quietly, consists of a glowing column of gas—the *positive column*—practically joining the two electrodes. In technical arcs, which are subjected to various deforming influences, the appearance presented is sometimes very different. The effect of pressure changes is similar to that in the case of the brush discharge. For pressures greater than a small fraction of an atmosphere, the voltage necessary for the arc to strike and play increases with the pressure. An increase in the length of the arc causes both an increase in the voltage necessary for a constant current, and also in the current furnished by a given voltage. The following approximate formula, which takes no account of the nature of the electrodes, holds [2]:

$$\mathrm{E} = a + \frac{b \, . \, l}{\sqrt{\mathrm{I}}},$$

where a and b are constants, and for air at atmospheric pressure are about 350 and 100–150 respectively. Thus, if the arc is 200 cm. long, and the current 100 amps.,

$$\begin{aligned}\mathrm{E} &= 350 + \frac{125 \times 200}{10} \\ &= 2850 \text{ volts.}\end{aligned}$$

It will be noticed that a is the minimum voltage necessary for the striking of a high-tension arc. The voltage drop across such a direct-current arc, consisting of a uniform column of glowing gas, is composed of three parts—the cathode and anode falls, and the voltage drop along the positive column. The structure of this column being uniform, so is also the potential gradient along it. In the example given it is $12{\cdot}5 \ \frac{\text{volts}}{\text{cm.}}$.

Fig. 53 represents diagrammatically for the same case the distribution of voltage along the length of the arc. The minimum value necessary for the arc to strike is given by the sum of the anode and cathode falls. Here, where two metal electrodes are assumed, the cathode is responsible for about 300, and the anode for 50, of the 350 volts. By using a hot cathode, covered with some

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[1] A choking coil is an impedance of high inductance and low resistance.

[2] Brion, *Zeitsch. Elektrochem.* **14**, 245 (*1908*).

metallic oxide (*e.g.* lime), the cathode fall can be very considerably reduced, owing to the large number of electrons such a cathode emits. The temperature of the high-tension arc varies in different parts, and also depends on the current and voltage relations. Using alternating current, it varies also with the time. It will be higher at the electrodes, owing to the bigger potential gradients. In the positive column it may perhaps be taken as 2200°–2500° C.

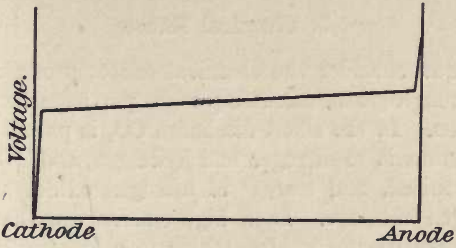

FIG. 53.

Low-tension Arc.—The low-tension arc discharge, the kind used in steel and carbide furnaces, etc., needs brief treatment only. It results from the breakdown of the high-tension arc when the latter is driven with too great a current. Its characteristic is first negative, then, with increasing current, positive. The equation connecting current, voltage, and length of arc differs slightly in form from that given for high-tension arcs. a is here only about 30 volts, and is chiefly due to the anode fall; b is also much smaller than with high-tension arcs.

The reasons why these low-tension arcs are not used for technical nitric oxide syntheses are that the *potential gradient* along the positive column is much lower than in high-tension arcs[1] and that the *temperature* is too high.[2] When metals and many metallic oxides are made incandescent, they shoot out large quantities of electrons. Further, certain metals at lower temperatures can give off positively charged particles, of sizes comparable to that of an ordinary chemical atom. The breakdown of the high-tension to the low-tension arc is really caused by the temperature of the electrode rising high enough for these processes to set in strongly. Electrons are shot off from the cathode, and positively charged ions from the anode. The impact of these particles on the gas molecules increases the ionisation enormously. The conductivity rapidly rises, the character of the discharge changes, and the temperature increases very considerably. In fact, a low-tension arc passes through an atmosphere very largely consisting of the vapours of the electrode material. It is chiefly the electrons discharged from the cathode which bring about the rapidly increasing

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[1] See pp. 191, 509.

[2] See pp. 192, 510.

ionisation in the gas. If the cathode has no spot sufficiently hot to emit these electrons in quantity, the low-voltage arc will not pass. The temperature of this arc varies essentially with the conditions. With carbon electrodes it is about 3500° C.

3. Chemical Effects

We must now consider the chemical effects produced by electrical discharges through gases, discussing more particularly the mechanism of the reactions. In the silent discharge CO_2 is partly decomposed to CO and O_2, ammonia to nitrogen and hydrogen, and HCl to H_2 and Cl_2. Oxygen is ozonised, and traces[1] of nitrogen oxides are formed in a nitrogen-oxygen mixture. In a high-tension arc the same mixture gives larger quantities of oxides, whilst in a low-voltage arc the proportion of nitrogen oxides again decreases. All these reactions, and others, result from two superimposed effects, varying greatly in different cases according to the conditions—the electrical and the thermal effects of the discharge.

Electrical Effect.—Consider first the electrical effect. We have seen that the power of gases to conduct electricity depends on the presence of free ions or charged particles, which traverse the path of the discharge between the electrodes. Only when a discharge passes are these ions numerous. If the current ceases they quickly disappear, oppositely charged ions neutralising one another, reforming neutral gas molecules. We must assume that this recombination of oppositely charged particles is continually proceeding whilst the current is passing. In an electrical discharge, indeed, a dynamic ionic equilibrium exists. In a given time interval, the sum of the ions formed by impact and those coming from the electrodes must be equal to those lost by recombination *plus* those giving up their charges to the electrodes. Now, in a gas containing several different kinds of gas ions, the products formed during the neutralisation may differ considerably from the original neutral molecules. Suppose an oxygen molecule ionised by impact into a negative electron and a positively charged oxygen molecule, and another oxygen molecule resolved into two oppositely charged oxygen atoms. Then, if positively charged oxygen molecule and negatively charged oxygen atom come into contact, combination may occur, resulting in a neutral ozone molecule. Similarly, if oppositely charged oxygen and nitrogen atoms come together, neutralisation may take place, giving a neutral molecule of nitric oxide.

In this way we can account for those chemical effects noticed in electrical discharges in gases which are specifically due to electrical action. Such chemical action will only occur to any extent when

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[1] Under suitable conditions, far larger quantities of nitrogen oxides are formed.

N^+ or active nitrogen is formed [illegible] passed through N_2 containing some electro- [illegible] impurity

there is a lively impact ionisation. For this not only the presence of ions is necessary, but also ions moving with a sufficient velocity. And this is only attainable when using a discharge of steep potential gradient.

Electrical Equilibria.—The new products thus formed by electrical discharge are subject to ionisation and decomposition by ionic impact just like the original molecules. At first more molecules will be formed in a given time than will be decomposed, but finally these quantities will become equal, and the composition of the gas will assume a definite value, corresponding to a definite **electrical equilibrium.** By this term is denoted a state stable only during the passage of an electrical discharge, and depending on the nature of this discharge. When the discharge is interrupted, the concentrations of the gaseous components correspond to a state unstable with respect to the state defined by the ordinary thermal equilibrium constant. The composition of the gas will hence tend to change. Whether it can do so with appreciable velocity depends on another factor which we shall presently discuss.

The general qualitative relation existing between electrical and thermal equilibria is simple. When an electrical discharge passes through a gas which is in thermal equilibrium, the new electrical equilibrium resulting corresponds to a thermal equilibrium at a *higher temperature*—*i.e.* to a shift from the thermal equilibrium in the *endothermic* sense. Thus the amount of ozone in thermal equilibrium with oxygen at room temperature is infinitesimal. At 1300° C. it is 0·1 per cent., at 2000° 1 per cent., and at 4500° perhaps 10 per cent. But by means of a silent discharge, oxygen can be 10 per cent. ozonised at room temperature. Similarly the quantities of CO and O_2 in thermal equilibrium with CO_2 at room temperature are very small, as are also the quantities of nitrogen and hydrogen in equilibrium with ammonia. But when a silent discharge passes through the respective gases, decomposition products in electrical equilibrium are formed to an extent corresponding to considerably higher temperatures.

Finally, we may take the equilibrium between N_2, O_2, and NO. The reaction $N_2 + O_2 \longrightarrow 2NO$ is endothermic. NO exists in considerable quantities in thermal equilibrium with N_2 and O_2 only at very high temperatures. At room temperature the equilibrium concentration of NO is exceedingly low. If a silent discharge be passed through air, some NO results, which, though small in amount, corresponds to a thermal equilibrium of a higher temperature. Complications are present, due to the ozone simultaneously produced forming higher oxides of nitrogen. But at 2000° C., in a high-tension arc, where such complications are impossible, NO can be produced in amounts which would not be in thermal equilibrium below 4500°–5000° C.

Thermal Effects.—But, besides the electrical effect of the discharge, we must consider its thermal effect. The electrical equilibrium only persists whilst the discharge is actually passing. When it ceases the system tends to lapse into thermal equilibrium, and reaches this state the more quickly it can react—*i.e.* the higher the temperature. Thus, highly ozonised air or oxygen is apparently stable at room temperatures simply because the rate of decomposition of ozone under such conditions is very slow. But no ozone results from a high-tension arc in oxygen or air because it decomposes rapidly already at moderate temperatures. On the other hand, the rate of decomposition of NO (experimentally determined) is much lower than that of ozone. Hence NO can be produced in concentrations corresponding to electrical equilibria by using forms of electric discharge of comparatively high temperature, followed by sufficiently rapid cooling to freeze the equilibrium when the gases have been removed from the influence of the electric discharge. A gas is thus obtained containing several per cents. of NO or its further reaction products (NO_2, N_2O_4, etc.), a quantity far in excess of that corresponding to the thermal equilibrium either at room temperature or at the temperature of the arc. The higher the temperature of the discharge, the more rapidly the thermal equilibrium will be reached in the arc itself, and the nearer will electrical and thermal equilibria approach one another. The greater, too, will be the change in concentration whilst cooling.

It is obvious that the gaseous product obtained by means of an electrical discharge is determined by several complicated factors. In the particular case of nitric oxide, the important rôle of electrical influences has only been recently recognised. It had previously been thought that thermal effects *only* came into play. The contrary view was first suggested by Warburg,[1] and shown experimentally to be correct by Haber and Koenig.[2]

One last point should be mentioned. Can the mass-action law be applied to electrical as to thermal equilibria ? The answer is uncertain, but is very probably *no*. In cases where the difference between electrical and thermal equilibrium is not great, and where the temperature is high, the law apparently holds. But in other cases that is not so. Nor can we expect it otherwise when we consider the complexity of the phenomena involved. The conditions in a high-tension arc are favourable, and Le Blanc and Nüranen and Grau and F. Russ have accordingly found the mass-action law to be applicable to the nitric oxide synthesis under most conditions. But in the silent discharge, the electrical, and hence other, conditions are obviously complex and varied, and Le Blanc and Davies consequently found that the $NH_3 - N_2 - H_2$ equilibrium was not governed by the mass-action equation.

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[1] *Zeitsch. Elektrochem.* 12, 540 (*1906*).

[2] See pp. 507–510.

PART II

SPECIAL AND TECHNICAL

CHAPTER XV

PRIMARY CELLS

1. General Considerations

APPLIED electrochemistry is chiefly concerned with the production of substances by means of the electric current, and the inverse operation, the conversion of chemical into electrical energy, is much less important. If it were possible to liberate the chemical energy obtainable from the combustion of fuels as electrical energy[1] this statement would be incorrect. But, as matters stand, the use of primary cells[2] is practically restricted to the intermittent production of small amounts of electrical energy, under conditions in which the installation of a generator or the taking of energy from a distributing system would be impossible or disproportionately expensive. Thus primary cells are largely used for electrotherapeutic purposes, electric bells, small private telephone systems, motor ignition, etc. The more efficient forms can be employed for small lighting installations in remote buildings, and for driving small motors and lathes. But the high cost renders the production of electricity in bulk from primary cells impracticable.

For an element of high E.M.F. we must combine two electrode systems, one with a high positive or oxidising potential, the other with a strongly negative or reducing potential. The E.M.F. of the resulting primary cell is then *potential positive-electrode* minus *potential negative-electrode.* From the table on p. 96 we see that if it were possible, for example, to combine a sodium electrode in a n. $Na^{\cdot}$ solution with a gold electrode in a normal $Au^{\cdot}$ solution, an E.M.F. of 4·2 volts would result; while a cell consisting of copper in a normal $Cu^{\cdot\cdot}$ solution and a chlorine electrode in a n. Cl' solution would have an E.M.F. of 1·023 volts (in both cases neglecting the liquid potential difference). Further, by decreasing the ionic concentration in the electrolyte the potential becomes more positive if the ion concerned is negative and more negative if the ion is a positive one. This furnishes a means of

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[1] P. 209.

[2] P. 3.

still further increasing the E.M.F. of a cell. Thus zinc in $\frac{n}{10}$ K_2ZnCy_4 solution, in which the $Zn^{\cdot\cdot}$ concentration is very low, has a potential of $-$ 1·033 volts, and, combined with copper in n. $CuSO_4$ solution, will give an E.M.F. of 1·35 volts, 0·25 volt higher than that of the ordinary Daniell cell.

Equally important for primary cells are the potentials of oxidation-reduction electrodes,[1] some of which are here collected.

TABLE XXX

Combination.	Electrode potential against indifferent electrode.
0·2 n. potassium stannite	$-$ 0·58 volt.
CuO in n. NaOH	$-$ 0·1
MnO_2 in 0·1 n. KOH	+ 0·42
Ni_2O_3 in 2·8 n. KOH	+ 0·48
6 per cent. HNO_3	+ 0·92
n. KClO	+ 0·94
n. KBrO	+ 1·08
35 per cent. HNO_3	+ 1·09
66 per cent. HNO_3	+ 1·12
n. CrO_3 in H_2SO_4	+ 1·20
95 per cent. HNO_3	+ 1·22
n. $HClO_3$	+ 1·38
MnO_2 in 0·5 n. H_2SO_4 + 0·05 n. $MnSO_4$	+ 1·46
n. $KMnO_4$	+ 1·52
n. $Ce(SO_4)_2$ in H_2SO_4	+ 1·55
PbO_2 in n. H_2SO_4	+ 1·595

All but two of these combinations give positive potentials, and the majority are known chemically as oxidising agents. The fact is that the reducing potentials given even by the most powerful reducing agents seldom approach the negative potential values for such metals as zinc, and, apart from the questions of relative cheapness, convenience of use, or atmospheric oxidation, they are consequently never used as the anode system in primary cells. With oxidising agents it is different, as we shall see. At present we may notice that the combination Zn | n. $Zn^{\cdot\cdot}$ solution | n. H_2SO_4 | PbO_2 would give an E.M.F. of 2·36 volts; the combination Fe | n. $Fe^{\cdot\cdot}$ solution | n. $KMnO_4$ | Pt 1·98 volts, etc., etc.

Irreversible Effects.—All these values assume the given combinations to work reversibly. This is very desirable, for otherwise the full amount of the available free energy of the chemical reaction which takes place in the cell is not obtained as electrical energy, but some is turned into heat, and thus lost. We already know that a cell or an electrode *never* behaves absolutely reversibly, and that often the degree of irreversibility is considerable. We have further (Chap. X)

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[1] P. 100.

discussed in detail in what ways irreversibility can enter into anodic and cathodic processes. In primary cells we must consider both these possibilities, and also concentration changes in the electrolyte. As anode, a soluble metal is invariably used in practice. Oxygen evolution never occurs, and the only irreversible effect to fear is passivity. It is therefore important that metal and electrolyte be so chosen that, under working conditions, the former does not appreciably become passive.

Cathodic Depolarisers.—At the cathode the matter is more complex. In some cases the cathodic process is the discharge of a metallion to metal. We know that such changes usually take place very nearly reversibly, though there are exceptions.[1] But more often the cathode system is an oxidation-reduction electrode, consisting of an oxidising agent in contact with an indifferent electrode, and serving to depolarise the discharge of $H^{\cdot}$ ions.[2] Suppose for the moment the primary cell to be Zn | n. $Zn^{\cdot\cdot}$ solution | n. $H^{\cdot}$ solution | indifferent metal. Then zinc would tend to dissolve and $H^{\cdot}$ ions to be discharged, and the reversible E.M.F. would be 0·77 volt (neglecting liquid potential difference). But in general, though the zinc enters solution almost reversibly, a considerable overvoltage[3] is needed for $H^{\cdot}$ discharge, and this figure must be subtracted from 0·77 to get the working voltage of the cell. Thus, if a copper cathode be used, at which the current density is 0·01 amp./cm.^{2}, then the overvoltage will amount to about 0·35 volt, and the E.M.F. of the resulting cell is only 0·42 volt.

But the result is different with a *depolariser*. It increases the E.M.F. of the cell above the value corresponding to reversible cathodic $H^{\cdot}$ discharge, and it effects this by reacting so quickly with the discharged hydrogen that the electrode never becomes saturated with the gas. The latter does not therefore exert its normal electrolytic solution pressure, and $H^{\cdot}$ discharge takes place at a correspondingly less negative cathode potential. It is essential for the efficiency of a depolariser that its interaction with hydrogen should be rapid.[4] The more rapid it is, the lower is the hydrogen concentration in the electrode, the more positive becomes the cathode potential and the more closely it approaches the equilibrium value (such as those given on p. 196).

As the table indicates, both solid and liquid depolarisers come into question. Generally speaking, liquids depolarise more quickly than solids, and hence give working potential values more nearly approaching the reversible figures. On the other hand, their power of diffusion towards the anode, which in most cases they strongly attack, usually renders it necessary to employ some kind of diaphragm between catholyte and anolyte. This increases the resistance of the cell, and complicates its construction. A satisfactory solid depolariser, besides

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[1] P. 120. [2] P. 128. [3] P. 118. [4] P. 128.

reacting rapidly with the discharged hydrogen, should have a high electrical conductivity, and be in good contact with the metallic part of the electrode. Where the conductivity is too low, it may be necessary to mix with it finely divided graphite or some indifferent metal. Whilst having such a mechanical structure that it does not crumble or flake away, it should nevertheless be so porous that the under layers can take part in the depolarisation without difficulty, and the reaction with hydrogen should not produce crusts or in any way tend to choke up these pores.

The polarisation resulting from *concentration changes* is less important. Round the dissolving electrode there will be an increased concentration of metallion, and at the cathode, assuming a liquid depolariser, there may be complicated concentration changes. With a solid depolariser, the only change usually noted is that the electrolyte becomes less acid or more alkaline, the magnitude of this effect depending on the porosity of the solid. But, except at high current densities, the effect of these changes on the E.M.F. is generally small, and they are largely neutralised by diffusion. In cells of the Daniell type, with two nearly reversible electrodes, concentration changes are, however, responsible for the greater part of the small polarisation. One further cause lowers the working voltage of a cell, viz. the *internal resistance.* This must be as low as possible. Diaphragms should be avoided (a consideration in favour of solid depolarisers), the electrodes should be as close together as possible, and the electrolyte of high conductivity.

Deterioration.—But galvanic cells, besides behaving satisfactorily when working, must do so when standing idle. They must not deteriorate owing to chemical changes in electrolyte or at the electrodes. Such changes can be of several kinds. The soluble anode may itself tend to dissolve spontaneously in the electrolyte, not doing so because of the high overvoltage needed for H_2 discharge at its surface. If now the electrolyte contains a dissolved trace of a more electronegative or noble metal, this metal will be chemically replaced from solution and deposited on the electrode. If the hydrogen overvoltage is sufficiently less at this second metal than it is at the electrode metal, the latter may commence to dissolve owing to the formation of a small local element—anode metal | electrolyte | electronegative metal. The anode metal dissolves, and hydrogen is evolved at the electronegative metal.[1] To avoid this, the electrolyte must therefore be free from traces of such salts. In the particular case of zinc anodes, any such action is further avoided by amalgamating the electrode with mercury, which tends to dissolve any trace of foreign metal deposited. At the smooth mercury or amalgam surface hydrogen overvoltage is very high.

We have already noticed the disadvantage of a liquid cathodic

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[1] Pp. 201, 227.

depolariser owing to its tendency to attack the anode chemically when the cell is standing. This is sometimes avoided by lifting the anode out of the electrolyte during idle periods. Atmospheric influences can also cause deterioration. The oxygen may attack the soluble anode if the electrolyte is suitable; and with alkaline solutions the cell should be protected against the action of CO_2.

Then comes the all-important question of price of materials. Many excellent depolarisers cannot be used on account of their high cost. Such depolarisers as can be regenerated after cathodic reduction by means of atmospheric oxygen are naturally very advantageous. CuO, which is much used, is thus regenerated. Ceric, titanic, and vanadic sulphates, which however must be used in the liquid form, would be excellent from this point of view. Other points to be weighed are simplicity and durability of construction and ease of working. Diaphragms should be as far as possible avoided, and refilling and recharging rendered easy.

Owing to one or more of the above considerations, a number of electrode systems, which, judging from their reversible potentials, appear very suitable for building up primary cells, are never used for that purpose. The alkali metals cannot, of course, be used as soluble anodes because of their chemical reactivity. Magnesium is also very reactive under certain conditions and is expensive; aluminium is sometimes strongly reactive chemically and sometimes electrochemically passive, and the same is true of iron; cadmium and chromium are too expensive, and the latter becomes easily passive. Of depolarising systems, PbO_2 in H_2SO_4 is too expensive, as it is not readily regenerated chemically; NaClO, NaBrO and $KMnO_4$ solutions do not depolarise quickly; and solutions of $HBrO_3$ and $HClO_3$ suffer from both disadvantages. In practice zinc is invariably the soluble anode. The anolyte can consist of a solution of $ZnSO_4$, $MgSO_4$, $ZnCl_2$, NH_4Cl, H_2SO_4, CrO_3 in H_2SO_4, or NaOH. As cathode systems we have copper in $CuSO_4$ (Ag in $AgNO_3$ would be expensive and inconvenient for other reasons) and carbon, whilst chromic and nitric acids are used as liquid, and MnO_2 and CuO as solid depolarisers.

2. Primary Cells in General Use

We will now consider the different primary cells still in general use; they are:—

(*a*) Daniell cells.
(*b*) Grove-Bunsen nitric acid cells.
(*c*) Poggendorff bichromate cells.
(*d*) Lalande cells. (Cupron cell: Neotherm or Wedekind cell.)
(*e*) Leclanché cells.
(*f*) Dry cells.

Daniell Cell.—We have several times already met with this well-known cell. We have seen that it consists of a zinc rod in zinc sulphate coupled with a copper rod in copper sulphate. The chemical reaction which takes place when it gives current is

$$Zn + CuSO_4 \longrightarrow Cu + ZnSO_4.$$

The salts must be regarded as reacting in the dissolved state if the cell electrolytes are unsaturated, in the solid state when using saturated solutions. We have further seen [1] that the voltage is given approximately by the formula

$$E = 1{\cdot}1 + 0{\cdot}029 \log \frac{[Cu^{\cdot\cdot}]}{[Zn^{\cdot\cdot}]} \text{ volts,}$$

where $\frac{[Cu^{\cdot\cdot}]}{[Zn^{\cdot\cdot}]}$ is the ratio of the molar $Cu^{\cdot\cdot}$ concentration in the catholyte to the molar $Zn^{\cdot\cdot}$ concentration in the anolyte. If the concentrations of zinc and copper sulphates do not widely differ, the ratio $\frac{[Cu^{\cdot\cdot}]}{[Zn^{\cdot\cdot}]}$ can be replaced by $\frac{[CuSO_4]}{[ZnSO_4]}$, as the degrees of dissociation of the two salts are very similar under similar conditions. We know also [2] that the electrical energy liberated by the cell when working is almost equal to the change in total energy which takes place, and that consequently the E.M.F. is nearly independent of temperature. The actual sign of its temperature coefficient (like the E.M.F. itself) depends on the concentrations of the electrolytes, becoming more positive with increase of the ratio $\frac{[Cu^{\cdot\cdot}]}{[Zn^{\cdot\cdot}]}$.

In its original form the Daniell cell consists of an outer glass vessel in which a porous pot stands. The outer vessel contains the copper sulphate solution, which is usually kept saturated (the E.M.F. is thereby kept up); the inner porous pot contains the $ZnSO_4$ solution. A cylindrical rod serves as zinc electrode, and a cylindrically bent piece of copper foil surrounding the porous pot as copper electrode, though thin sheet lead on which a layer of copper has been deposited is also used. If the porous pot be properly chosen the resistance of the cell will be low. The E.M.F. is also very constant, showing only a slight decrease owing to the accumulation of zinc ions. But in most forms the maximum current is very small, not exceeding 0·2 ampere. The great drawback of the Daniell cell, however, is the severe chemical corrosion of the zinc. The diffusion of $CuSO_4$ through the wall of the porous cell cannot be avoided except during continuous working (when the cationic migration away from the anode chamber overcomes this

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[1] P. 99.

[2] P. 82. For a more detailed consideration of the thermodynamics of this cell see Cohen, Chattaway and Tombrock, *Zeitsch. Phys. Chem.* **60**, 706 (*1907*).

tendency). This means chemical replacement of a certain amount of zinc and destruction of far larger quantities owing to local action started by the deposited copper. Hydrogen overvoltage at this metal is much less than at zinc, and dissolved oxygen also plays a part in the corrosion. According to Haber,[1] even under favourable conditions only 30 per cent. of the zinc is electrochemically utilised.

Various improved forms of the cell have been suggested and widely used in America and Germany. They are particularly designed to give a higher E.M.F., larger currents and capacities,[2] and lower resistances. To avoid using porous pots, the difference in densities between the solutions employed has been utilised. Saturated copper sulphate is covered with a lighter solution of $MgSO_4$, in which the zinc electrode dips. Even after the cell has been working for some time the $Zn^{\cdot\cdot}$ concentration is low, and the ratio $\frac{[Cu^{\cdot\cdot}]}{[Zn^{\cdot\cdot}]}$, and consequently the E.M.F., high. In the Meidinger element, for example, the voltage at the start is 1·18 volts, though rapidly falling to 1·12–1·13 volts. Its resistance is, however, not low. Other designs provide a large electrode surface, thus allowing larger currents to be taken off without undue polarisation. But in no case has it proved possible to exclude local action, and this is quite sufficient to prevent a wider use of the cell.

Grove-Bunsen Cell.—This is also a two-fluid cell. The anode consists of amalgamated zinc, usually in 8 per cent. H_2SO_4. As cathode depolariser, nitric acid is used, usually 66 per cent. In the first form of the cell, due to Grove, the cathode consisted of platinum. Bunsen replaced this by the cheap retort carbon, which alteration hardly affects the E.M.F. In most Bunsen cells, the carbon electrode (a rectangular plate) and the HNO_3 are contained in a rectangular-shaped porous pot, which stands in an outer larger rectangular glass jar containing the H_2SO_4. The zinc is used in the form of a single sheet, bent parallel to the sides of the porous pot, and underneath it.

The anode process in the Bunsen cell consists in zinc ions entering the solution. The cathodic process depends essentially on the concentration of the nitric acid. The matter has not been fully investigated, but we know that, with the strongest acid, NO_2 first results, and as the acid becomes weaker NO appears. With still more dilute acid, N_2O is formed, then nitrogen, and finally ammonia. Pure aqueous HNO_3, whether strong or dilute, is not a reversible depolariser. Its rate of reaction with the discharged hydrogen is very slow, and such an electrode becomes rapidly polarised. A number of substances, however, catalyse this depolarisation, and such substances are usually added to the

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[1] *Grundriss der technischen Elektrochemie,* p. 156 (1898).

[2] The capacity of a cell under given conditions is the quantity of electricity it can furnish, usually expressed in ampere-hours.

cathodic nitric acid of the Bunsen cell. HCl, H_2SO_4, $H_2Cr_2O_7$ all act thus. Most important is nitrous acid, itself formed in the first stages of reduction. It increases enormously the rate of oxidation of the hydrogen, and thus keeps the E.M.F. near to the equilibrium value.[1] It is particularly effective if the acid has a concentration of $<$ 30 per cent., as polarisation is then very easy. As a matter of fact, these different catalysts render the depolarisation in the Bunsen cell very good, and large currents can be taken from it without any serious drop in voltage.

The E.M.F. is about 1·96 volts if fuming HNO_3 be used, but with 45 per cent. to 65 per cent. acid it is 1·8–1·9 volts. This figure is composed of the difference of the anode potential difference, about $-$ 0·8 volt, and the cathode potential difference, $+$ 1·0 to 1·1 volts. The conductivities of the electrolytes are high, and the resistance consequently low—0·1 to 0·2 ohm. An objection to the cell is the evolution of nitrous fumes when working.

Poggendorff Bichromate Cell.—This cell resembles the above in using a liquid depolariser, but differs from it in containing only one liquid and in dispensing with a diaphragm. The electrolyte is a solution containing H_2SO_4 and either potassium or sodium bichromate. It of course evolves no fumes. The total reaction at the cathode can be expressed thus—

$$Cr_2O_7'' + 14H^{\cdot} \longrightarrow 2Cr^{\cdot\cdot\cdot} + 7H_2O + 6\oplus,$$

and that in the whole cell by

$$3Zn + Cr_2O_7'' + 14H^{\cdot} \longrightarrow 2Cr^{\cdot\cdot\cdot} + 3Zn^{\cdot\cdot} + 7H_2O.$$

The electrolyte very slowly attacks the zinc electrode chemically, and, in order completely to avoid local action during long idle periods, the latter is usually arranged so that it can be lifted out of the solution or immersed in it at will. The use of $Na_2Cr_2O_7$ in the electrolyte is preferable to that of the potassium salt, owing to its greater solubility. This means a higher capacity, and a lesser tendency to depolarisation. If potassium bichromate be used, the solution contains 8–10 parts of this salt and 10–18 parts H_2SO_4 per 100 parts water; and with sodium bichromate, 17–20 parts of salt and 20–24 parts of H_2SO_4 per 100 parts water. The resistance of the cell is about 0·3 ohm—low, though higher than that of the Bunsen cell. The cathodes are of carbon.

We have seen [2] that the potential of a chromic acid solution in H_2SO_4 is higher than the potential of 66 per cent. HNO_3. It follows that the E.M.F. of the Poggendorff cell should exceed that of the Bunsen cell, which is the case. It is usually 2·0 volts. On the other hand, it polarises more easily. This is partly due to sluggishness in oxidising

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[1] Ihle, *Zeitsch. Elektrochem.* **2**, 174 (*1895*).

[2] Table, p. 196.

the discharged hydrogen, but also to concentration polarisation. The Cr_2O_7'' ions around the cathodes and in their pores become exhausted and are replaced by $Cr^{\cdots}$ ions.[1] On standing, these concentration changes are neutralised by diffusion and the cell recovers. The polarisation due to slow action between the chromic acid and hydrogen can be largely removed by adding some soluble chloride, which acts as a catalyst. It unfortunately also increases the rate of chemical solution of the zinc by the electrolyte. Owing to the high voltage, and its comparatively ready polarisability, the bichromate cell is particularly suitable for furnishing large currents for short periods, between which it is allowed to recover.

Lalande Cells.—These cells also have a soluble zinc anode. But, unlike those already considered, the electrolyte is alkaline, not acid, and the cathodic depolariser a solid, viz. CuO. The system is

Copper | Oxides of copper . Alkali | Zinc.

First invented by Lalande, they were worked on by Edison and others, and successful forms developed by Messrs. Umbreit and Matthes of Leipzig (Cupron element) and by Wedekind (in England known as the Neotherm cell). These latest types are undoubtedly the best and most efficient primary cells we possess.

In construction the Cupron element consists of a rectangular glass trough, with an ebonite lid through which pass the nickel terminals of the plates inside. These number three, and hang parallel to one another. The two outer are of amalgamated zinc, the inner is the porous copper oxide plate. This is constructed by filling a flat cage of copper gauze with cupric hydroxide, compressing strongly, and subsequently baking. 15 per cent. to 18 per cent. NaOH solution is used. The Cupron cells have an E.M.F. (open circuit) of about 1·0–1·1 volts. This very rapidly falls when current is furnished to about 0·9 volt, and then slowly decreases to 0·75 volt during the discharge. At this point it commences to again rapidly fall and the cell polarises. As long, however, as the active material is still not all reduced, very considerable currents can be given without causing the working voltage to appreciably fall. The depolariser acts quickly, and the internal resistance is very low—0·03 to 0·05 ohm. When run down, fresh zinc plates and NaOH are put in, and the cupric oxide plate regenerated by heating it to 150°—in an oven for example.

The Neotherm element consists of a rectangular iron containing vessel, closed with an indiarubber gland and an iron lid. Through the lid pass ebonite bushes, insulating the terminals. There is one zinc electrode, a vertical plate suspended in the middle of the cell.

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[1] In the Bunsen cell, although the HNO_3 is consumed, there is no accumulation of other products, as the gases formed stream away.

The copper oxide depolariser is caused by a special process to adhere to the cell wall, and this is directly connected with the positive terminal. Like the Cupron cell, the E.M.F. of the Neotherm cell is 1·0–1·1 volts, and its discharge voltage 0·90–0·75, though it is customary to take it down to 0·5–0·6 volt when working. Below that limit it drops very rapidly. The internal resistance is even smaller than that of the Cupron cell. The copper oxide is regenerated by heat, the whole cell body being warmed up.

In spite of its low voltage, the Lalande cell, now that difficulties inherent in the CuO plate have been overcome, has won considerable favour, and is undoubtedly to be preferred to any other type of primary cell. It is compact in structure, and has a high capacity per unit-weight. (A Neotherm cell weighing 12 lbs. will give 150 ampere-hours if discharged at 1 amp.) The zinc consumption is practically theoretical during discharge, and local action whilst standing is negligible, as the solubilities of CuO and Cu_2O (particularly the latter) in the electrolyte are very small. The alkali is well protected against atmospheric CO_2. The positive plate depolarises rapidly, and admits of large currents, whilst the regeneration is quick and convenient. There are no diaphragms or similar complications, and the resistance is very low.

In the Lalande element the zinc dissolves as a complex anion, probably according to the equation

$$Zn + 3OH' \longrightarrow ZnO_2H' + H_2O + 2\ominus.$$

Owing to the exceedingly low $Zn^{\cdot\cdot}$ concentration in equilibrium with this complex, the anode potential will have a high negative value. Measured against a normal calomel electrode, Lorenz[1] found a voltage difference of 1·55 volts, which would correspond to a single potential of about − 1·3 volts. We know that such an electrode is 0·4 volt more negative than a hydrogen electrode in the same solution, and about − 1·24 volts is a more probable average figure for this single potential (assuming $Zn \mid n.\ Zn^{\cdot\cdot} = -0{\cdot}77$ volt).

The change of the copper oxide plate potential during working has been studied by Johnson,[2] and his results are expressed in Fig. 54. The initial potential is 1·4 volts positive to hydrogen in the same solution (this is probably too high), but very rapidly falls to 0·6 volt. At this value it keeps constant for some time, then falls quickly to 0·4 volt, and remains nearly constant during the greater part of the discharge. Towards the end there is another rapid drop in potential, and the point of reversible hydrogen evolution is passed. But no

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[1] *Zeitsch. Elektrochem.* **4**, 308 (*1898*).

[2] *Trans. Amer. Electrochem. Soc.* **1**, 187 (*1902*). The 'charge' curve refers to the attempted use of the copper oxide plate in secondary cells. See p. 221.

hydrogen is evolved until a potential corresponding to an overvoltage of about 0·3 volt[1] is reached. During the first horizontal stage of the discharge, CuO is reduced to Cu_2O. Before all the CuO has disappeared, however, polarisation has lowered the potential to the point at which Cu_2O is reduced to copper. Along the main horizontal part of the curve this is the chief process, though the further reduction of CuO to Cu_2O occurs simultaneously.[2] When the Cu_2O in the plate approaches

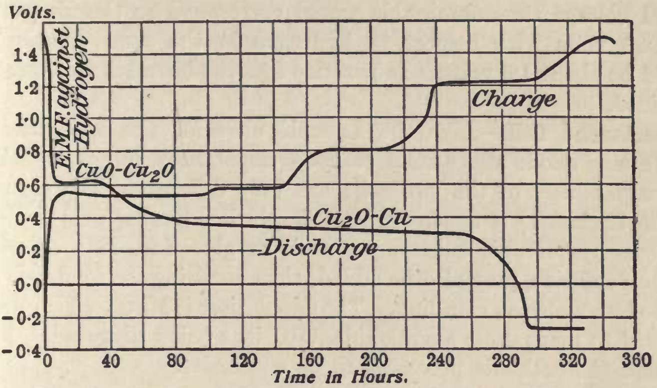

FIG. 54.—Discharge Curve of Lalande Cell Positive Electrode.

exhaustion, the potential rapidly falls to the value necessary for hydrogen evolution. During this stage Johnson noticed that the small quantities of Cu_2O left suffered further reduction to green copper quadrantoxide – Cu_4O. The potentials of the two stages of the discharge (0·6 and 0·4 volt respectively, referred to a hydrogen electrode in the same solution) lie somewhat below the equilibrium values. These are[3] 0·75–0·66 volt for the $CuO-Cu_2O$ mixture, depending on the method of preparation of the CuO, and 0·47 volt for the Cu_2O-Cu electrode. The discrepancies—up to 0·15 volt—are due to concentration polarisation, as the amounts of the oxides dissolved in the electrolyte at any moment are exceedingly small.

Johnson found for the system $Cu \mid CuO\ KOH\ Pt \mid H_2$ the E.M.F. 0·73 volt. This value is probably too high, owing to the presence of dissolved oxygen. The most probable figure is + 0·68 volt referred to hydrogen in the same solution. If we subtract from this – 0·41 volt, the potential of the zinc anode, we get 1·09 volt as the E.M.F. of the cell, which is the value actually obtained. Its working voltage

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[1] Cf. values for copper on pp. 118–119.

[2] The Lalande cell cannot be strictly regarded as a form of the Daniell cell, as is sometimes done. The process $Cu^{\cdot} \longrightarrow Cu$ does *not* take place, but instead we have the two successive reactions $Cu^{\cdot\cdot} \longrightarrow Cu^{\cdot}$ and $Cu^{\cdot} \longrightarrow Cu$.

[3] Allmand, *Trans. Chem. Soc.* **95**, 2151 (*1909*); **97**, 603 (*1910*).

during the first stages is somewhat lower, and during the chief part of the discharge is made up of the difference of the potentials of the CuO plate + 0·4 volt and the zinc plate − 0·4 volt, *i.e.* 0·8 volt. Lorenz[1] has shown that the zinc electrode behaves nearly reversibly except at very high current densities. Finally the initial high voltage stages of the discharge are due to depolarisation by air dissolved in the electrolyte and adsorbed on the positive plate. Its presence keeps the $Cu^{\cdot}$ concentration low and the potential high. The highest possible initial voltage thus obtainable would correspond to the air potential (+ 1·22 volts with respect to hydrogen in the same solution) and would be about 1·6 volts. In practice figures above 1·2 volts are never obtained.

Leclanché Cell.—Like the Lalande element, the Leclanché cell[2] uses a zinc anode and a solid cathodic depolariser, but the efficiencies and capabilities of the two cells are very different. The electrolyte in the Leclanché is a strong NH_4Cl solution (perhaps 20 per cent.). Various hygroscopic substances, such as glycerine, zinc chloride or calcium chloride, may also be added, thus lessening the tendency of the cell to lose water on standing. The depolariser is MnO_2, which becomes reduced to manganese sesquioxide, OH' ions being liberated. We can suppose the cathodic processes to be successively

$$MnO_2 + 2H_2O \longrightarrow Mn^{\cdot\cdot\cdot\cdot} + 4OH'$$
$$Mn^{\cdot\cdot\cdot\cdot} \longrightarrow Mn^{\cdot\cdot\cdot} + \oplus$$
$$Mn^{\cdot\cdot\cdot} + 3OH' \longrightarrow \tfrac{1}{2}Mn_2O_3 + \tfrac{3}{2}H_2O.$$

The total result is

$$MnO_2 + \tfrac{1}{2}H_2O \longrightarrow \tfrac{1}{2}Mn_2O_3 + OH' + \oplus.$$

The exact form in which the Mn_2O_3 is precipitated is not known. This depolariser has several disadvantages. It does not react as rapidly as the CuO plate of the Lalande cell. One or other of the above reactions takes place comparatively slowly, and, unless the current density be kept low, the polarisation increases to such an extent that the potential necessary for $H^{\cdot}$ discharge is reached. The cathode potential[3] also becomes more negative owing to the formation of OH' ions. This formation occurs in all the primary cells we have considered with the exception of the Daniell cell. In elements with acid depolarisers it is neutralised, and in the Lalande cell its effect is small in comparison with

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[1] *Loc. cit.*

[2] Friedrich, *Elektrochem. Zeitsch.* **16**, 219, 252, 287 (*1909–10*).

[3] In the present case

$$\mathcal{E} = (E.P.) + 0{\cdot}058 \log \frac{[MnO_2]}{[Mn_2O_3]^{\frac{1}{2}} \, . \, [OH']}$$
$$= \text{constant} - 0{\cdot}058 \log [OH']$$

See p. 102.

the OH′ ions already present. But in the Leclanché element, with a neutral electrolyte, the effect on the cathode potential can be marked. On standing, the greater part of the alkali of course diffuses away.

Finally the specific resistance of the MnO_2 is high. Not only does this mean an increased cell resistance, but it renders it difficult to make the mass so porous that the full capacity of the depolariser can be utilised. It is always necessary to mix some highly-conducting powdered graphite or carbon with the MnO_2 on this account.

At the anode zinc dissolves, forming $ZnCl_2$. The OH′ ions produced at the cathode give undissociated NH_4OH with the $NH_4^{\cdot}$ ions, which in its turn furnishes ammonia gas. Some of this escapes into the atmosphere. But the greater part remains dissolved and sets itself into equilibrium with the $ZnCl_2$ as follows:

$$ZnCl_2 + 2NH_3 \rightleftarrows Zn(NH_3)_2Cl_2.$$

This last salt, the chloride of a complex zinc-ammonium cation, is sparingly soluble and gradually separates out. The equation expressing the main reaction in a Leclanché cell is therefore $Zn + 2NH_4Cl + 2MnO_2 \longrightarrow Mn_2O_3 + Zn(NH_3)_2Cl_2 + H_2O$. Whether water actually separates or not depends on the form in which the Mn_2O_3 is precipitated. Besides $Zn(NH_3)_2Cl_2$, basic insoluble zinc ammonium salts can be formed. Another effect of the cathodic production of OH′ ions is to precipitate zinc hydroxide where their concentration is greatest, *i.e.* in the porous MnO_2 mass. This precipitation naturally still further raises the resistance of the depolariser. The conductivity of the cathodic mass of an exhausted element is exceedingly low, due to this cause and to the production of the manganese sesquioxide.

There is one further complication. In a working Leclanché cell it is usually observed that the upper end of the zinc electrode is far more attacked than the lower end. The cause is as follows. The $ZnCl_2$ solution formed anodically is heavier than the rest of the electrolyte, and falls to the bottom of the vessel. We have then a zinc rod, its two ends dipping into solutions of $ZnCl_2$ of different strengths, in other words a concentration cell.[1] This cell will furnish a current that will tend to neutralise the concentration difference. Zinc is deposited at the bottom end of the rod and dissolves at the upper end, whilst positive electricity flows along the rod from bottom to top. The result is the phenomenon observed.

The actual construction of the Leclanché cell shows many variations, designed to increase capacity and lessen resistance. A common type is a glass vessel containing the NH_4Cl solution. The zinc anode is an amalgamated rod, whilst the cathode is a carbon rod surrounded by a cylindrical mass of the depolariser. This consists of powdered pyrolusite intimately mixed with excess of graphite or carbon. Various additions

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[1] P. 103.

are sometimes made, such as MgO, CaO, Fe_2O_3, but their function is doubtful. The mass is held together by a suitable cement. In other types the depolarising mixture is packed round the carbon into a porous pot.

The voltage of the Leclanché on open circuit is 1·4–1·65, but, owing to polarisation, drops to 1·1–1·2 volts when furnishing even small currents (0·1–0·2 amperes for an ordinary cell). The value 1·4 volts corresponds to the MnO_2–Mn_2O_3 electrode; the higher figure, 1·65 volts, is due to depolarisation by air dissolved and adsorbed in the active mass, and is only given for a very short time by fresh cells. The air potential is about + 0·81 volt, and the potential of the zinc electrode at the prevailing low $Zn^{\cdot\cdot}$ concentration can be taken as – 0·84 volt. The current furnished depends on the active area of the depolariser. Generally (to avoid hydrogen evolution) it should not exceed 0·1 amps. /d.m.^{2}, *i.e.* 0·1—0·2 amps. for an average cell. The resistance varies enormously with the construction (0·05–10 ohms), but averages 0·4–2 ohms. Despite its many disadvantages, the Leclanché is widely used for purposes requiring small intermittent currents (bells, telephones, etc.). The reasons are that it is readily set up, requires but little attention, and is cheap. For larger continuous currents it is useless.

Dry Cells.—These cells[1] are Leclanché elements in which the electrolyte is contained in some porous material with which the cell is filled. Such cells can be placed in any position without losing liquid, often a great convenience. Millions are made yearly, all of small capacity, and used for small handlamps, telephones, door bells and motor ignition. The outer containing vessel can be of zinc and form the anode, or of impregnated cardboard, enamelled iron, celluloid, etc. The zinc is best amalgamated, taking the form of a rod or a cylindrical piece of foil. The carbon rod (cathode) is surrounded with the depolariser, a mixture of graphite or carbon powder and MnO_2, the latter as pure as possible. The electrodes are placed closely together.

As porous material are used paper-pulp, sawdust, cotton-wool, cocoanut charcoal, clay, infusorial earth, etc. Gypsum, magnesia, and ZnO have the disadvantage of setting into a solid mass under the action of the electrolyte and increasing the cell resistance. The electrolyte contains usually NH_4Cl (25 per cent.) and $ZnCl_2$. The latter decreases the local action at the zinc electrode and also the polarisation. As in the Leclanché, hygroscopic substances such as $CaCl_2$ and glycerine are also added, it being essential that the cell does not become too dry.

The cells being intended for intermittent use, and having to stand idle for long periods, great care must be taken in their construction

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[1] *Trans. Amer. Electrochem. Soc.* **16**, 97 (*1909*); **17**, 341 (*1910*).

to avoid defects that may lead to local action,[1] and the materials used must be very pure. A trace of copper is fatal. The cells are usually closed up with hard pitch, an opening being left for the escape of the ammonia when working.

On open circuit the voltage of a dry cell is equal to that of a Leclanché, perhaps 1·6 volts. But if discharged at an average rate only about one volt is obtained. The capacity depends largely on the rate of discharge. A normal cell under normal conditions will furnish perhaps 30 ampere-hours before its voltage falls to 0·5 volt. The resistance increases continually during working, the evaporation of water and the deposition of basic zinc compounds being responsible.

3. Fuel Cells[2]

The Problem. — When mechanical energy (or electrical energy) is produced from fuel by means of boiler and steam engine (and dynamo), only some 10 per cent. to 15 per cent. of the total amount of energy liberated by the complete combustion of the fuel is obtained,[3] and with a gas engine some 25 per cent. One of the most important technical problems is a better utilisation of this available chemical energy of oxidation of fuel, and many attempts have been made to convert it directly into electrical energy without the intermediate production of heat, *i.e.* to bring about the combination of the fuel and atmospheric oxygen *electrochemically*. If it were possible to do this, and reversibly, not merely a small fraction of the free energy of combustion of the fuel would become available as mechanical energy, but the whole of it, and this naturally would mean an industrial revolution only comparable with the first introduction of steam engines. Besides the enormous drop in the cost of power, resulting in a great extension of its use and in the unquestioned supremacy of coal as against water-power (this fact would be of particular economic importance to industrial electrochemistry), a successful fuel cell would mean a great mitigation of the smoke nuisance and vast changes in the engineering and chemical industries. Obviously all schemes so far proposed have been fruitless, but in view of the extreme importance of the subject we must consider it at some length here.

The chief constituent of our fuels is carbon. If burnt to CO_2 at room temperature, one gram-atom (12 grams) liberates 97,650 cals. This is U,[4] the decrease of total energy. A, the decrease of free energy, the measure of the maximum amount of useful work obtainable from

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[1] In some types the water necessary is only added immediately before use. Such cells can be stored indefinitely till required without fear of deterioration.

[2] Ostwald, *Elektrotech. Zeitsch.* **15**, 329 (*1894*). Haber, *Grundriss der Technischen Elektrochemie*, p. 178 (1898). *Zeitsch. Elektrochem.* **11**, 264 (*1905*).

[3] P. 10.

[4] P. 78.

the combustion, is rather less, 96,635 cals. Carbon is tetravalent, and its electrochemical combustion would necessitate the passage of four faradays per gram-atom. If E is the voltage of a $C - O_2$ cell at room temperature, we have then

$$E \times 96540 \times 4 = 4{\cdot}19 \times 96635$$
$$E = 1{\cdot}05 \text{ volts.}$$

If air be used instead of oxygen, the E.M.F. will be about 0·01 volt lower, *i.e.* 1·04 volt, and the reversible combustion of one kilo. of carbon in this way will furnish about 8,940 ampere-hours at this pressure. The coulombs are high and the voltage low.

The Difficulties.—To effect the electrochemical combination of carbon and oxygen, the obvious procedure is to construct a cell with a carbon anode, an oxygen cathode, and a suitable electrolyte. Oxygen or oxygen-containing substances and carbon must of course be kept out of contact with one another. The earlier cells (Becquerel; Jablochkoff) erred in this way, other considerations apart. But we at once encounter two main difficulties. *It is essential that the carbon should ionise* (not necessarily as carbon ions, for ions containing carbon and some constituent of the electrolyte would suffice), otherwise the electrochemical solution of the carbon anode cannot take place. Now, carbon stands in the middle of the first horizontal series of the Periodic System, and one characteristic of these horizontal series is that the end members show very marked electrochemical properties, and have high electrolytic solution pressures, whilst this tendency steadily diminishes towards the middle of the series. Carbon is almost electrically neutral, and has resisted all attempts to make it ionise, whatever the electrolyte.

The second difficulty is that the forms of carbon which constitute our fuels[1] are *by no means pure.* The presence of inorganic ash constituents apart, the carbon itself does not really occur as elementary carbon, but rather as highly complex substances, containing also hydrogen, oxygen, and nitrogen. Considering that carbon itself does not ionise, it is difficult to imagine what ions these carbon-rich complexes could give. The anodic impurities would also mean a foul electrolyte, and we have already seen how essentially important it is for an electrolytic process that this fouling be minimised.

The recognition of these facts has led later experimenters to employ a different principle. This consists in first allowing the carbon to react chemically with other substances, forming an electromotively active product, and using this product in the primary cell. The final result is that the fuel is burnt to CO_2 (also water, etc.). For example, one could imagine the carbon to be used to produce zinc from ZnO, giving at the same time CO_2, and the zinc subsequently electrochemically oxidised to ZnO (assuming these reactions to be possible). Or Fe_2O_3

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[1] These, and not electrode carbons, would form the active anodes in a fuel cell!

could be reduced by carbon to iron and afterwards electrochemically regenerated from the iron and air. The equations would be

$$(a) \quad 2ZnO + C \longrightarrow CO_2 + 2Zn.$$
$$2Zn + O_2 \longrightarrow 2ZnO.$$
$$(b) \quad 2Fe_2O_3 + 3C \longrightarrow 4Fe + 3CO_2$$
$$4Fe + 3O_2 \longrightarrow 2Fe_2O_3.$$

The above examples, if feasible, would of course furnish a large quantity of electrical energy during the second stage of the reaction, but the first stage of the cycle is strongly endothermic, absorbing heat and requiring a high temperature, and the wastage of fuel involved would render the processes impracticable. To be successful, the first (chemical) stage of the cycle must not take place with any great absorption of heat. If, on the contrary, it take place with evolution of heat, the smaller this evolution, other things being equal, the better; for then a greater fraction of the original heat of combustion of the carbon will be available for the production of electrical energy in the second part of the process. This method of procedure frankly abandons the attempt to obtain the whole of the available energy of combustion as electrical energy.

Three such processes have been suggested. One is that used in the Jungner cell.[1] Carbon acts on strong H_2SO_4. The SO_2 formed is conducted to the cell, and there combines electromotively with atmospheric oxygen, the resulting SO_3 dissolving in the H_2SO_4 electrolyte. The latter is continually drawn off, and used to generate more SO_2. The second process is of considerable interest, and has been much investigated.[2] It consists in principle in converting the fuel into producer gas, and causing the resulting CO to enter solution anodically in a suitable electrolyte.

Generator-gas Cells.—The decrease of available energy corresponding to the reaction $[C] + [O_2] \longrightarrow [CO_2]$ is 96,635 cals. at room temperature. When carbon is burnt to CO, much heat is liberated—29,650 cals. for the reaction

$$[C] + \tfrac{1}{2}[O_2] \longrightarrow [CO].$$

Consequently the free energy decrease during the reaction

$$[CO] + \tfrac{1}{2}[O_2] \longrightarrow [CO_2].$$

is much less than the decrease during the reaction

$$[C] + [O_2] \longrightarrow [CO_2].$$

At room temperature it is 61,880 cals. It follows that if carbon is burnt to CO, and this gas combined electrochemically with oxygen at room temperature, the electrical energy obtained will only be $\frac{619}{966}$, or

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[1] P. 215.

[2] Originally by Grove.

64 per cent. of that which the reaction $C + O_2 \longrightarrow CO_2$ would furnish if electrochemically carried out. But if even this could be managed in practice it would be a great advance. To the 64 per cent. must also be added the energy which can be generated from the 29,650 cals. liberated in the gas producer. This might amount to another 5 per cent. of the original 96,635 cals., making the maximum possible utilisation of energy 69 per cent. The $CO - O_2$ cell would have one advantage over the $C - O_2$ cell, however. Its E.M.F. would be higher. The combination of one mol. CO with half a mol. O_2 necessitates the passage of only two faradays, and we have

$$E \times 96540 \times 2 = 4{\cdot}19 \times 61880$$
$$E = 1{\cdot}34 \text{ volts,}$$

compared with 1·05 volts, the E.M.F. of the $C - O_2$ cell.

All attempts to construct a practicable CO—O_2 cell working at room temperature have failed (the best known, that of Borchers, we shall presently discuss). The difficulty of finding a suitable electrolyte in which the CO can ionise has been insuperable. Another difficulty encountered in all gas cells is their easy polarisability. This is due to the fact that the concentration of the gas in the ionising electrode material is nearly always very low, and can only be renewed by diffusion from the gas atmosphere surrounding the latter. This process is invariably slow in comparison with the rate of ionisation, and, unless the current density is exceedingly small, polarisation at once occurs. This fact has led to experiments with generator-gas cells at high temperatures. Under these conditions the rate of diffusion is vastly increased, and polarisation should be consequently diminished. There is also the possibility that electrochemical combination of CO and O_2 may be accelerated at high temperatures just as their chemical combination is accelerated, *i.e.* that the CO may ionise. It must, however, not be forgotten that working at high temperatures still further limits the electrical energy obtainable by the combustion of the fuel. We have seen that the E.M.F. of the $CO - O_2$ cell at 17° is 1·34 volts. But it falls to

1·25 volts at 200°
1·18 volts at 350°
1·11 volts at 500°
0·88 volt at 1000°.

If the cell were worked at 500°, instead of getting 64 per cent. of the maximum value, as at room temperature, only 53 per cent. would be obtained, a fraction further diminished by the heat consumed in keeping the cell at its working temperature.

Bucherer[1] worked in this way, employing fused alkaline carbonates

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[1] D. R. P. 88327.

as electrolytes, and using as electrodes a platinum tube through which oxygen was led, and a nickel tube through which CO was passed. One might suppose the cell to function as follows :

At anode :

$$CO + CO_3'' \longrightarrow 2CO_2 + 2 \ominus \text{ (formation of } CO_2\text{).}$$

At cathode :

$$\tfrac{1}{2}O_2 \longrightarrow O'' + 2 \oplus \text{ (formation of } Na_2O\text{).}$$

In electrolyte :

$$O'' + CO_2 \longrightarrow CO_3'' \text{ (reformation of } Na_2CO_3\text{).}$$

Total reaction :

$$CO + \tfrac{1}{2}O_2 \longrightarrow CO_2.$$

But in practice complications entered, reactions taking place between electrodes and electrolyte, and the rate of diffusion of the gases through the metal electrodes being too slow. The cell proved unworkable. Later experiments were undertaken by Haber and Moser.[1] Using glass as electrolyte, platinum black electrodes, and temperatures of 450°–500°, they succeeded in showing that the combinations $CO-O_2$ and $C-O_2$ could be made electromotively active, giving the calculated E.M.F.s. But, owing to the extreme ease with which these cells became polarised, their results are without practical value.

In the third combined chemical and electrical process, the carbon reduces hydrogen from water, and this hydrogen subsequently combines electrochemically with oxygen. The hydrogen is prepared in the form of water-gas in a low temperature gas producer, and suitably separated from the accompanying oxides of carbon. The most notable attempt on these lines was made by L. Mond and Langer, and will presently be described. But it has had no technical success, despite the time and skill spent on it. Mond and Langer worked at room temperature, and were much troubled by the easy polarisability of their electrodes.[2] As with the generator-gas element, the idea of working at higher temperatures was obvious, and more likely of success in this case, there being no difficulty about the actual ionisation (qualitative) of the hydrogen as there was with CO.

But no suitable electrolyte has so far been found. Haber and Fleischmann[3] and Haber and Foster[4] have shown that at high temperatures glass and porcelain allow the electrochemical combination of the gases to proceed, and that the theoretical voltage results on open circuit.

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[1] *Zeitsch. Elektrochem.* **11,** 593 (*1905*).

[2] On the anodic passivity of hydrogen, see Sackur, *Zeitsch. Phys. Chem.* **54,** 641 (*1906*).

[3] *Zeitsch. Anorg. Chem.* **51,** 245 (*1906*).

[4] *Zeitsch. Anorg. Chem.* **51,** 289 (*1906*).

But the cells polarise with the smallest current. The experiments of Beutner[1] were hardly more successful. He used an experimental arrangement very similar to Bucherer's, employing molten mixtures of various halides as electrolytes. On open circuit he obtained rather low values for the E.M.F. of the H_2-O_2 cell, owing to diffusion of the gases through the electrolyte to the opposite electrode, and to the oxygen electrode functioning imperfectly. And a current density of 0·8 amps./d.m.^{2} lowered the cell voltage to 0·25 volt. Addition of substances such as CuO to the melt to act as oxygen carriers had no success.

The four best-known attempts to utilise electrochemically the free energy of carbon combustion, or a part of it, are due to Jacques, to Jungner, to Borchers, and to Mond and Langer.

Jacques Cell.—This consisted of electrodes of battery carbon and iron in molten NaOH. Round the iron air was blown in. An E.M.F. was obtained of about one volt, the iron being the positive electrode, and, according to the inventor, represented the free energy of combination of the carbon anode and atmospheric oxygen to CO_2. He asserted moreover that the CO_2 formed did not dissolve in the electrolyte, but was evolved as gas. Neglecting this statement, it is assumed that the reaction at the anode is

$$C + 6OH' + 4\oplus \longrightarrow CO_3'' + 3H_2O$$

and at the cathode

$$2H_2O + O_2 + 4\ominus \longrightarrow 4OH'$$

the total reaction being

$$C + O_2 + 2OH' \longrightarrow CO_3'' + H_2O.$$

It was shown by Haber and Bruner[2] that, though the last equation expresses the total result, the mechanism of the cell's action differs from that sketched above. The iron cathode, which at first dissolves chemically in the alkali, soon becomes passive, and then indeed acts as an air electrode. It does so by virtue of the presence of some manganese in the melt, either there originally or dissolved out of the iron. This manganese exists as a mixture of manganate and manganite (MnO_4'' and MnO_3'') in equilibrium with the atmospheric oxygen. The manganate preponderates. When the cell is working, the cathodic process consists in the discharge of $H^{\cdot}$ ions (from the water present in the melt) and the interaction of the hydrogen with the MnO_4'' ions, reducing them to MnO_3'' ions. The latter are almost instantaneously reoxidised by the air, so rapidly that the iron electrode behaves almost

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[1] *Zeitsch. Elektrochem.* **17,** 91 (*1911*).

[2] *Zeitsch. Elektrochem.* **10,** 697 (*1904*); **12,** 78 (*1906*). Bechterew [*Zeitsch. Elektrochem.* **17,** 851 (*1911*)] has recently published a detailed experimental investigation of the Jacques cell. His work confirms that of Haber and Bruner in essential particulars.

perfectly as a reversible air electrode. The successive reactions are therefore

$$
\begin{gathered}
2H^{\cdot} \longrightarrow H_2 + 2\oplus \\
H_2 + MnO_4'' \longrightarrow MnO_3'' + H_2O \\
MnO_3'' + \tfrac{1}{2}O_2 \longrightarrow MnO_4''
\end{gathered}
$$

or, in total,

$$2H^{\cdot} + \tfrac{1}{2}O_2 \longrightarrow H_2O + 2\oplus.$$

At the carbon electrode, the first effect is the production of CO by local combustion. This gas, with or without the intermediate formation of sodium formate, produces Na_2CO_3 and liberates hydrogen. If CO is blown in, or sodium formate or oxalate added, the same result is obtained. And it is this hydrogen dissolved in the carbon electrode which is electromotively active.[1] The anodic reactions are therefore

$$
\begin{gathered}
C + \tfrac{1}{2}O_2 \longrightarrow CO \\
CO + 2NaOH \longrightarrow Na_2CO_3 + H_2 \\
H_2 + 2\oplus \longrightarrow 2H^{\cdot}
\end{gathered}
$$

or, in total,

$$C + \tfrac{1}{2}O_2 + 2NaOH + 2\oplus \longrightarrow Na_2CO_3 + 2H^{\cdot}.$$

The total result of the action of the cell is therefore

$$C + O_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O,$$

and the E.M.F. is the E.M.F. of a H_2-O_2 cell, working at that temperature and under those conditions. Later work by Taitelbaum[2] has shown many carbonaceous substances to behave thus in molten NaOH. Sugar, charcoal, sawdust, lignite, coal, and coal gas all give hydrogen which becomes electromotively active. The number of coulombs obtained is often a surprisingly high fraction of the theoretical number. But the cell polarises very easily, as the velocity with which the ionised hydrogen is replaced by chemical action is very low. This fact, coupled with the conversion of expensive NaOH into cheap Na_2CO_3 makes the Jacques cell a technical impossibility.

Jungner Cell.—As we have seen, we have here the electromotive combination of oxygen and sulphur dioxide, the latter being prepared by the action of the fuel on strong H_2SO_4. The cell contains two chambers separated by a vertical porous diaphragm. The two electrodes are of graphite. The cathode compartment is packed with pieces of graphite, and through it air passes; the anode compartment is packed with porous coke or gas coal, and a stream of moist SO_2 passed through. The anode chamber contains sulphuric acid, and the diaphragm is well

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[1] Nobis [*Dissertation* (Dresden, 1909)] showed hydrogen dissolved in carbon to be electromotively inactive at room temperature and in acid electrolytes.

[2] *Zeitsch. Elektrochem.* **16**, 286 (*1910*).

saturated with the same. The cathode chamber contains nitrosyl-sulphuric acid of high concentration. This depolarises the $H^{\cdot}$ discharge, and is supposed to be immediately reoxidised by the air, thus acting as an oxygen carrier. In the anode compartment, H_2SO_4 is continually formed, drawn off, and used to produce more SO_2. The E.M.F. is dependent on the concentration of the acid, and is stated to vary from 0·5 volt at medium concentration to 0·3 volt or less with strong acid. Jungner says that 70 per cent. to 80 per cent. acid is the most convenient working strength, the temperature being 70°.

Taitelbaum has studied cells of this type also.[1] He showed that the anodic process *is* due to the electromotive activity of the SO_2. The potentials given by different fuel stuffs placed in the anode chamber vary, depending on the rate at which the H_2SO_4 attacks them, but all approach the value corresponding to SO_2. He also investigated several oxygen carriers for the catholyte. Ferro-ferri and mercuro-mercuri sulphate mixtures came too slowly into equilibrium with atmospheric oxygen, and were therefore unsuitable. But mixtures of thallous and thallic sulphates or the sulphates of tetra- and penta-valent vanadium reacted very quickly, soon showing the air potential ($+$ 1·35 volts at 250° under the conditions prevailing). He finally constructed cells containing the vanadium depolariser in the catholyte and different fuels in the anolyte. At 250° he obtained on open circuit 0·4–0·6 volt, depending on the fuel used. The figure was usually higher, the more rapidly fuel and acid reacted. But all these elements polarised quickly, though not as rapidly as the Jacques cell. Thus, whilst a small Daniell cell of similar dimensions only dropped in voltage from 1·08 to 0·99 volts at a current of 0·1 ampere, a fuel cell using charcoal was polarised from an open circuit voltage of 0·45 volt to 0·25 volt. Cells with the nitrosyl-sulphuric acid recommended by Jungner behaved far worse, the oxygen carrier evidently acting slowly and irreversibly.

Considering these results, one must conclude that the Jungner element leaves the problem unsolved. Though less easily polarisable than the Jacques element, its very low E.M.F., corresponding to about a 30 per cent. utilisation of the free energy of carbon combustion, renders its further development highly unlikely.

Borchers Cell.—This was a very ingenious attempt to effect the electrochemical combination of CO and O_2, but as it has been conclusively shown that its E.M.F. did not depend on the presence of the CO we need only very briefly consider it. CO dissolves in a hydrochloric acid solution of CuCl, forming a loose additive compound. The anode chamber in Borchers' cell was filled with this solution, and CO gas was bubbled through. The cathode compartment contained the HCl-CuCl solution, but with oxygen instead of carbon monoxide

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[1] *Loc. cit.*

bubbling through it. Copper electrodes were used. Borchers hoped that changes on the following lines would occur :

At cathode :

(*a*) $2Cu^{\cdot\cdot} \longrightarrow 2Cu^{\cdot} + 2\oplus$
(*b*) $\frac{1}{2}O_2 + 2Cu^{\cdot} + 2H^{\cdot} \longrightarrow 2Cu^{\cdot\cdot} + H_2O.$
Total : $\frac{1}{2}O_2 + 2H^{\cdot} \longrightarrow H_2O + 2\oplus.$

At anode :

(*a*) $2Cl' \longrightarrow Cl_2 + 2\ominus$
(*b*) $Cl_2 + CO$ (of dissolved complex) $+ H_2O \longrightarrow CO_2 + 2H^{\cdot} + 2Cl'.$
Total : $CO + H_2O \longrightarrow CO_2 + 2H^{\cdot} + 2\ominus,$

giving a total cell reaction

$$CO + \tfrac{1}{2}O_2 \longrightarrow CO_2.$$

But the small E.M.F.s. observed cannot be ascribed to any such reaction. R. Mond showed that if the copper electrodes were replaced by carbon the E.M.F. sank almost to zero, and Barnes and Veesenmayer[1] failed to detect any CO_2 in the anode gases. As Mond's observation indicates, the probability is that the observed E.M.F.s. depended essentially on the presence of the copper electrodes.

Mond-Langer Cell.[2]—These workers were guided by the following principles :—

(*a*) The current density must be exceedingly low.

(*b*) The gases must only have a short distance to diffuse through before reaching the surface at which they ionise.

(*c*) The electrodes must be kept free from any film of liquid, otherwise the solution of the gas is hindered. These three conditions are essential for supplying gas to the electrodes as quickly as it is ionised, and therefore for the reversible working of the cell.

One of the constructions they used is shown in Fig. 55. The electrolyte—dilute H_2SO_4—is contained in the porous diaphragm C (stone, gypsum, asbestos, pasteboard), just as it is in dry cells. The two sides of C are covered with very thin platinum sheets, pierced with a large number of tiny holes, some 1500 per cm.^{2} These sheets, which constitute the electrodes, are backed with leaden strips to decrease the internal resistance, provided with leads of copper wire, and finally painted on the back with platinum black.[3] The diaphragm and electrodes are then set in an ebonite frame A, and clamped together between two other ebonite frames B, B′, the frames being separated by

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[1] *Zeitsch. Angew. Chem.* **8**, 101 (*1895*).

[2] *Proc. Roy. Soc.* A. **46**, 296 (*1889*).

[3] Best prepared by precipitating boiling H_2PtCl_6 with Na_2CO_3, and reducing with H.COONa.

rubber rings. Through the shallow chambers behind the electrodes (of the depth of the rubber rings) the reacting gases are led, one on each side, and commence to ionise.

The results given depend largely on the quality of the platinum black.

On open circuit about 0·97 volt was usually got. The reversible value is 1·23 volts, and the highest figure ever got with platinum electrodes about 1·15 volts. The inner resistance depended on the diaphragm, its nature, thickness, and amount of electrolyte present; but it was generally low. A gypsum diaphragm of area (one side) 350 c.m.^{2} and thickness 8 m.m. had a resistance of only 0·02 ohm. Such an element furnished currents up to 8 amperes, but its E.M.F. rapidly fell. As typical of the final results obtained, it may be recorded that a cell with a total active surface of 700 c.m.^{2} and containing 0·35 gram Pt foil and 1 gram Pt black could give a current of 2 to 2·5 amperes at 0·73 volt. This was reckoned to correspond to an energy efficiency of about 50 per cent.

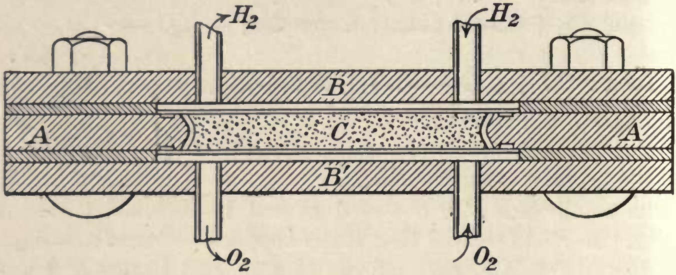

FIG. 55.—Mond-Langer Cell.

Good as this result appears compared with those of other cells, it was only achieved by using an impracticable apparatus. Technically, the first cost would be too high, and the complications impossible. The platinum black is also very sensitive to the presence of traces of impurities. Haber[1] found that 2·5 per cent. of CO present in the hydrogen seriously affects the absorption of the latter by the platinum electrode. Finally, great concentration changes go on during the electrolysis. If sulphuric acid is the electrolyte, this will concentrate in the layer of the diaphragm next to the anode (hydrogen electrode) owing to the migration of the HSO_4' and SO_4'' ions, and water will collect in the cathode layer, enormously increasing the internal resistance. These changes cannot be neutralised by circulation of the electrolyte or by stirring. The only possibility would be to frequently interchange the

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[1] *Grundriss der Technischen Elektrochemie*, p. 199 (1898).

streams of gas, and thus alter the direction of the current. All these facts help to render the Mond-Langer cell technically impracticable.

Hydrogen-chlorine Cell.—For completeness, one other gas cell should be discussed. It would be of great importance for the alkali-chlorine industry[1] if a technical cell could be constructed in which hydrogen and chlorine gases could be caused to combine electrochemically to hydrochloric acid. The hydrogen in most alkali-chlorine works is allowed to escape, the chlorine is converted into bleach, the market for which is very depressed at present. In many cases, even to allow hydrogen and chlorine to combine chemically might be advantageous. There is no doubt that their electrochemical combination would be. If reversibly carried out, giving a concentrated acid, the cell would have an E.M.F. of about 1·2 volts at room temperature.[2] Supposing the brine electrolysis to require 4·5 volts, the manufacturer would save 25 per cent. to 30 per cent. of his power, and would make strong HCl instead of bleach. This is doubtless a difficult problem, but nevertheless far easier than effecting the combination of hydrogen and oxygen, as chlorine ionises readily, very differently from oxygen. Nor would there be serious difficulties due to concentration changes, as in the Mond-Langer cell.

Nobis[3] has studied the subject. He found the ionisation of chlorine to take place easily at platinum, graphite or carbon. Such electrodes were not readily polarisable. Hydrogen was electromotively inactive at carbon, but ionised at platinum or platinised carbon. These electrodes were very polarisable. This is essentially due to the low solubility of hydrogen in aqueous solutions. The gas must pass from electrolyte into electrode before it can ionise, and the amount dissolved in the electrolyte becomes quickly exhausted. The more rapidly hydrogen is bubbled through, the better the results obtained. Nobis constructed a small diaphragm cell, about 6″ × 5″ × 4″, and was able to take continuously from this at room temperature a current of 0·63 ampere at 0·73 volt. By working at 60°, the power furnished could be increased by 50 per cent. These results however, necessitated passing hydrogen gas very rapidly through the cell, less than 1 per cent. being utilised. This would introduce great difficulties technically.

Literature

Bein. *Elemente und Akkumulatoren.*

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[1] P. 385.

[2] P. 82.

[3] *Dissertation* (Dresden, 1909).

CHAPTER XVI

SECONDARY CELLS

1. General Considerations

ELECTRICAL energy can only be conveniently stored in quite small amounts. The storage of large quantities is possible *indirectly* by transforming the electrical energy into some kind of energy which can be stored and retransformed into electrical energy at will. Such a form of energy is chemical energy, and a system in which these reciprocal transformations of chemical and electrical energy can take place is termed a *secondary cell* or *accumulator*, as distinguished from primary cells, which are only concerned with the transformation of chemical into electrical energy.

We have discussed at length[1] the conditions fulfilled by an ideal primary cell. They are

(*a*) High capacity of energy and current per unit weight and volume. A high voltage is thus desirable.

(*b*) No chemical action.

(*c*) Reversibility.

(*d*) Low resistance.

(*e*) Simplicity and strength of construction. Conditions (*b*), (*d*), and (*e*) all declare disadvantageous the use of two liquids and the diaphragm thereby rendered necessary.

(*f*) Durability.

(*g*) Low cost of materials.

These conditions should also be satisfied by secondary cells, and most are even more important than is the case with primary cells. Thus :—

(*a*) The capacity per unit weight is of prime importance, as they are used on a large scale compared with primary cells, and form a convenient means of transporting electrical energy.

(*b*) As they are meant for continued use, their life not being limited to a single discharge, and as they may have to stand idle for long

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[1] Pp. 195–199.

periods, it is essential that even very slight chemical effects causing deterioration or loss of stored electrical energy should be excluded.

(*c*) As they store up electrical energy in order to give it out later, it is desirable that the losses during these operations be minimal. Hence, both the transformation of electrical into chemical energy (*charging*) and that of chemical into electrical energy (*discharging*) should proceed nearly reversibly.

(*d*) The losses are lower, the lower the resistance of the cell.

(*e*) A general principle for the construction of all chemical, and particularly electrochemical, apparatus.

(*f*) Of the highest importance, secondary cells being intended for long continued use.

(*g*) Provided (*f*) is fulfilled, less important than with primary cells.

Successful Cells.—Only two secondary cells need to-day be considered. The one is the universally used lead accumulator [Lead peroxide | sulphuric acid | lead], the other the Edison nickel-iron accumulator [Nickelic hydroxide | caustic potash | iron], which will probably, in its improved form, become extensively used. The former adequately fulfils conditions (*b*), (*c*), (*d*), and (*g*), and, if well treated, also (*f*). Its construction is very simple, but the mechanical strength of the lead plates rather low, and their great weight a drawback. The improved Edison accumulator fulfils conditions (*a*), (*b*), (*d*), (*f*). Its first cost is somewhat high, owing to the materials and to complexities in construction; but, as the cell is mechanically strong and durable, that is of minor importance. Unfortunately, the charging and discharging losses considerably exceed those of the lead accumulator.

Unsuccessful Attempts.—Of the numerous other attempts made to construct practicable accumulators a few may be mentioned. With an acid electrolyte, the best known is perhaps the combination PbO_2 | acid $ZnSO_4$ | Zn. Its E.M.F. is 2·47 volts, but local action, chemical solution of the zinc, and the impossibility of reversibly depositing the latter during charging, render its use impossible. v. Welsbach's cell,

$$\text{Carbon} \mid Ce_2(SO_4)_3 + Ce(SO_4)_2 \mid ZnSO_4 \mid \text{amalgamated zinc},$$

infringed several principles of secondary cell design, particularly in using two fluids and a diaphragm. Many cells with alkaline electrolytes have been proposed, with oxides of copper, silver, nickel, or mercury at the positive pole, metallic zinc, cadmium, cobalt, or iron at the negative; but none have proved successful.

At one time hopes were entertained that the Lalande primary cell[1] would also function satisfactorily as an accumulator, and extensive tests were carried out. But its behaviour during charging was very unsatisfactory: the CuO plate did not behave reversibly, and an energy efficiency of only 35 per cent. to 50 per cent. usually resulted;[2] whilst

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[1] P. 203.

[2] Johnson, *Trans. Amer. Electrochem. Soc.* **1**, 187 (*1902*); and Figure 54.

the zinc deposited with difficulty unless the electrolyte was previously saturated with zinc oxide. Local action, negligible during the short life of the primary cell, played a part, and it was found necessary to surround the CuO plate with a diaphragm; whilst the gradual absorption of atmospheric CO_2 lowered the solvent properties of the electrolyte for ZnO, and led to the latter being slowly deposited in the cell.

2. The Lead Accumulator

The chemical changes taking place in this cell were first made clear by Gladstone and Tribe. When in a condition to furnish electrical energy it consists of the system $PbO_2 \mid H_2SO_4 \mid Pb$. During discharge the lead peroxide is reduced to lead sulphate, and at the other electrode lead is oxidised to lead sulphate. The discharged system is therefore $PbSO_4 \mid H_2SO_4 \mid PbSO_4$. On charging the process is reversed, and the system $PbO_2 \mid H_2SO_4 \mid Pb$ regenerated. The chemical action involved is

$$Pb + PbO_2 + 2H_2SO_4 \rightleftarrows 2PbSO_4 + 2H_2O$$

taking place from left to right during discharge, and from right to left during charge. During charge, therefore, the acid electrolyte becomes more concentrated, during discharge more dilute. The positive pole is the PbO_2 electrode. Positive electricity passes out from it during discharge and enters through it during charge.

Construction.—Accumulators are made in all sizes, from very small elements with two or three plates for experimental work up to cells furnishing 16,000 amp.-hours on discharge and weighing some tons. The containing vessels for the smaller units are of glass, and for the larger ones of lead-lined wood. For transportable cells they are constructed of celluloid or hard rubber. The plates are hung vertically, positives and negatives alternately, similar plates being connected in parallel. Sometimes they are guided by grooves in the sides of the cell. Their distance apart is generally 8–15 mm., being greater the larger the cell. For transportable cells, where the utmost lightness is of importance, this distance may fall to 3–5 mm.

To guard against short-circuiting, glass tubes or rods are inserted between adjacent plates. Between the lower ends of the plates and the bottom of the container is a free space. Besides supplying a reservoir of acid, short-circuiting due to conducting material dropping from the plates is thus avoided.[1] The two end plates are always

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[1] There is an accompanying drawback. The extra layer of liquid decreases the resistance locally in comparison with the resistance between other parts of the plates. The current density thereby proportionately rises, causing concentration differences, and tending to make the plates 'buckle.' See Schoop, *Electrochem. Ind.* **4**, 268, 307 (*1906*).

negatives, as positive plates, if only active on one side, become deformed owing to volume changes during working. The electrolyte is usually H_2SO_4 of S.G. 1·15, a 21 per cent. (weight) solution, but up to S.G. 1·20 can be used.

The Plates.—Accumulator plates consist of (*a*) the supporting and conducting framework, and of (*b*) the active mass. The framework is usually of hard lead, containing 4–6 per cent. antimony, and on to it the active mass is brought by one of two distinct methods. The first is due to Planté, and consists in starting with a solid lead plate of one piece with the framework, and transforming its surface layers either chemically or electrochemically into the PbO_2 or spongy lead required. In the second method, that of Faure, the framework is of somewhat complicated construction, provided with projections, cavities, pockets, etc. In these interstices is placed a paste of suitable materials, and this paste changed electrochemically into PbO_2 or finely divided lead. The process of producing active material on an accumulator plate is (in both cases) termed *forming*, and the layer produced must be sufficiently thick and mechanically strong.

Planté Plates.—In the original Planté process a current was passed between two sheets of lead in dilute H_2SO_4, its direction being frequently reversed. At the one electrode a thin layer of PbO_2 was first produced, hydrogen being liberated at the other plate. On reversing the current, the latter became superficially oxidised, the PbO_2 on the first plate being reduced to spongy lead. This process, many times repeated, finally resulted in the formation on one plate of a layer of PbO_2, on the other of a layer of spongy lead. By thus electrolysing for a year a thickness of about 1 mm. could be reached. Such an active deposit is naturally very strong mechanically, but the process has otherwise two great disadvantages. The capacity of the finished plate is very low, compared with its weight and volume, and the time (and electrical energy) needed for the forming is excessive. As the capacity depends on the total weight (or volume) of active material present, it is evident that it can be increased by increasing

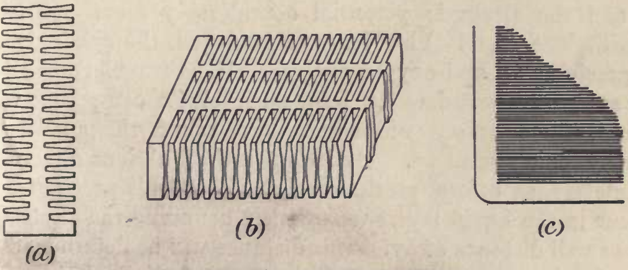

FIG. 56.—Types of Planté Plates.

either the area of lead affected or the thickness of the layer. To increase the latter beyond a certain limit is not desirable. Its mechanical strength is lessened, and the underlying parts are not in good contact with the mass of the electrolyte.

Accordingly it has become usual to employ plates of highly-developed surface for forming. Fig. 56 (*a*) shows in side section the ribbed plate with a solid lead core introduced by the Brothers Tudor. In Fig. 56 (*b*) is shown a plate manufactured by the A.F.A.G. of Berlin-Hagen. The lead core is dispensed with, supporting ribs being used. The weight is thereby decreased, and free circulation allowed to the acid. Fig. 56 (*c*) shows the D.P. (Dujardin-Planté) plate, consisting of parallel lead strips, burnt together at the ends.

Rapid Forming.—The second improvement introduced allows of a far more rapid forming than heretofore. To the dilute H_2SO_4 is added a small quantity of some 'catalyst' such as $HClO_4$, $HClO_3$, HNO_3, SO_2, $CH_3.COOH$.[1] The result is the anodic production of an adherent layer of $PbSO_4$ instead of the PbO_2. This is more porous than the latter, and allows further action to proceed. By thus electrolysing with a current density of about 0·8 amp./d.m.^{2}, as much active material can be produced in a week as by the original Planté process in a year.[2] Before treating the plates further, they must be very carefully washed free from every trace of the addition agent used. Cathodic reduction will then give a plate of spongy lead, and anodic oxidation in dilute H_2SO_4 a plate of PbO_2.

The explanation of the action of the addition agents is that in solutions containing only the one anion SO_4'', the $Pb^{\cdot\cdot}$ ions, on entering solution, are immediately precipitated as a dense non-conducting $PbSO_4$ crust on the anode. Current can only penetrate this with difficulty. At those points where it does so the current density is very high, and the electrode potential considerably more positive than the equilibrium value. $Pb^{\cdot\cdot\cdot\cdot}$ ions are produced, the sparingly soluble PbO_2 precipitated, and oxygen evolved. If, however, a small fraction of the anions present does *not* form an insoluble compound with the $Pb^{\cdot\cdot}$ ions, these anions will accumulate round the anode, carried thither by ionic migration. And though the $Pb^{\cdot\cdot}$ ions dissolving will be ultimately, as before, precipitated as $PbSO_4$, this precipitation will not occur in the liquid layers *immediately* bounding the electrode, but at some small distance away. This distance will be determined by the current density, temperature, and the concentration of the SO_4'' and added ion in the electrolyte. If the ratio $\frac{SO_4''}{\text{added ion}}$ be very great, no appreciable effect will be produced. If it be rather less, then a

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[1] Fischer has suggested phosphoric acid. *Zeitsch. Elektrochem.* **16**, 355 (*1910*).

[2] Methods have been recently so much improved that, by working at high current densities, the whole process of forming can be completed in half a day.

layer of $PbSO_4$ will be formed which, though adherent, is still sufficiently porous to allow electrolytic conduction to take place through it. These are the conditions aimed at during forming. If the ratio be still further lowered, a loose precipitate of $PbSO_4$ will result, which will stream away continuously from the electrode.[1] For an investigation of the influence of current density, temperature, and the concentrations of the electrolyte constituents when using HNO_3, see Just, Askenasy, and Mitrofanoff.[2] Schleicher[3] has published a similar investigation, using chlorate and perchlorate as additions.

In practice, negative lead sponge Planté plates are never used, as the finely divided lead originally present agglomerates together, and the diminution in surface leads in time to a serious diminution in capacity. Negative plates are always pasted, and of about twice the capacity of a positive of equal size. On the other hand, Planté positives are widely used. Owing to their great surface they are particularly suitable for high rates of discharge, and distortion and losses due to volume changes in the active material are negligible. For portable accumulators their weight renders them unsuitable.

Faure Plates.—In Faure plates the holders for the active material are of the most varied description, designed to secure a maximum weight of paste of sufficient mechanical strength, making maximum contact with electrolyte and supporting frame. The construction of the positives and negatives also differs because the positive and negative active materials show opposite volume changes in course of time. Thus, whilst the conversion of $PbSO_4$ to spongy lead or PbO_2 during charging involves an increase of volume in both cases, the negative active mass shows a decrease in volume on standing, the positive material an increase.

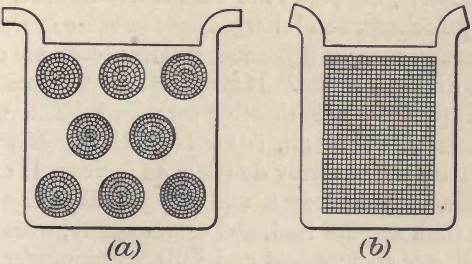

FIG. 57.—Types of Faure Plates.

Fig. 57 (*a*) shows the positive plate of the Chloride Co.'s accumulator, consisting of a lead frame pierced with a number of circular holes,

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[1] See p. 388.

[2] *Zeitsch. Elektrochem.* **15,** 872 (*1909*).

[3] *Ibid.* **17,** 554 (*1911*).

each of which contains a corrugated lead spiral, projecting out for 2–3 mm. on either side of the plate. The interstices in these spirals contain the active mass. Fig. 57 (*b*) shows a plate consisting of a simple lead grating or lattice-work, its meshes being filled with active material. The Tudor negative plates are of this type. Some plates consist almost entirely of active material, and must be discharged very slowly, as the surface of contact of the latter with the lead frame is small, and the resistance consequently high. Further, a rapid rate of discharge, in consequence of the large and rapid volume changes it would produce, would soon lead to disintegration of the plate.

In the case of positive plates of this kind, there is a limit which it is impossible to exceed in increasing the ratio of active material to inactive lead frame. Gladstone and Tribe showed that the positives of an accumulator undergo slow self-discharge, the PbO_2 and the lead of the supporting frame acting as a short-circuited cell. In this way some of the lead of the frame is converted into $PbSO_4$, and, on recharging, into PbO_2. Thus a constant corrosion of the lead grating proceeds, with formation of sulphate and peroxide, and if the grating is initially too weak, the whole plate may later collapse.

The paste with which the plates are treated generally consists of PbO (for positives, Pb_3O_4 can be used), worked up with H_2SO_4 or an $NaHSO_4$ solution. Shortly after pasting on, it sets to a hard mass of basic lead sulphate. The plates are formed electrochemically in a solution of magnesium or aluminium sulphate, kept as nearly neutral as possible. When the reduction to spongy lead and oxidation to peroxide is complete, the plates are washed free from all traces of salts, and alternately discharged and charged once or twice in H_2SO_4. Various organic substances, such as glycerine, gelatine, etc., are often added to the electrolyte during forming. It is claimed that capacity, mechanical strength, and porosity are thereby increased. The way in which these substances act, if at all, is far from clear. Mercury salts are also added. They undoubtedly do effect an increase in capacity. The overvoltage for both hydrogen and oxygen discharge is higher at amalgamated than at pure lead, and consequently, when charging, the useful production of spongy lead and PbO_2 continues for a longer time, gas evolution commencing later.

The great disadvantage of pasted plates is their mechanical weakness. In spite of great care, the active material tends to fall out in time, and particularly so at high current densities, with consequent rapidly succeeding volume changes.

Effect of Impurities.—The purest materials are necessary in constructing and setting up accumulators. The lead must be free from zinc and copper. The H_2SO_4 and active material must contain no HNO_3 or HCl. Otherwise local chemical solution of the lead will be increased, and during charge a certain amount of forming will occur every time at the positive electrode. Iron must be absent, or it will cause a lowering of electrical efficiency, owing to its being alternately anodically oxidised to the ferric state and cathodically reduced to the ferrous condition.[1] Manganese salts behave similarly. And all traces of copper, silver, gold, platinum, or arsenic must be absent. If any one of these is deposited on the lead (all are electronegative to it, and have lower hydrogen overvoltages) local action will be rapidly increased. It must be remembered that lead would dissolve chemically in H_2SO_4, liberating hydrogen, only for the high overvoltage necessary for $H^{\cdot}$ discharge at that metal (even at the spongy metal). A normal cell standing charged loses 1–2 per cent. of its energy content daily, owing to chemical and electrical local action. With a bad electrolyte this can rise to 50 per cent.

Reversible Voltage Relations.—The voltage of the lead accumulator depends essentially on the strength of the acid, and also, to a less extent, on the temperature. Dolezalek found the following values at 15°:

TABLE XXXI

Density of acid	Percentage of acid	Voltage
1·05	7·37	1·906
1·15	20·91	2·010
1·20	27·32	2·051
1·30	39·19	2·142
1·40	50·11	2·233

He showed that these and other figures corresponded very closely to values calculated thermodynamically from the vapour pressures of the acids used. In practice, acid of density 1·15–1·20 is used. The temperature coefficient of E.M.F. is very small, and also depends on the acid concentration, becoming more positive as the latter increases. Our most reliable measurements are due to Dolezalek, and a selection is here given in Table XXXII:

TABLE XXXII

Per cent. H_2SO_4 (by weight)	Density	$\frac{dE}{dT}$
1·57	1·01	$-0{\cdot}00045\ \frac{\text{volt}}{\text{degree.}}$
6·53	1·044	$\pm 0{\cdot}0000$
11·6	1·08	$+0{\cdot}00025$
17·0	1·12	$+0{\cdot}00038$
20·9	1·15	$+0{\cdot}00037$
27·3	1·20	$+0{\cdot}00032$

With very dilute acid the temperature coefficient is negative, becomes zero with acid of S.G. 1·044 ($[H_2SO_4] = 0{\cdot}7$), increases to a maximum

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[1] Cf. pp. 162, 417.

positive value of $0{\cdot}00039 \frac{\text{volt}}{\text{degree}}$ with 1·13 S.G. acid, and slowly falls as the acid concentration further increases. Using the figure for 1·15 S.G. acid, we calculate that the E.M.F. of a technical accumulator will fall from 2·010 volts to 2·004 volts at 0°, and rise to 2·023 volts at 50°.

Charge and Discharge Curves.—The above are all reversible values, and hold only for cells with a negligibly small current. In working cells the relations are rather different. Fig. 58 shows charge and discharge[1] curves for an accumulator working at normal current densities.

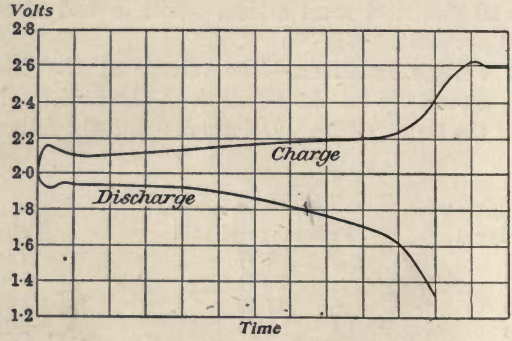

FIG. 58.—Charge and Discharge Curves of Lead Accumulator.

The discharged cell has the normal voltage of slightly over 2·0 volts. On leading in current this rises rapidly to 2·1 volts, slowly increases during the charge, and shortly before the end rises quickly to about 2·6 volts. These changes are accompanied by gas evolution at the plates. Oxygen is already evolved in small quantities at the positive when 2·2 volts are reached, and the liberation of hydrogen at the negative commences at 2·3 volts. Charging is stopped when this hydrogen evolution has become considerable. The voltage then rapidly falls to its normal value. When discharged, the voltage drops quickly at the commencement to about 1·9 volts, and then falls slowly to 1·8 volts. At this point, when it again commences to decrease rapidly, the discharge is stopped. The usual rule is to discharge until the drop in voltage is one-tenth the initial voltage of the cell. Left to itself after discharge, the accumulator rapidly recovers, the voltage rising to its normal value.

Electrical Losses.—It is clear that the voltage difference between charge and discharge curves means that the accumulator stores up

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[1] The discharge curve of an accumulator can be regarded as a particular case of the *polarisation discharge curves* discussed on p. 113, only differing in the quantity of products present on the electrodes.

electrical energy and gives it out again with an efficiency falling considerably below 100 per cent. One could suppose the voltage loss to result from two causes: (*a*) voltage required to overcome the internal resistance of the accumulator, and (*b*) voltage losses from irreversible electrode effects. Owing, however, to the very high conductivity of the electrolyte (accumulator acid has usually a resistance of only $1{\cdot}4\text{–}1{\cdot}5\ \frac{\text{ohms}}{\text{cm.}^3}$), the resistance of technical accumulators is very small, and the difference thus arising between the two curves does not exceed 0·05 volt. The remaining voltage difference, amounting to about 0·2 volt in the above case, must therefore result from some irreversible electrode effect.

This point also has been investigated by Dolezalek, who has shown the polarisation to be undoubtedly due to concentration changes in the electrolyte, occurring at the electrodes. During charge, we know that at the positive electrode $PbSO_4$ is changed to PbO_2, water disappears from the electrolyte, and H_2SO_4 is formed, whilst at the negative electrode $PbSO_4$ is reduced to metallic lead, with formation of H_2SO_4. The effect of charging therefore is to tend to increase the acid concentration at the electrodes. With free diffusion possible between the main bulk of the electrolyte and that in immediate contact with the electrodes, very little effect would be observed, as the quantity of H_2SO_4 thus produced is very small compared with the total acid in the electrolyte. But when, as in the present case, the concentration increase takes place inside the porous masses of lead and PbO_2 which cover the electrodes, diffusion outwards is hindered, and consequently, during charge, the electrodes are in contact with H_2SO_4 of a higher concentration than that in the body of the cell. As the E.M.F. rises with increase in strength of acid, it follows that the voltage of a charging accumulator must exceed that of the same accumulator when idle. During discharge the reverse changes occur, the solution in the electrode pores becomes diluted, and the E.M.F. falls below the reversible value.

The increase and decrease in acid concentration which must be assumed are quite modest. If during charge the concentration in the pores rose to 30 per cent., and during discharge dropped to 10 per cent., this would suffice to explain the voltage differences in Fig. 58. The gradual rise or fall in voltage during working results from increasing difficulty of diffusion between the electrolyte and the inner pores, as the surface layers of the active material become exhausted. When standing, diffusion no longer being counteracted by the production of further concentration changes, equilibrium must quickly be established with the main electrolyte.

This explains the rapid rate at which overcharged and discharged accumulators assume their normal voltage on standing. The polarisation in cells with weak acid exceeds that in cells with strong acid discharged at the same current density. This is to be expected, as the percentage difference in concentration resulting is greater. The structure of the positive plate being much denser than that of the negative, and the concentration changes produced there being greater than those at the negative, would indicate the peroxide plate as the chief contributor towards this polarisation. That is in fact so. Streintz showed that the difference between the electrode potentials at the positive electrode during charge and discharge was about twice as great as that between the negative electrode potentials under the same conditions. Finally, with decrease of current density, the difference between charge and discharge curves continuously diminishes until it practically disappears at low current densities. This simply means that diffusion nullifies concentration changes more quickly than they can be produced by electrolysis. All facts then support the view that the polarisation in working accumulators is essentially concentration polarisation.

Similarly the rapid fall in voltage at the end of the discharge must be ascribed to the same cause. It certainly only depends *indirectly* on the exhaustion of active material, as some of the latter is always present in a discharged plate. The rapid rise in voltage at the end of the charge is caused by the high overvoltage necessary for the discharge of hydrogen and oxygen gases at lead and PbO_2 respectively. We have no exact data for the current densities used, but the 2·5 volts finally required probably consist of 1·2 volts for reversible electrolysis *plus* 0·8 volt for hydrogen overvoltage *plus* 0·5 volt for oxygen overvoltage.

Capacity.—The quantity of energy an accumulator can furnish depends on its capacity as well as on its voltage. An element of high capacity must allow of a good utilisation of the inner layers of the active material. We have seen how this utilisation essentially depends on the possibility of rapid diffusion between the main electrolyte and that contained in the porous mass. Any circumstance favouring this diffusion will increase the cell capacity. The more porous the active material is, the better will be its utilisation. And the higher the temperature, the greater will be the cell capacity. Similarly the capacity will be greater the lower the current density, as then the concentration changes causing polarisation are less rapidly produced, whilst the rate of diffusion remains unaffected. The capacity also depends to some extent on the concentration of the acid, reaching a maximum figure with 30 per cent. acid. The conductivity of H_2SO_4 is also a maximum at this strength, and there is a close connection between these two facts. Stationary cells are now manufactured to give up to 10–15 watt-hours per kilo. (including weight of acid). Transportable batteries furnish up to 30 watt-hours. But the plates contain so large a proportion of paste that they are often too fragile.

In course of time, particularly if the cell stands in a discharged state, the capacity becomes permanently lower, owing to the agglomeration of the finely divided active material. This phenomenon, termed *sulphating*, is particularly marked in the negative plate, and, as we have seen, the original capacity of negatives is made considerably to exceed that of positives for this reason. The process essentially consists in the dissolving of the finer particles of $PbSO_4$ in the electrolyte, and their reprecipitation as larger and more insoluble crystals, possessing relatively much less surface.

Efficiency.—The ampere-hour efficiency of the lead accumulator is usually about 95 per cent. The slight losses are due to self-discharge and local action, and to gas evolution during charging.[1] The watt-hour or energy efficiency depends on the rate of charge and discharge, decreasing as these increase, and is usually 75–85 per cent. The greater part of the loss, as we have seen, is essentially due to concentration polarisation.

Theory.—The theory of the lead accumulator has been fully developed by Dolezalek in his well-known monograph. Some points we have already discussed, and we will here consider two or three other aspects of the question, though anything like a full treatment is impossible. We have seen that for reversibly working galvanic cells the following form of the Gibbs-Helmholtz equation holds, $96540nE - 4{\cdot}19\ U = T\ 96540\ n\ \frac{dE}{dT}$, where U is the heat of reaction of the corresponding chemical change, n the number of faradays corresponding to the same amount of chemical change taking place electrochemically, and $\frac{dE}{dT}$ the temperature coefficient of E.M.F. The value of U for the reaction

$$PbO_2 + Pb + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$$

has been determined by Streintz and by Tscheltzow. They obtained values of 86,800 and 88,800 cals. respectively, figures however which only hold good for very dilute solutions, about $1[H_2SO_4] : 400[H_2O]$. We will take the mean of 87,800 cals. The acid used in practice has S.G. 1·15, and contains $1[H_2SO_4] : 21[H_2O]$. The heat of dilution of this acid to the concentration ratio 1 : 400 is 800 cals. per mol. Hence the value of U for 1·15 S.G. acid is $87{,}800 + 2 \times 800 = 89400$ cals. E as measured at 15° by Dolezalek is 2·01 volts, n is two. If therefore, using the above equation, we calculate $\frac{dE}{dT}$, we have

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[1] On the influence of gas evolution on the capacity, see papers by Rumpf and by Streintz, *Zeitsch. Elektrochem.* **16**, 163, 747 (*1910*).

$$\frac{dE}{dT}=\frac{96540 \times 2 \times 2{\cdot}01 - 4{\cdot}19 \times 89400}{288 \times 96540 \times 2}$$
$$= +0{\cdot}00024\,\frac{\text{volt}}{\text{degree}}.$$

The actual value is $+0{\cdot}00037\,\frac{\text{volt}}{\text{degree}}$, the agreement being excellent considering the nature of the calculation.

A – U being positive—*i.e.* more electrical energy being given out by the accumulator than corresponds to the heat of reaction—it follows that, joule heat apart, heat must be absorbed by the accumulator during discharge and evolved during charge. Direct temperature measurements and quantitative experiments carried out by Streintz by the method described on p. 81 have confirmed this.

The different electrode processes are best considered in the light of the theory first put forward by Le Blanc. According to this view, the following reactions take place during discharge and are reversed during charge:

Positive Electrode—

(*a*) PbO_2 solid $\longrightarrow$ PbO_2 dissolved
$\longrightarrow \text{Pb}^{\cdot\cdot\cdot\cdot} + 2\text{O}''$.
(*b*) $4\text{H}^{\cdot} + 2\text{O}'' \longrightarrow 2\text{H}_2\text{O}$.
(*c*) $\text{Pb}^{\cdot\cdot\cdot\cdot} \longrightarrow \text{Pb}^{\cdot\cdot} + 2\oplus$.
(*d*) $\text{Pb}^{\cdot\cdot} + \text{SO}_4'' \longrightarrow \text{PbSO}_4$ undissociated
$\longrightarrow \text{PbSO}_4$ solid.

Negative Electrode—

(*a*) $\text{Pb} + 2\oplus \longrightarrow \text{Pb}^{\cdot\cdot}$.
(*b*) $\text{Pb}^{\cdot\cdot} + \text{SO}_4'' \longrightarrow \text{PbSO}_4$ undissociated
$\longrightarrow \text{PbSO}_4$ solid.

The total reaction at the positive is then

$$\text{PbO}_2 + 4\text{H}^{\cdot} + \text{SO}_4'' \longrightarrow \text{PbSO}_4 + 2\text{H}_2\text{O} + 2\oplus;$$

at the negative

$$\text{Pb} + \text{SO}_4'' + 2\oplus \longrightarrow \text{PbSO}_4;$$

and in the whole cell

$$\text{PbO}_2 + \text{Pb} + 2\text{H}_2\text{SO}_4 \longrightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}.$$

The positive electrode potential at room temperature will therefore be

$$\mathcal{E}_1 = \text{E.P.}_{\text{Pb}^{\cdot\cdot\cdot\cdot}\rightarrow\text{Pb}^{\cdot\cdot}} + \frac{0{\cdot}058}{2}\log\frac{[\text{Pb}^{\cdot\cdot\cdot\cdot}]}{[\text{Pb}^{\cdot\cdot}]},$$

the negative electrode potential

$$\mathcal{E}_2 = \text{E.P.}_{\text{Pb}^{\cdot\cdot}\rightarrow\text{Pb}} + \frac{0{\cdot}058}{2}\log\,[\text{Pb}^{\cdot\cdot}],$$

and the E.M.F. of the cell

$$\text{E} = \mathcal{E}_1 - \mathcal{E}_2 = \text{E.P.}_{\text{Pb}^{\cdot\cdot\cdot\cdot}\rightarrow\text{Pb}^{\cdot\cdot}} - \text{E.P.}_{\text{Pb}^{\cdot\cdot}\rightarrow\text{Pb}} + 0{\cdot}029\log\frac{[\text{Pb}^{\cdot\cdot\cdot\cdot}]}{[\text{Pb}^{\cdot\cdot}]^2}.$$

Cumming,[1] from experiments with HNO_3 solutions of PbO_2 and $Pb(NO_3)_2$, has determined the value of $E.P._{Pb^{\cdot\cdot\cdot\cdot} \rightarrow Pb^{\cdot\cdot}}$ as + 1·8 volts. The value of $E.P._{Pb^{\cdot\cdot} \rightarrow Pb}$ is – 0·12 volt. The ionic concentrations of $Pb^{\cdot\cdot\cdot\cdot}$ and $Pb^{\cdot\cdot}$ in 1·15 S.G. H_2SO_4 are somewhat difficult to calculate. To calculate $[Pb^{\cdot\cdot\cdot\cdot}]$ we will use an expression[2] deduced by Cumming to express the solubility of PbO_2 in HNO_3, and which will probably furnish fairly correct results for H_2SO_4 also. It is

$$[Pb^{\cdot\cdot\cdot\cdot}] = (\text{acid normality})^4 \times (\text{active mass of water})^2 \\ \times 0{\cdot}00024 \text{ millimols.}$$

To get the active mass of the water, 3·6 per cent. must be subtracted from unity for each equivalent of acid present. 1·15 S.G. H_2SO_4 is 4·88 equivalent normal, and we calculate

$$[Pb^{\cdot\cdot\cdot\cdot}] = 0{\cdot}91 \times 10^{-4} \text{ mols.}$$

The value of $[Pb^{\cdot\cdot}]$ can only be estimated at this concentration by extrapolating from experimental figures for more dilute acids. The most probable value is about $5 \times 10^{-6} \frac{\text{mols.}}{\text{litre}}$. Substituting in the above formula, we have

$$E = 1{\cdot}8 + 0{\cdot}12 + 0{\cdot}029 \log \frac{0{\cdot}91 \times 10^{-4}}{25 \times 10^{-12}} = 2{\cdot}11 \text{ volts}$$

(correct figure 2·01 volts).
The discrepancy of 0·1 volt is not great, considering the assumptions made.

The formula can also be somewhat differently written. We have

$$[Pb^{\cdot\cdot\cdot\cdot}] \times [O'']^2 = K_1,$$

where K_1 is the solubility product of PbO_2.[3] As also $[H^{\cdot}]^2 . [O''] = K_2[H_2O]$ we obtain

$$[Pb^{\cdot\cdot\cdot\cdot}] = \frac{K_1[H^{\cdot}]^4}{K_2^2[H_2O]^2}.$$

Similarly
$$[Pb^{\cdot\cdot}] = \frac{K_3}{[SO_4'']},$$

where K_3 is the solubility product of $PbSO_4$. We have then

$$E = 1{\cdot}92 + 0{\cdot}029 \log \frac{K_1[H^{\cdot}]^4[SO_4'']^2}{K_2^2 . K_3^2[H_2O]^2}.$$

The influence exerted by the acid concentration is thus very clearly shown.

For other important points, particularly details on this effect of acid concentration, the reader is referred to Dolezalek's monograph.

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[1] *Zeitsch. Elektrochem.* **13,** 19 (*1907*).

[2] Really only empirical.

[3] P. 74.

3. The Iron Accumulator

This accumulator, developed to some extent by Jungner, but chiefly by Edison and his co-workers, and usually known as the Edison cell, is the only competitor of the lead accumulator which has to-day even a limited use. It is probable that, as the result of certain constructional improvements, this use will receive a great extension in the near future. The electrochemical system of the charged Edison cell is $Ni(OH)_3$ | concentrated KOH | Fe, the $Ni(OH)_3$ forming the positive pole. On discharge this $Ni(HO)_3$ is reduced to $Ni(OH)_2$, the iron being simultaneously oxidised to $Fe(HO)_2$. The state of the discharged cell is therefore $Ni(HO)_2$ | concentrated KOH | $Fe(OH)_2$. On charging, the reverse action takes place, $Ni(OH)_3$ and iron being regenerated. The equation representing these changes is

$$2Ni(OH)_3 + Fe \rightleftarrows 2Ni(OH)_2 + Fe(OH)_2,$$

taking place from left to right during discharge, from right to left during charge. One important point is at once noticeable in which the lead and iron accumulators differ. Not only is the electrolyte here alkaline and not acid, but no water is separated from or taken up by the plates during the working of the cell.[1] The electrolyte concentration remains practically constant during charge and discharge, and the E.M.F. is almost independent of the same.

The Plates.—In the Edison cell,[2] the active mass is present in a condition corresponding to the Faure pasted plates of the lead accumulator. But owing to its small cohesion, to the large volume changes which take place on working, particularly in the nickel hydroxide plates, and to the fact that the light Edison cells are particularly intended for transport purposes, and are therefore liable to be subject to joltings and rough usage, any kind of open grid arrangement is impossible. The active mass is instead packed into closed containers of thin nickel-plated steel called 'pockets,' pierced with numbers of tiny holes to allow of access of the electrolyte. Plates of extraordinary rigidity and permanence can thus be made, buckling and loss of active material being completely avoided.

Negative Plates.—The negative plate of the new A type of cell (Fig. 59) consists of a nickel-plated steel frame, provided above with a flange for electrical connection with other plates, and containing twenty-four pockets arranged in three horizontal rows. These pockets are rectangular in shape, 3″ × ½″ × ⅛″, and are filled with finely divided iron, made by reducing iron oxide with hot gases. A little mercury is

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[1] For a slight modification of this statement, see p. 240.

[2] For details of construction and working of the latest types of Edison cells, see papers by Holland and others, *Electr.* **64**, 741, 764; **65**, 185; **66**, 47, 83 (*1909–10*).

also added (as oxide, subsequently reduced). This increases the conductivity of the mass when discharged, and has also a markedly favourable effect on the capacity. When the pockets are filled and in position, the whole plate is so compressed that the surfaces of the pockets are no longer plane, but curved. The effect of expansion and contraction during working is thus neutralised, and the active material kept in continual good contact with itself and the conducting steel containers.

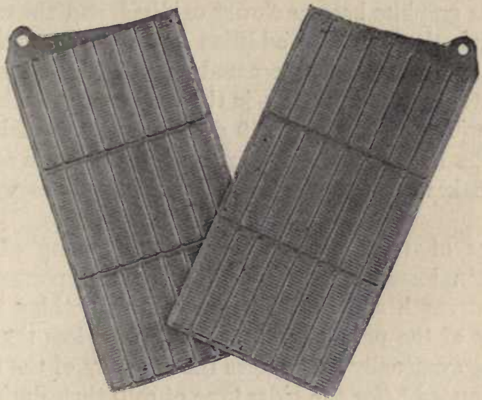

FIG. 59.—Negative Plates of Edison Accumulator.

FIG. 60.—Positive Plates of Edison Accumulator.

Positive Plates.—These were formerly made in the same way, but owing to the exceptionally large volume changes to be dealt with, their mechanical strength proved insufficient. The new construction is shown in Fig. 60. A steel frame contains two rows of fifteen pencil-shaped pockets. These pockets are of nickel-plated steel, about 4″

long and ¼″ in diameter, perforated as before, and provided with a double-lapped spiral seam. They are further strengthened by eight steel rings, closely fitting on the outside. The active filling consists of $Ni(OH)_2$. To increase its conductivity graphite was formerly added (as also in the negative plate). It was however found that, on charging, this graphite became slowly oxidised, and the capacity of the plate consequently fell. The addition now used consists of very thin flakes[1] of electrochemically prepared nickel. These flakes alternate with horizontal layers of $Ni(OH)_2$ in the vertical pencil-shaped tube. A single tube will contain about 350 double layers of nickel and nickel hydroxide, the hydroxide having an average thickness of about 0·01″. The nickel makes contact all around its circumference with the nickel container.

By means of these improvements the capacity of the positive plate has been increased and made much more permanent, and its mechanical strength and durability leave now nothing to be desired. The capacity of the positive is nevertheless far less than that of the negative, and eventually determines the capacity of the cell itself. It has been estimated[2] (for the older type of cell) that, during an average discharge, 75 per cent. of the active material of the positive, but only 10 per cent. of that of the negative, plate is utilised.

General Construction.—As large low-voltage currents are not required for traction work, the Edison accumulator units are of moderate size. As made now, they contain either four, six, or eight positive plates, the number of negatives being one greater. These plates are arranged alternately, a few mm. apart, in suitable grooves in a hard-rubber framework, rods of hard rubber being also inserted between them. All like plates are connected together by nickelled steel rods passing through holes provided in their flanges, and these are in their turn connected with vertical leads of the same material. The whole frame, with its system of plates, is placed inside a container of nickelled sheet steel. The two leads pass up through bushes of hard rubber in the lid of this container, which is also provided with a valve permitting the escape of gases during charge, but preventing entrance of atmospheric CO_2, and with a suitable opening for filling. The electrolyte is 21 per cent. KOH solution (S.G. 1·21). Lately it has been usual to add a little LiOH, which is said to improve the behaviour of the positive electrode. It is difficult to see how this addition is effective.

The electrolyte must be replaced about every twelve months. As there is a continual loss of water due to gassing during charging, and as the quantity of electrolyte in the cell is small in comparison with a lead cell of similar capacity, it is necessary regularly and frequently to add water during working.

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[1] Cf. p. 294.

[2] Gräfenberg, *Zeitsch. Elektrochem.* **11**, 736 (*1905*).

Reversible Voltage Relations.—The E.M.F. of the Edison cell is 1·33–1·35 volts. It is only very slightly dependent on the concentration of the potash, as Foerster has shown between the limits of 0·2 N–6 N. The following are some of his figures for 25°[1]:

Electrolyte	Voltage
5·3 N . KOH	1·3349 volts
2·82 N . KOH	1·3377
1·0 N . KOH	1·351

The temperature coefficient of E.M.F., as measured by Thompson and Richardson,[2] is positive, and increases as the alkali concentration diminishes. They obtained the following values:

$$\begin{aligned}
50 \text{ per cent. KOH } &+0{\cdot}00008 \frac{\text{volt}}{\text{degree}},\\
23{\cdot}8 \text{ per cent. KOH } &+0{\cdot}00026\text{–}0{\cdot}00022,\\
6{\cdot}25 \text{ per cent. KOH } &+0{\cdot}00069.
\end{aligned}$$

The Edison cell will therefore cool slightly during discharge. The resistance of a cell depends somewhat on its size and on the stage of discharge reached, but varies between 0·0015–0·006 ohm.

Charge and Discharge.—The above reversible values for E.M.F. hold good of course only for cells standing idle. When current passes irreversible effects come into play, and these are unfortunately of considerable magnitude in the present case. Fig. 61 contains typical charge and discharge curves, taken at a normal rate. If discharged immediately after charging, the initial voltage is about 1·45 volts.

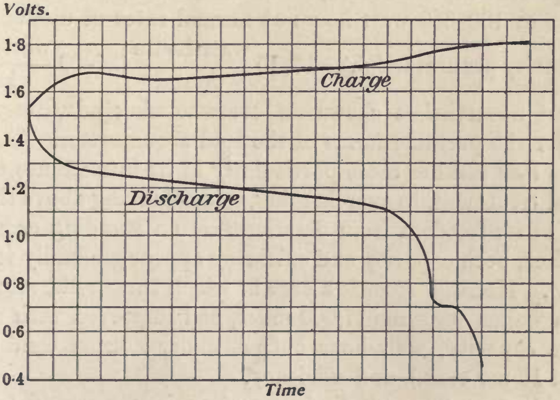

Fig. 61.—Charge and Discharge Curves of Edison Accumulator.

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[1] *Zeitsch. Elektrochem.* **14**, 285 (*1908*).

[2] *Trans. Amer. Electrochem. Soc.* **7**, 95 (*1905*).

This rapidly falls to 1·3 volts, and then drops very slowly during the course of the discharge to 1·15 volts. At this point it begins to fall more rapidly, and drops to zero, showing a second short halt at about 0·7 volt. Under normal working conditions this stage is not reached, the discharge being interrupted when the voltage has fallen to 0·9 volt. On charging, the curve shows a small maximum shortly after the start, and a subsequent continuous rise from 1·65 to 1·8 volt. From the beginning, an evolution of hydrogen, which finally becomes considerable, is noticed at the negative plate. Oxygen evolution at the positive does not commence immediately, but is very brisk before the end of the charge.

Efficiency.—Owing to these facts, the ampere-hour efficiency of the iron accumulator is low—82 per cent. under normal conditions compared with the 95 per cent. of the lead accumulator. It depends largely, however, on the rate of discharge and charge. If these are low, or if a small fraction only of the possible capacity of the cell is utilised, then the ampere-hour efficiency can be much higher. The voltage efficiency is about 72 per cent. (roughly $\frac{1{\cdot}2}{1{\cdot}7}$), and consequently the watt-hour efficiency 59 per cent., whereas that of the lead accumulator averages 80 per cent. The voltage losses are not in this case due to concentration polarisation, but, as we shall see, are essentially connected with the current losses.

As at present manufactured, iron accumulators will furnish 150–300 amp.-hours or 180–360 watt-hours at normal rates of discharge. The energy capacity per unit weight—13–15 $\frac{\text{watt-hours}}{\text{pound}}$ (28–33 $\frac{\text{watt-hours}}{\text{kilo}}$)—is high, but nevertheless shows no overwhelming advantage in that respect over the portable forms of the lead accumulator. The advantage of the iron cell lies more particularly in its indifference to violent mechanical treatment, to overcharging, to discharging above the normal rate, and in its freedom from deterioration on standing or after long use. In fact, both capacity and efficiency appear gradually to increase during use. Holland records a case in which three cells, after helping to drive a wagon for some 17,000 miles, had improved with respect to overcharge capacity, watt-hour output under normal conditions (an increase of 16 per cent.), and efficiency.

Self-discharge.—The self-discharge of an iron accumulator is considerable at first, even 8–10 per cent. in the first twenty-four hours. After that, however, it becomes very much less, and only reaches 15 per cent. after weeks. This initial drop in capacity, which is very sensitive to temperature, is associated with evolution of oxygen from the Ni $(OH)_3$ plate, and is accompanied by the drop in voltage already mentioned. The iron electrode also slowly decreases in capacity, owing to chemical solution of the finely divided metal in the alkali, with evolution of hydrogen. But as the capacity of the negative plate is so great, this self-discharge never becomes noticeable.

Theory.—Our knowledge of the theory of the iron accumulator has in recent years become very complete, chiefly owing to the comprehensive researches of Foerster,[1] though contributions have also been made by others, notably Schoop,[2] Zedner, and Faust. In its simplest form, we can write the equation representing the iron accumulator processes thus—

$$Fe + Ni_2O_3 \rightleftarrows FeO + 2NiO.$$

In that case, the potential of the positive electrode at 18° is given by

$$\begin{aligned}\mathcal{E}_1 &= \text{E.P.}_{Ni^{\cdots} \rightarrow Ni^{\cdot\cdot}} + 0{\cdot}058 \log \frac{[Ni^{\cdots}]}{[Ni^{\cdot\cdot}]} \\ &= \text{E.P.}_{Ni^{\cdots} \rightarrow Ni^{\cdot\cdot}} + 0{\cdot}058 \log \frac{K_1^{\frac{1}{2}}[O'']}{[O'']^{\frac{3}{2}}K_2} \\ &= \text{E.P.}_{Ni^{\cdots} \rightarrow Ni^{\cdot\cdot}} + 0{\cdot}058 \log \frac{K_1^{\frac{1}{2}}}{K_2[O'']^{\frac{1}{2}}},\end{aligned}$$

where K_1 and K_2 are the solubility products of nickelic and nickelous oxides respectively, and $[O'']$ the molar O'' concentration in the electrolyte. Similarly the potential of the negative electrode at 18° is

$$\begin{aligned}\mathcal{E}_2 &= \text{E.P.}_{Fe^{\cdot\cdot} \rightarrow Fe} + 0{\cdot}029 \log [Fe^{\cdot\cdot}] \\ &= \text{E.P.}_{Fe^{\cdot\cdot} \rightarrow Fe} + 0{\cdot}029 \log \frac{K_3}{[O'']},\end{aligned}$$

K_3 being the solubility product of ferrous oxide. Combining these values we obtain

$$\begin{aligned}E &= \mathcal{E}_1 - \mathcal{E}_2 \\ &= \text{E.P.}_{Ni^{\cdots} \rightarrow Ni^{\cdot\cdot}} - \text{E.P.}_{Fe^{\cdot\cdot} \rightarrow Fe} + 0{\cdot}058 \log \frac{K_1^{\frac{1}{2}}}{K_2 \, . \, K_3^{\frac{1}{2}}},\end{aligned}$$

a value for the E.M.F. which is independent of the alkali concentration, and determined only by the electrolytic potentials of the two electrode processes concerned and by the solubility products of the different oxides. We arrive at the same conclusion if, instead of writing the equation as above, we write it as is usually done—viz.:

$$Fe + 2Ni(OH)_3 \rightleftarrows Fe(OH)_2 + 2Ni(OH)_2.$$

Effect of Alkali Concentration.—But we have seen that the E.M.F. really *is* slightly affected by the alkali concentration, and Foerster has shown the explanation to be that the colloidal hydroxides of nickel and iron are, as Van Bemmelen showed, not definite compounds, but rather

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[1] *Zeitsch. Elektrochem.* **13**, 414 (*1907*); **14**, 285 (*1908*); and with Herold, **16**, 461 (*1910*).

[2] *Electrochem. Ind.* **2**, 272, 310 (*1904*).

oxides containing more or less adsorbed or occluded water. A very nearly correct equation is the following:

$$Fe + Ni_2O_3, 1{\cdot}2H_2O + 2{\cdot}9H_2O \leftrightarrows FeO, xH_2O + 2(NiO, y\ H_2O)$$

where $x + 2y = 4{\cdot}1$.

The exact values of x and y are unknown. If we arbitrarily assume that $x = 1{\cdot}5$ and $y = 1{\cdot}3$ (very possible values), we obtain for the total equation

$$Fe + Ni_2O_3, 1{\cdot}2H_2O + 2{\cdot}9\ H_2O \leftrightarrows FeO, 1{\cdot}5H_2O + 2(NiO, 1{\cdot}3H_2O);$$

for the equation representing the reaction at the negative plate

$$Fe + 2OH' + 0{\cdot}5H_2O \rightleftarrows FeO,1{\cdot}5H_2O + 2\ominus;$$

and for the equation at the positive

$$Ni_2O_3,1{\cdot}2H_2O + 2{\cdot}4H_2O \rightleftarrows 2(NiO,1{\cdot}3H_2O) + 2OH' + 2\oplus.$$

The electrolyte as a whole therefore becomes more concentrated on discharge, owing to the absorption of water by the active material; the electrolyte in the neighbourhood of the positive becomes considerably more concentrated, water being taken up and OH′ ions entering solution; and the solution around the negative becomes somewhat diluter, the absorption of water not compensating for the disappearance of OH′ ions. In fact, as Foerster and Schoop have shown, these specific gravity changes can be followed experimentally. The phenomena are reversed on charging. But, compared with the concentration differences produced in the pores of the lead accumulator plates, these effects are small, and do not account for the low efficiency of the iron cell, the explanation for which is furnished by Foerster's studies of the processes taking place at the two electrodes.

Nickel Oxide Plate.—He worked chiefly with 2·8 *n.* KOH and at room temperature. Under these conditions a freshly charged nickel oxide electrode shows an initial potential $\mathcal{E}_h = + 0{\cdot}60$ volt. This falls rapidly at first, then more slowly, till after six weeks it finally reaches the value + 0·47 volt. At this figure it will remain constant indefinitely, and Foerster showed that the value represents the equilibrium potential of the hydrated nickel sesquioxide. The initial potential fall is accompanied by an oxygen evolution, and analysis showed that the freshly charged plate contains considerably more oxygen than corresponds to Ni_2O_3. That this oxygen is not present as adsorbed gas is shown by the fact that it will react with H_2O_2.

If the freshly charged positive plate be discharged, the potential follows a course corresponding with the changes shown by the plate on standing. There is an initial rapid fall of potential (unaccompanied by oxygen evolution), followed by a long discharge during which the potential, though slowly dropping, is almost constant, and about 0·04 volt lower (at a normal rate of discharge) than the equilibrium value for the hydrated Ni_2O_3. Finally it drops rapidly, and there is a second short halt at about $-0·1$ volt. The different stages thus correspond exactly to the stages in the discharge of the accumulator as a whole. This is because a small fraction only of the total capacity of the iron electrode is utilised, the conditions there remaining practically constant throughout. On charging, the potential of the positive plate rises rapidly and then more slowly to about $+0·65$ volt. Towards the end it becomes practically constant. Oxygen evolution begins after some time, and then rapidly increases until it corresponds fully to the current passing.

To explain these phenomena, Foerster assumes that the first process taking place at the positive plate during charging is OH' discharge to oxygen, which at once combines with the depolariser present—viz. NiO. Arguing from certain known analogies the oxide supposed to be thus formed is not Ni_2O_3, but NiO_2. This peroxide then reacts chemically according to the equation

$$NiO_2 + NiO \longrightarrow Ni_2O_3,$$

the sesquioxide resulting from a *secondary chemical* reaction. Anodic polarisation therefore produces a solid solution of NiO, Ni_2O_3, and NiO_2, the proportions of the two latter oxides gradually increasing during the charge. Of these oxides, NiO_2 is unstable, and rapidly evolves oxygen in the pure condition, forming Ni_2O_3. Only the fact that it is dissolved in the sesquioxide (and monoxide) lends it a certain stability and lowers its rate of decomposition. But finally, as the quantity of monoxide decreases, the combination of the two to form sesquioxide is unable to take place so rapidly, the concentration of dioxide in the solid solution grows, and the point is reached at which it begins to decompose appreciably, evolving oxygen. At the same time, also owing to the decreasing quantity of NiO present, the depolarisation of discharged oxygen with formation of NiO_2 takes place less quickly, and some of the gas is liberated in the free state. (Ni_2O_3 depolarises the oxygen discharge, only less readily.)

A state is finally reached in which the active mass consists of a solid solution of NiO_2 in Ni_2O_3. The concentration of NiO_2 is an equilibrium one, determined by equal rates of (*a*) spontaneous chemical decomposition of NiO_2 ($2NiO_2 \longrightarrow Ni_2O_3 + \frac{1}{2} O_2$), and (*b*) reformation by reaction between the Ni_2O_3 and anodic oxygen. The total oxygen evolved corresponds to the total current passing—a small fraction results chemically from the decomposition of the dioxide, the greater part comes from direct anodic discharge. The greater the current density, the quicker the rate of production of NiO_2 from Ni_2O_3—the higher therefore the concentration of NiO_2 in the solid solution.

On interrupting the current, oxygen will be evolved by the activ mass owing to the decomposition of the dioxide. This evolution wi be rapid at first, corresponding to the initial high concentration c NiO_2; later, as this concentration sinks, the gas will be given o more and more slowly, ceasing of course when the active mass contain all its nickel as Ni_2O_3. If, immediately after charging, the plate b discharged, there will be an initial high potential value correspondin to the high NiO_2 concentration, which, as this concentration become less, will continually fall until the value corresponding to Ni_2O_3 i reached.

The short halt at — 0·1 volt Foerster attributes to some other oxid produced during the decomposition of the NiO_2.

The whole explanation, which is amply supported by experimenta evidence, and which accounts satisfactorily for all the phenomen observed, is summarised below.

Charging.

$$\left.\begin{array}{lrcl}\text{(i)} & 2OH' & \longrightarrow & H_2O + O + 2\ominus \\ \text{(ii)} & NiO + O & \longrightarrow & NiO_2 \\ \text{(iii)} & NiO_2 + NiO & \longrightarrow & Ni_2O_3\end{array}\right\}\text{with much NiO present.}$$

$$\left.\begin{array}{lrcl}\text{(i)} & 2NiO_2 & \longrightarrow & Ni_2O_3 + \tfrac{1}{2}O_2 \\ \text{(ii)} & Ni_2O_3 + O & \longrightarrow & 2NiO_2 \text{ (with difficulty)} \\ \text{(iii)} & 2OH' & \longrightarrow & H_2O + \tfrac{1}{2}O_2 + 2\ominus\end{array}\right\}\begin{array}{c}\text{with little or no} \\ \text{NiO present.}\end{array}$$

Standing.

$$2NiO_2 \longrightarrow Ni_2O_3 + \tfrac{1}{2}O_2.$$

Discharging.

$$\begin{array}{ll}\text{(i)} & 2NiO_2 + H_2O \longrightarrow Ni_2O_3 + 2OH' + 2\oplus \text{ (if soon after charge)} \\ \text{(ii)} & Ni_2O_3 + H_2O \longrightarrow 2NiO + 2OH' + 2\oplus.\end{array}$$

Iron Plate.—We have already[1] mentioned Foerster's views on th passivity of iron and similar metals, and how he supposes that whe pure these metals are passive, and only become active when they hav received a charge of nascent hydrogen, the degree of activity corre sponding to the concentration of the hydrogen. In the present case it is well known that finely divided iron is, under ordinary condition passive in alkaline solutions. But if cathodically charged wit hydrogen it becomes active, showing a potential in 2·85 *n.* KOH c — 0·87 volt. It will now readily dissolve anodically, and Foerste and Herold have conclusively shown the electrode process to be

$$Fe + 2\oplus \longrightarrow Fe^{\cdot\cdot} \qquad \text{(i)}$$

the product being ferrous hydroxide.

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[1] P. 142.

At the same time, this anodic polarisation tends to cause the dissolved hydrogen to ionise, and thus diminishes the hydrogen charge in the original iron. Consequently the potential becomes more and more noble, and the metal dissolves less and less easily. Finally, when the limit of $-0{\cdot}75$ volt is reached, passivity sets in and the iron no longer dissolves as $Fe^{\cdot\cdot}$ ions. Another process instead commences—viz.

$$Fe^{\cdot\cdot} + \oplus \longrightarrow Fe^{\cdot\cdot\cdot} \qquad \text{(ii)}$$

involving the transformation of ferrous into ferric hydroxide. (Some ferrous hydroxide will be present, formed electrochemically in the first stage: more will result from chemical interaction between the ferric hydroxide now produced and the finely divided iron. So the total result of this second stage will be the transformation, partly chemical and partly electrochemical, of iron into ferric hydroxide.)

But we know that in an iron accumulator under ordinary conditions the capacity of the iron electrode greatly exceeds that of the nickel hydroxide electrode. Consequently, before the potential of the iron electrode has fallen to $-0{\cdot}75$ volt, the discharge is finished, and the electrode receives a fresh treatment with nascent hydrogen during charging which once more renders it active.[1] The second discharge stage is never reached under normal technical conditions. Foerster and Herold showed, however, that small quantities of iron oxides in the iron powder considerably decrease the capacity of the first stage of the discharge, and accelerate the commencement of the second stage. This is, however, neutralised in the technical cell by the mercury present. The nature of its action is far from clear, but it certainly keeps the capacity of the iron electrode corresponding to stage (i) high and constant, and prevents any production of ferric hydroxide.[2]

On charging, stage (i) is by no means reversed. Hydrogen is evolved very soon after the start and in gradually increasing quantities until it corresponds to the total current passing. The potential rises sharply from the equilibrium value of $-0{\cdot}87$ volt through a slight maximum to about $-1{\cdot}05$ volts, and then gradually during the charge approaches its final value of about $-1{\cdot}15$ volts.[3] We have seen that an increase of hydrogen concentration in the iron makes it less passive—*i.e.* makes its potential less noble. It follows therefore that, as the hydrogen evolution during charge increases, and with it the hydrogen concentration in the iron, the polarisation necessary for the iron deposition must become greater and greater.

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[1] It is observed in practice that, if the charging be carried out at too low a current density, the capacity of the negative during the succeeding discharge is small. The reason is that the potential of the iron depends on the concentration of dissolved hydrogen, and this in its turn on the current density and potential prevailing during charge.

[2] Cf. perhaps its action in the lead accumulator (p. 226).

[3] These figures are for $2{\cdot}8$ *n*. KOH.

If we tabulate the potentials and voltages in the cell during charge and discharge, we obtain the following approximate figures :

TABLE XXXIII

	Charge	At rest	Discharge
Cell	1·65 ⟶ 1·80 (average 1·67)	1·34	1·3 ⟶ 0·9 (average 1·2)
+ Electrode	+ 0·60 ⟶ + 0·65	+ 0·47	+ 0·45 ⟶ + 0·10
− Electrode	− 1·05 ⟶ − 1·15	− 0·87	− 0·85 ⟶ − 0·80

It is clear that much the greater part of the irreversible voltage losses is due to the charging, and that the positive electrode behaves rather better than the negative in this respect. During discharge, on the other hand, the losses are very evenly divided between the two plates, it only being towards the end that the potential of the positive quickly falls off. It is interesting to compare these data with those for the lead accumulator, where the losses are mostly of an entirely different nature (concentration polarisation), are distributed pretty evenly between charge and discharge, and are mostly due to the positive plate.

Literature

Dolezalek. *Theory of the Lead Accumulator.*
Bein. *Elemente und Akkumulatoren.*
Holland. *The 1910 Edison Storage Battery.*

CHAPTER XVII

COPPER—SILVER—GOLD

In this chapter we shall deal with the electrometallurgy of copper, silver, and gold. The very important subject of electrolytic copper refining will be first treated. We shall then discuss in turn the various attempts made to win copper by electrochemical methods from its ores, the electrolytic refining of silver and gold, and the electrolytic modification of the cyanide process for gold extraction.

1. Copper Refining. Theory

We are here concerned with the anodic solution of crude copper in aqueous $CuSO_4$ and its cathodic deposition in the pure state. When copper electrodes are dipped into a $CuSO_4$ solution, the reaction

$$Cu^{\cdot\cdot} + Cu \longrightarrow 2\,Cu^{\cdot} \qquad (a)$$

sets in, and, disturbing influences apart, continues until equilibrium prevails at the surface of copper and electrolyte. The equilibrium constant of this reaction $\left(K = \frac{[Cu^{\cdot}]^2}{[Cu^{\cdot\cdot}]}\right)$ is $0{\cdot}5 \times 10^{-4}$ at room temperature. A molar normal $CuSO_4$ solution may have $[Cu^{\cdot\cdot}] = 0{\cdot}5$, and we calculate $[Cu^{\cdot}] = 0{\cdot}005$. At higher temperatures, the equilibrium moves strongly over in favour of the $Cu^{\cdot}$ ions, and K consequently increases. Thus if acid $CuSO_4$ solution be boiled with finely divided copper powder and filtered, crystals of metallic copper will be deposited on cooling.

Let us now particularly consider a cathode at which the above equilibrium has been set up and persists while current is flowing. Three electrochemical reactions are possible—

$$Cu^{\cdot\cdot} \longrightarrow Cu + 2\oplus \qquad (b)$$
$$Cu^{\cdot} \longrightarrow Cu + \oplus \qquad (c)$$
$$Cu^{\cdot\cdot} \longrightarrow Cu^{\cdot} + \oplus \qquad (d)$$

and it is clear that all must proceed equally easily—otherwise one particular ion would be produced or removed preferentially, and the equilibrium thus become disturbed. The relative magnitudes of the different reactions, determined by the condition that equilibrium persists, will depend on the concentrations of the ions involved. Hence reaction (*b*) will preponderate because of the far greater concentration of the $Cu^{\cdot\cdot}$ ions. Further if $[Cu^{\cdot\cdot}]$ is only varied slightly, reactions (*c*) and (*d*) will take place to an equal extent, otherwise the equilibrium will be disturbed. We see then that the result of the passage of two faradays is the conversion of one $[Cu^{\cdot\cdot}]$ to metallic copper, as the sum of the effects of (*c*) and (*d*) equal the effect of (*b*). Copper is therefore deposited as a di-valent metal in accordance with Faraday's Law.

But if the equilibrium point of the reaction (*a*) is not reached, or is passed, things are different. That electrochemical action will proceed most easily which tends to restore equilibrium. Thus if it were possible to produce near the cathode an excess of $Cu^{\cdot}$ ions beyond the amount demanded by the $Cu^{\cdot\cdot}$ concentration and the constant K, reaction (*c*) would preponderate, and an excess of $Cu^{\cdot}$ ions deposit until equilibrium were reached. The yield would exceed that demanded by Faraday's Law if copper be taken as a di-valent metal. If, on the contrary, the $Cu^{\cdot}$ concentration were below the equilibrium value, reaction (*d*) would commence, tending to restore equilibrium. A lower yield of copper than the theoretical would result. And this last case is important in the theory and practice of copper refining. For efficient working, the $Cu^{\cdot}$ concentration at the cathode must not become low. Now it may fall below the equilibrium value for two reasons. Firstly, the $Cu^{\cdot}$ concentration necessary for equilibrium may be raised as the result of an increase in the constant K, due to a rise in temperature. Secondly, the $Cu^{\cdot}$ ions may be continually removed by some subsidiary chemical reaction. Two such reactions must be taken into account. They are oxidation by atmospheric oxygen,

$$2Cu^{\cdot} + 2H^{\cdot} + \tfrac{1}{2}O_2 \longrightarrow 2Cu^{\cdot\cdot} + H_2O \qquad (e)$$

and hydrolysis of the cuprous sulphate,

$$Cu^{\cdot} + OH' \longrightarrow \tfrac{1}{2}(Cu_2O + H_2O) \qquad (f)$$

In the one case, $Cu^{\cdot\cdot}$ ions are formed, in the other, Cu_2O precipitated.

The effect of different conditions on the *cathodic yield* of metal will now be discussed in the light of the above considerations.

(1) Presence of dissolved oxygen from air. To be avoided as it directly leads to reaction (*e*), and hence to a low yield, owing to the preference thereby given to the electrochemical process (*d*).

(2) Influence of temperature. A high temperature is disadvantageous. It increases the velocity of (*e*), whereby $Cu^{\cdot}$ ions are used up. It favours the right-hand side of the equation (*f*). And lastly, as we have seen, it causes an increase in the constant K. More $Cu^{\cdot}$ ions must be electrochemically produced to satisfy the equilibrium conditions.

(3) $H^{\cdot}$ concentration. A high value increases the rate of (*e*), in

accordance with the laws governing reaction velocity. On the other hand, too low a value allows the hydrolysis (*f*) to take place, with consequent removal of $\mathrm{Cu}^{\cdot}$ ions as insoluble $\mathrm{Cu_2O}$. In practice, an electrolyte containing free acid is always used.

(4) $\mathrm{Cu}^{\cdot\cdot}$ concentration. This should not be *too* high, as, in accordance with the equation $K = \frac{[\mathrm{Cu}^{\cdot}]^2}{[\mathrm{Cu}^{\cdot\cdot}]}$, it would necessitate a correspondingly high $\mathrm{Cu}^{\cdot}$ concentration to satisfy the equilibrium conditions.

(5) Current density. This must not be too low, as it gives a relatively long time for the reactions (*e*) and (*f*) to take place in. On the other hand, it must not become too high.[1] If it does, the copper is produced as a dark-coloured spongy mass which does not adhere to the cathode. Hydrogen is also evolved, owing to exhaustion of the $\mathrm{Cu}^{\cdot\cdot}$ ions, and the resulting lowering of the $\mathrm{H}^{\cdot}$ concentration may cause precipitation of $\mathrm{Cu_2O}$. By using a hot strong $\mathrm{CuSO_4}$ solution, and a low current density, it is easily possible for practically all the current passing to be concerned with the reaction $\mathrm{Cu}^{\cdot\cdot} \longrightarrow \mathrm{Cu}^{\cdot} + \oplus$, and thus for *no* copper to be deposited. If the electrolyte is sufficiently acid, the $\mathrm{Cu}^{\cdot}$ ions are oxidised as in (*e*). In the absence of acid, the hydrolysis (*f*) takes place, and almost pure $\mathrm{Cu_2O}$ results. Table XXXIV, containing figures from the papers of Foerster and Seidel[2] and Schwab and Baum,[3] shows how the current efficiency of copper deposition varies with temperature and current density.

TABLE XXXIV

Temperature	Current density in amps. /metre²									
	0·3	1·0	13·5	30	37	100	120	200	300	400
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
20°	80	90				100		100	100	100
50°				100		100		100	100	100
70°				96		98		100	100	100
90°						91		96	99	99
100°			3	47	60	83	83			

Owing to differences in the electrolytes used, the figures are not all strictly comparable, but only inessential alterations are thereby produced.

From the above discussion, we gather that the best cathodic conditions for copper refining are—

(1) Absence of dissolved oxygen or other oxidising agent.

(2) Low temperature.

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[1] P. 124.

[2] *Zeitsch. Anorg. Chem.* **14,** 106 (*1897*).

[3] *Jour. Phys. Chem.* **7,** 493 (*1903*).

(3) Acid solution.
(4) Moderate $Cu^{\cdot\cdot}$ concentration.
(5) Fairly high current density.

The successful functioning of a copper voltmeter depends of course on the same conditions being observed.

At the anode we have a very similar state of things. The same equilibrium as at the cathode $Cu^{\cdot\cdot} + Cu \rightleftarrows 2Cu^{\cdot}$ strives to set itself up. The participating electrochemical reactions are :

$$\begin{aligned} Cu + 2\oplus &\longrightarrow Cu^{\cdot\cdot} \qquad && (g)\\ Cu + \oplus &\longrightarrow Cu^{\cdot} && (h)\\ Cu^{\cdot} + \oplus &\longrightarrow Cu^{\cdot\cdot} && (k). \end{aligned}$$

The disturbing chemical influences are the same, and the resulting continual removal of $Cu^{\cdot}$ ions tends to be neutralised by the reaction (*h*). Copper therefore dissolves anodically in quantity exceeding that demanded by Faraday's Law, assuming the metal to be di-valent. We have already seen that it deposits cathodically in amounts less than correspond to Faraday's Law. Combining these two facts, it is obvious that the electrolyte must gradually become richer and richer in copper. At the same time it becomes poorer in acid, as at both electrodes $Cu^{\cdot}$ ions are produced and subsequently oxidised throughout the bath according to the equation (*e*). Wohlwill states that the acid consumption is also caused by solution of the finely divided copper[1] in presence of air—thus :

$$Cu + 2H^{\cdot} + \tfrac{1}{2}O_2 \longrightarrow Cu^{\cdot\cdot} + H_2O.$$

One other interesting point must be noticed. The cuprous copper is practically entirely present as the complex anion $CuSO_4'$. We have the equilibria—

$$[Cu^{\cdot}]^2 = K[Cu^{\cdot\cdot}] \text{ and}$$
$$[Cu^{\cdot}] \, . \, [SO_4''] = K_1 \, . \, [CuSO_4'],$$

whence
$$[CuSO_4']^2 = \frac{K}{K_1^2} \, . \, [SO_4'']^2 \, . \, [Cu^{\cdot\cdot}],$$

or, as
$$[SO_4''] = [Cu^{\cdot\cdot}] \text{ (approximately)}$$
$$[Cu_2SO_4]^2 = K_2[CuSO_4]^3.$$

We thus see that the equilibrium quantity of cuprous salt decreases more quickly on dilution than does that of the cupric salt. Consequently when the concentrated equilibrium solution produced at the anode has diffused away a little into the bulk of the electrolyte, it will have become supersaturated with respect to cuprous copper, and the reaction $2Cu^{\cdot} \longrightarrow Cu^{\cdot\cdot} + Cu$ will take place. Finely divided crystals of copper are precipitated and afterwards found in the anode slimes.

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[1] See below.

This phenomenon becomes less and less marked as the current density increases, and it has been suggested that the degree of supersaturation is so great that copper precipitation sets in whilst the cuprous salt is still in the immediate neighbourhood of the anode, and the metal is practically redeposited chemically on the electrode.

For another reason a high anodic current density is desirable—less time comparatively being available for the oxidation and hydrolysis of the $Cu^{\cdot}$ ions. There is a limit, however, to its increase, as, if the $CuSO_4$ solution becomes too concentrated in the neighbourhood of the anode, it will crystallise out with formation of a badly conducting solid layer. A consideration of the anode processes in the electrolysis of a $CuSO_4$ solution between copper electrodes confirms, therefore, the conclusions already reached as to the most favourable working conditions.

In actual copper refining, with the crude metal forming the anode, the conditions are somewhat different, owing to the impurities dissolved anodically, some of which accumulate in the electrolyte. For several reasons it is generally impracticable to electrolytically refine a metal containing less than 97 per cent. copper. The electrolyte quickly becomes foul and needs frequent renewal. And the percentage of unattacked copper remaining in the anode residue is too high. Typical analyses of anode copper are given in Table XXXV:

TABLE XXXV

	American Converter Copper		English		German
	I	II	III	IV	V
Cu	99·25	99·35	98·60	98·24	98·87
Ag	0·34	0·24	0·05	0·10	0·11
Au	0·001	0·02		0·0003	0·0007
Pb	0·01		0·10	0·02	0·08
Bi	0·002		0·05	0·04	0·09
As	0·03	0·02	0·80	0·94	0·39
Sb	0·05	0·007	0·10	0·40	0·34
Fe	Trace	0·01	0·10	Trace	0·05
Ni	0·002		0·10	0·28	0·02
Se + Te	0·01				
Insoluble					0·04
Oxygen	0·30	Present		0·05	
S			0·10	0·03	

Several points may be noticed. The two samples of American metal have more silver and gold than the raw European copper. This is simply because of the nature of the ore. On the other hand, the low percentages of arsenic, antimony, and bismuth are due to the treatment with air in the converter, whereby these substances are driven off as volatile oxides. The impurities in anode copper that must be considered are therefore nickel, iron, lead, gold, silver, selenium, tellurium, arsenic, antimony, bismuth, and sulphur and oxygen present as Cu_2O and Cu_2S. Traces of platinum, zinc, cobalt, and tin sometimes occur.

Behaviour of Anodic Impurities.—The behaviour of these impurities during the electrolysis was carefully investigated by Kiliani,[1] and the great majority of his observations and conclusions have been repeatedly confirmed. Nickel, iron, and lead, together with any zinc, cobalt, and tin which may happen to be present, are electropositive with respect to copper and completely dissolve. As the current is simultaneously removing copper from the electrolyte cathodically, their presence makes the electrolyte poorer in copper. The lead of course is at once precipitated as $PbSO_4$, and is found in the anode slimes. Any tin will slowly come down as insoluble basic sulphate. The other four metals mentioned will collect in the electrolyte. Being so much more electropositive than copper, they will require a far higher cathodic polarisation than does the latter before being deposited on the cathode, and can therefore be allowed to accumulate. Thus, for electrodeposition from a solution of the same normality, nickel requires a cathodic polarisation 0·7 volt greater than does copper. This is partly due to a reaction resistance. A limit to the accumulation of these salts is set, however, by their own solubility, the corresponding depletion of the $Cu^{\cdot\cdot}$ ions, and the alterations in the nature of the cathodic deposit thereby produced.

The following substances less electropositive than copper remain undissolved at the current densities used, and are afterwards found in the anode slimes—Au, Ag, Pt, Se, Te. With high current densities and high percentages of silver, a little of that metal may dissolve, when, if remaining in solution, it would deposit on the cathode. As we shall see, a little HCl or other soluble chloride is usually added to the electrolyte, and the $Ag^{\cdot}$ concentration thus kept exceedingly low.[2] Cu_2S is unattacked and is found in the slimes, whilst Cu_2O partially dissolves. This reaction is probably merely chemical, depending on the acid content of the electrolyte.

The most important impurities, because of their deleterious effect on the properties of the refined copper and the ease with which they enter solution and are cathodically precipitated, are arsenic, antimony, and bismuth. Small quantities—up to 0·8 per cent.—of antimony or arsenic improve the tensile properties of copper; bismuth on the other hand is harmful. But all three metals, even when only a few

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[1] *Berg- und Hütten-Zeit. 1885*, 249, 260, 273.

[2] It should be noted that from Fig. 36 we should expect the anodic silver to dissolve as readily as the copper. We are here, however, dealing with a complex system containing other substances than silver and copper, and a huge excess of the latter metal. It is partly due to the presence of these other metals, which lower the electrolytic solution pressure of the silver, and partly because the anodic polarisation is always kept very low, that the proportion of silver actually dissolving is so small.

thousandths per cent. are present, cause a very considerable fall in the electrolytic conductivity of the copper, its most valuable property, the increasing of which is the very purpose of electrolytic refining. The possibility of the precipitation of these three impurities is clear when we consider the data available on the single potential differences which they show against solutions of the corresponding ion. Neumann[1] using normal solutions of $SbCl_3$, $Bi_2(SO_4)_3$, and $AsCl_3$, to a great extent hydrolysed and with indefinite and very low ionic concentrations, found

$$\begin{array}{ll} As \mid solution & +\ 0{\cdot}27 \text{ volt,} \\ Bi \mid solution & +\ 0{\cdot}21 \text{ volt,} \\ Sb \mid solution & +\ 0{\cdot}10 \text{ volt,} \end{array}$$

whilst for $Cu \mid n.\ CuSO_4$, $\mathcal{E}_h = +\ 0{\cdot}308$ volt. As the potentials, even for very small ionic concentrations and with electrodes of the pure metal, approach so nearly the value for $Cu \mid n.\ CuSO_4$, one can well imagine that, with the discharge somewhat depolarised by the copper cathode, with increased amounts of ionic impurity in solution, or with a low $Cu^{\cdot\cdot}$ concentration at the cathode, or an increased cathodic polarisation, produced by using a high current density, a potential may be reached at which arsenic or bismuth will deposit.

The best remedy is to use anodes containing as little as possible of these constituents. We have seen that converter copper is better than reverberatory furnace copper in this connection. When that is impossible, the ionic concentration of these impurities in the electrolyte must by other means be kept very low.

$As^{\cdot\cdot\cdot}$ ions on entering solution are immediately almost completely hydrolysed as follows:

$$2As^{\cdot\cdot\cdot} + 6OH' \longrightarrow As_2O_3 + 3H_2O,$$

the free $As^{\cdot\cdot\cdot}$ concentration being exceedingly small. As OH' ions are used up, and as copper is simultaneously deposited cathodically, the effect of the presence of arsenic in the anode is to decrease the $CuSO_4$ content and to increase the acidity of the electrolyte. As the concentration of the As_2O_3 increases, it can begin to act as an anodic depolariser, and be oxidised to As_2O_5. The antimony dissolves as $Sb_2(SO_4)_3$. This salt again is very strongly hydrolysed, this time giving a sparingly soluble basic sulphate or oxide. Its effect on the electrolyte is similar to that of arsenic. Bismuth behaves exactly like antimony. The equations controlling the ionic concentrations of these metals are

$$\begin{array}{l} As\,(HO)_3 \rightleftarrows As^{\cdot\cdot\cdot} + 3OH' \\ Sb_2(SO_4)_3 \rightleftarrows 2Sb^{\cdot\cdot\cdot} + 3SO_4'' \\ Bi_2(SO\ \ ) \rightleftarrows 2Bi^{\cdot\cdot\cdot} + 3SO_4''. \end{array}$$

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[1] *Zeitsch. Phys. Chem.* **14**, 193 (*1894*).

To keep the $As^{\cdots}$ content low, the OH' concentration should be high—*i.e.* the $H^{\cdot}$ concentration should be low. On the other hand, the $Sb^{\cdots}$ and $Bi^{\cdots}$ concentrations are essentially determined by that of the SO_4''; and this again, owing to the far greater dissociation of H_2SO_4 than of $CuSO_4$, is chiefly a matter of the H_2SO_4 content. If this is kept high, it favours the non-production of $Sb^{\cdots}$ and $Bi^{\cdots}$ ions, but also favours the *production* of $As^{\cdots}$ ions.

As a matter of fact, owing to arsenic being a much more weakly basic metal than antimony or bismuth, with a smaller ionising tendency, its effect can be neglected in comparison with theirs, and it is found that the bath is best made pretty strongly acid. The concentrations of $Sb^{\cdots}$ and $Bi^{\cdots}$ are also kept low by the presence of the small quantity of soluble chloride already mentioned, which causes the formation of the very insoluble oxychlorides SbOCl and BiOCl. Foerster gives the following figures showing how the last three impurities divide themselves between slimes and electrolyte:

Original anode		Percentage in electrolyte	Percentage in slimes
As	0·059	77 per cent.	23 per cent.
Sb	0·065	39 per cent.	61 per cent.
Bi	0·032	22 per cent.	78 per cent.

The **products of electrolysis** are:

(1) Cathode copper.

(2) Anode residues and slimes.

(3) Impure electrolyte.

The following table contains the extreme analysis figures for ten different samples of *electrolytically refined copper*. The figures in brackets denote the number of samples containing the particular constituents.

Cu		99·85–99·99	Bi	(1)	0·0002
Ag	(5)	0·0001–0·004	Fe	(4)	0·004–0·01
Sb	(7)	0·0008–0·003	Pb	(4)	0·001–0·01
As	(4)	0·001	O	(9)	0·002–0·07

The *anode slimes* will contain first finely divided copper from the reaction $2Cu^{\cdot} \longrightarrow Cu^{\cdot\cdot} + Cu$.[1] Then gold, silver, and platinum, with which will be alloyed more copper. Then sulphur, selenium, and tellurium, in all cases probably combined with copper. Finally, basic bismuth and antimony salts, $PbSO_4$, some AgCl, Cu_2O, and oxides of arsenic. The actual percentage composition of the slimes can naturally vary within wide limits. The nature of the original ore, the previous metallurgical treatment of the anode metal, the composition of the electrolyte, and the current density, are all essential factors in deter-

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[1] See p. 248.

mining their composition. The following Table XXXVI contains the extreme percentage figures of analysis of fourteen different samples :

TABLE XXXVI

Cu	11·01–57·00	Bi	0·34–5·70
Ag	12·90–55·15	Pb	Trace–5·26
Au	0·034–5·1	Te	1·0–3·97
Sb	2·00–7·86	Se	0·39–1·72
As	1·09–3·80	SO_4	5·27–10·68

The *electrolyte* becomes gradually richer in $CuSO_4$ during the electrolysis, and its H_2SO_4 content decreases. The causes have already been discussed.[1] At the same time, nickel and iron sulphates accumulate, as also do Sb, Bi, and As. An analysis of a typical foul solution gave—

Cu	51·8	grams per litre
Fe	13·2	,, ,,
As	14·06	,, ,,
Sb	0·62	,, ,,
H_2SO_4	48	,, ,,

The treatment of both slimes and electrolyte will be shortly discussed.

2. Copper Refining. Practice

Two distinct arrangements of baths and electrodes are used in technical practice. The *multiple system* is employed in Europe and also in the majority of the great American refineries. The *series or Hayden system* is worked, however, in two of the largest American plants—the Nichols Refinery, Brooklyn, and that at Baltimore. In the multiple system, all the anodes in each tank are connected in parallel, also all the cathodes (just as in Fig. 38), and a large number of such units is connected in series. Through each tank therefore flows a heavy current at a low voltage. In the series system the arrangement is as in Fig. 39, the tank being filled with bi-polar electrodes, from one side of which crude metal dissolves, on the other side of which the refined metal is deposited. Each unit carries a much smaller current, but absorbs a far greater voltage than a unit of the multiple system containing the same weight of copper.

Multiple System.—In the multiple system the electrolysis tanks are generally of wood—lead-lined. They vary considerably in size. An average American vat is about 9′ × 3′ × 3′. Those used in Europe are smaller. They are very carefully insulated on glass or porcelain, and are placed so that any leak of electrolyte can be at once detected. The electrodes can be suspended inside the tank either by providing

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[1] Pp. 248, 251.

them with lugs, and allowing these to bear directly on the corresponding busbar and (carefully insulated) on the other side of the tank, or, better, by laying crossbars over the tank, resting on the busbar and on the side of the tank, and from these suspending the electrodes by hooks. This second method has the advantage that, owing to the absence of lugs, a much smaller fraction of the anode remains unattacked after the electrolysis. It averages only 7 per cent., whereas using anodes with lugs, it may easily average 20 per cent. of the original weight. This represents a considerable saving of interest charges, besides meaning less subsequent melting up to new electrodes.

The anodes are of cast copper, and in all large refineries are prepared by a special casting machine. Their size corresponds with that of the vat. In the American refineries, an average anode is 35″ × 22″ × 1·5″. The time they remain in the tanks depends on their thickness and on the current density. To keep down interest charges it is advantageous to make them thin, but the increased labour charges for more frequent renewal must then be reckoned in. An upper limit to the possible current density is set by the percentage of impurities present. Only with comparatively pure anodes are high current densities and therefore quick working possible. The average duration of treatment in American practice has been recently much reduced, and is now 20–24 days.

The cathodes are prepared electrolytically in separate tanks, often in the ‘regenerating tanks.’[1] The metal is deposited on a sheet of pure rolled copper, which has been lightly coated with graphite or grease to facilitate subsequent removal. The length and breadth of the electrode are the same as those of the anodes. The thickness is far less, generally 1–2 mm. and never exceeding 3 mm. They require about two days to make, and are in the refining tank for one to two weeks. A unit of the size described will contain about 23 cathodes and 22 anodes arranged alternately, the distance between adjacent electrodes being 1½–2″. It will carry about 4000 amperes at 0·3 volt. Some hundreds of such units will be arranged in series, and driven off one generator.

The circulation of the electrolyte is an important matter. Methods have been proposed and indeed employed involving the blowing of air into the electrolyte. It must be emphasised that such methods, as they bring about a continual oxidation of the cuprous copper in the solution, are essentially irrational. The current efficiency of the process is lowered and the increase of $CuSO_4$ concentration, and consequent deterioration of the electrolyte, accelerated, as has already been discussed. The system generally adopted is gravity circulation. The electrolyte flows out of the lowest set of baths into a supply tank, where it is reheated to the working temperature by leaden steam coils, and thence pumped

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[1] See p. 257.

up to the highest level again. The velocity of circulation depends on the working conditions. With large current densities, associated perhaps with the use of high-quality anodes, or at low working temperatures, or with low copper concentrations, the rate of flow must be greater. If again the electrolyte traverses a large number of vats before again reaching the heating and supply tank, the rate of circulation should be greater, owing to the cooling which otherwise would take place. The temperature is of course partly kept up by the current.

Electrolyte.—The composition of the electrolyte is determined by several factors. A high $CuSO_4$ concentration is favourable, as there is then less chance of cathodic deposition of impurities, or of a non-adherent copper deposit being produced. And higher current densities and a lower rate of circulation of the electrolyte may be used. But it must not be too high, as a correspondingly high $Cu^{\cdot}$ concentration is necessary for equilibrium, to reach which entails current losses. Further there is a danger of crystallisation of copper sulphate at the anode. The electrolyte almost universally used contains about 16 per cent. of $CuSO_4, 5H_2O$ crystals.

A high H_2SO_4 concentration is advantageous because (i) of the increased conductivity thus obtained; (ii) it lowers the $Bi^{\cdot\cdot\cdot}$ and $Sb^{\cdot\cdot\cdot}$ concentrations; (iii) it prevents precipitation of Cu_2O and consequent current losses. A limit to its increase is set by its effect in (*a*) diminishing the solubility of $CuSO_4$; (*b*) increasing the $As^{\cdot\cdot\cdot}$ concentration; (*c*) rendering cathodic $H^{\cdot}$ discharge more easy. In practice 6–10 per cent. H_2SO_4 is present. We have already mentioned the customary addition of a little NaCl, $MgCl_2$, or HCl. In one particular refinery, the chlorine concentration is kept at 0·04 $\frac{\text{gram}}{\text{litre}}$. Besides keeping the $Sb^{\cdot\cdot\cdot}$, $Bi^{\cdot\cdot\cdot}$, and $Ag^{\cdot}$ concentrations low, it seems to stop the formation of nodules on the cathode. Finally, the addition of $(NH_4)_2SO_4$ is stated to work well if much arsenic be present. The composition of the electrolyte is constantly controlled, determinations being made of conductivity, acidity, and copper.

Temperature.—A high working temperature is advantageous, on account of the higher conductivity of the electrolyte and the increased rates of diffusion, which allow of higher current densities being used. On the other hand, more cuprous copper is needed for equilibrium at the electrodes, which means current losses and a larger amount of copper in the anode slimes. And the rate of oxidation of the $Cu^{\cdot}$ ions and the deterioration of the electrolyte thereby caused are increased. In America it is customary to work at 40°–50°, in many European refineries at about 35°.

Current Density.—This all-important question is decided by a consideration of the following points. If it is high, the rate of working is rapid, and there is a consequent saving in space and in interest charges. It is favourable to the electrolysis in that it brings about the establishment of a smaller $Cu^{\cdot\cdot}$ concentration at the cathode, a smaller $Cu^{\cdot}$ concentration being thus needed ; also because it allows proportionately less time for the oxidation of $Cu^{\cdot}$ to $Cu^{\cdot\cdot}$ ions, and gives an anode slime containing a smaller copper percentage. But too high a current density may lead to hydrogen evolution and to the production of spongy copper and Cu_2O at the cathode, also to the deposition of such impurities as Bi, As, and Sb. With impure anodes it may cause material to dissolve which otherwise would enter the slimes (*e.g.* silver). It may further cause crystallisation of copper sulphate on the anodes, and in any case necessitates a more rapid circulation of the electrolyte. It also, of course, increases the voltage and the necessary energy expenditure.

In view of these conflicting influences it is not surprising to find that current densities used in practice in the multiple system vary very considerably. In the Norddeutsche Affinerie in Hamburg, the current density is 0·4–0·5 amp./dm.^{2}. In certain American refineries, where very pure anodes are used and power is cheap, current densities up to 4·3 amp./dm.^{2} have been employed. If still further increased, spongy copper begins to be deposited. The average American practice is 1–2 amps./dm.^{2}. In England and on the Continent it is rather less.

Voltage.—The voltage difference across an average multiple system vat is 0·2–0·25 volt, and rarely exceeds 0·3 volt. Of this, the polarisation voltage, due to the difference between composition of anode and cathode, amounts to about 0·02 volt. The greater part of the remainder is spent in overcoming the ohmic resistance of the electrolyte, but a considerable fraction is nevertheless due to defective contacts. According to Magnus,[1] this loss may even amount to 20 per cent. of the total potential drop across the tank.

An elaborate investigation was carried out by Schwab and Baum[2] on the effect of changes of current density and temperature on voltage and current efficiency in copper refining. The electrolytes used were acid $CuSO_4$ solutions of concentrations employed in practice, and the copper electrodes were placed 1 cm. apart. Fig. 62 expresses the relationships existing between voltage, current density, and temperature. During the current efficiency tests it was found that even at 70°, working with technical current densities, excellent current efficiencies of practically 100 per cent. resulted. The contrary results of Foerster and Seidel[3] are easily explained by their using much lower current densities. With Schwab and Baum, the ratio $\frac{\text{anode loss}}{\text{cathode gain}}$ which determines the rate of deterioration of the electrolyte was only 1·01–1·02 at 70°

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[1] *Electrochem. Ind.* **1**, 561 (*1903*).

[2] *Jour. Phys. Chem.* **7**, 493 (*1903*).

[3] *Zeitsch. Anorg. Chem.* **14**, 106 (*1897*).

and with high current densities. Fig. 63 gives the relations between the K.W.H. necessary for the production of one kilo. of copper, current density, and temperature. They finally deduced that, working with the series (Hayden) system, with a current density of 3·5–3·75 amps./dm.^{2}, and with covered tanks to avoid loss of heat, after taking all charges into account, 70° is the best economic working temperature. This conclusion has however been received with criticism in technical circles.

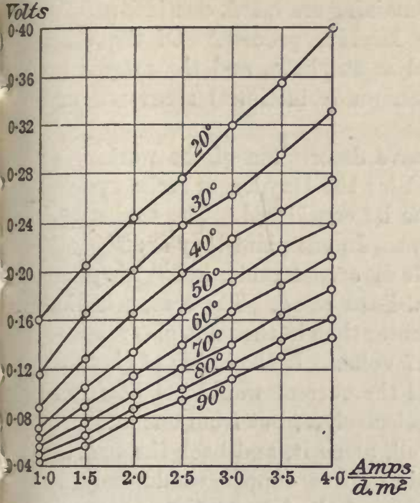

FIG. 62.

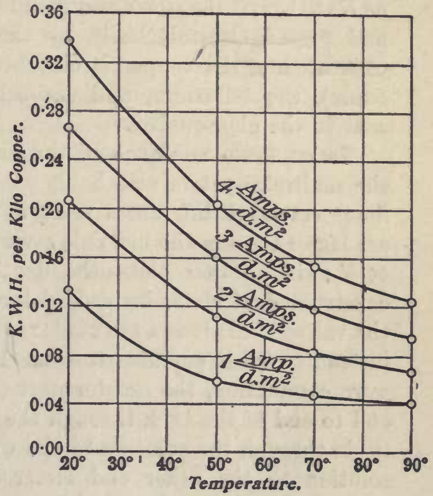

FIG. 63.

During the process of refining, the electrolyte steadily deteriorates. The H_2SO_4 is gradually neutralised, and impurities accumulate which will finally deposit on the cathode. *Regeneration* is necessary. To correct the acid concentration, the whole electrolyte is often circulated through a certain number of baths which contain copper cathodes and insoluble lead anodes. At the latter, oxygen and H_2SO_4 are liberated, whilst the cathodic reaction is utilised for the production of copper cathodes for the refining tanks. Thus both the H_2SO_4 and $CuSO_4$ concentrations are corrected. About 2–2·5 volts are absorbed in these tanks, which may amount to 1 per cent. of the total number. To avoid undue accumulation of impurities such as As, Sb, Bi, Fe, Ni, etc., some 20–30 per cent. is periodically withdrawn and treated in various ways according to local circumstances.[1] The copper may be electrolysed out. Or the acid may be neutralised by passing the hot liquors together with air over shot copper, and the copper content of the solution removed by crystallisation as $CuSO_4, 5H_2O$, and finally by treatment with iron. Having removed

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[1] See, for example, *Metall. Chem. Engin.* **9**, 154 (*1911*).

the copper, the residue may be discarded or worked up for As, Sb or Bi by blowing in air in the hot; and nickel sulphate may be recovered.

The anode slimes are generally first treated with hot H_2SO_4 and air blown in. Cu, As, Sb and Bi are thus largely dissolved. The undissolved portion is washed and cupelled with the addition of some lead. Se and Te are removed from the residue by fluxing with Na_2CO_3 or $NaNO_3$, and the silver and gold remaining are fused, cast into anodes, and parted electrolytically by the Moebius process.[1] Of the other constituents, the copper is obtained as sulphate, and the arsenic (as oxide), the tellurium, and the selenium (sometimes) recovered and sent to the glass-maker.

Series System.—Much of the above description of the working of the multiple system also holds good for the Hayden or series system. Some essential differences must now be considered. The tanks used are larger than in the multiple system. In one plant they are 16′ × 5′ × 5′; in another plant the depth is considerably less. They are constructed of slate, instead of lead-lined wood. The reason is that the voltage fall along a tank is far greater than in the multiple system—instead of 0·3 it amounts to some 17 volts. If the lining of the tank were conducting, the greater part of the current would not flow from end to end of the tank through the electrolyte, but from one end electrode through the solution to the wall, along it, and back through the solution to the other end electrode. Thus copper would only be deposited on the end cathode, on none of the intermediate ones. As it is, there is always a certain current loss through part of the current flowing directly down the tank from end anode to end cathode, and thus doing the minimum amount of chemical work. *The gain in weight of the end cathode always exceeds the gain in weight of any intermediate cathode.*

The series system requires no special cathodes.

On the other hand, the anodes need careful preliminary treatment. They must, to begin with, consist of good quality copper which easily dissolves anodically, leaving only a small residue.[2] Otherwise portions remain unattacked, and the cathodic deposit which forms on the other side of the disappearing anode is liable to be dissolved. For the same reason all surface and structural irregularities must be avoided, and it is found necessary to employ copper plates which have been rolled and finally hammered. This treatment still further restricts the nature of the anode material, as certain kinds of copper, otherwise suitable for refining, cannot be worked mechanically.

A bath of the dimensions given will contain 100–200 bi-polar electrodes, placed 1–2 cm. apart. They are generally 6–8 mm. in thickness, and about 60 cm. square. They fit into slots, cut into suitable

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[1] See p. 266.

[2] This condition, as we have seen, can be fulfilled in America.

wooden uprights, and are thus kept vertical. Their edges are smeared beforehand with some grease, which assists the subsequent detaching of the finished cathodes from the anode residue, the great bulk of which consists of the unattacked portions protected by the slots. The end anode is often made of lead for the purpose of correcting the acid concentration. Owing to the proximity of adjacent electrodes, the voltage drop between each pair is low—0·13 volt. With 130 in series the voltage along the bath is 17 volts, and assuming a current density of 1·9 amps./dm.^{2} the current carried by such a series will be $36 \times 1{\cdot}9 = 68$ amperes. In some cases, several such series of electrodes are connected in parallel in the one bath, thus increasing the current taken by a single unit. Owing to the smaller thickness of the anodes, the time during which they remain in the bath is less than in the multiple system. It averages about twelve days.

The electrolyte used is of much the same composition as in the multiple process. Less of it is needed for the same weight of electrode copper, and it must be circulated more rapidly and regenerated more often. The current density employed is seldom below 1·6 amps./dm.^{2} and is generally nearer 2 amps./dm.^{2}. Owing to the compactness of the plant, close proximity of the electrodes, etc., the heat produced by the current is more effective in keeping the temperature up than in the multiple system, and the working temperature is a little higher, averaging about 50°.

Comparative.—The first advantage which the Hayden process possesses over the multiple process is an economic one. For the same copper output, a smaller plant is needed with less electrolyte, the weight of anodes locked up is far less, as is also the percentage of unattacked anode at the end of the electrolysis, and most of the copper leads and busbars are avoided. No special cathodes need be prepared. On the other hand, the process is less adaptable and needs careful supervision. Copper anodes of moderate or poor quality cannot be used, and, owing to the need for their corrosion to be absolutely uniform, very high current densities cannot be employed. The electrodes require more frequent changing, and the electrolyte more rapid circulation and more frequent regeneration. Above all, the preliminary preparation of the anodes is tedious and costly.

The *current efficiency* of the multiple system is decidedly better than that of the series system, being generally 96 per cent., whereas the latter furnishes only 90 per cent. The deficiency in both cases is chiefly due to short circuit and shunt current losses, and these are far greater in the series process. But, on the other hand, the *voltage* drop per pair of electrodes is about twice as great with the multiple as with the series system—0·25 volt as against 0·13 volt. Hence the multiple process requires $\frac{0{\cdot}9}{0{\cdot}96} \times \frac{0{\cdot}25}{0{\cdot}13} = 1{\cdot}8$ times as much electrical energy as does the Hayden process for the refining of the same weight of copper. When all allowances have been made for losses in leads and in the dynamos it is found that about 150 K.W.H. are needed with the series system and about 300 K.W.H. with the multiple system for the production of one ton of refined copper. Against this must be set the cost of preparing the anodes and the small adaptability of the Hayden system. This last reason makes it exceedingly improbable that it will ever be introduced into Europe.

3. Copper Extraction

Marchese Process.—In striking contrast to the present position of copper refining stands the problem of electrolytic production of pure copper from its ores without the intermediate formation of crude metal. We have seen that a chief essential to the success of an electrolytic process is that the electrolyte shall be pure and of constant composition, and this condition is the main obstacle which has prevented the success of the hitherto proposed processes. The Marchese process is a striking example. The proposal was to use anodes cast from copper-iron matte, in a solution containing $CuSO_4$, $FeSO_4$ and free H_2SO_4, copper being deposited cathodically. It was hoped that the anodes would dissolve easily, partly by direct oxidation and partly by the action of the ferric salt present, and that sulphur would be deposited. The process was tested on a large scale,[1] but proved a complete failure. As electrolyte was used the liquor obtained by extracting the matte with dilute H_2SO_4, and containing free acid, $CuSO_4$, $FeSO_4$ and $Fe_2(SO_4)_3$—about 27–28 grams Cu and 15 grams Fe per litre. The anodes, which were cast with difficulty, had the composition: Cu 15–16 per cent.; Pb 14 per cent.; Fe 41–42 per cent.; S 25 per cent. (on another occasion Cu 30 per cent.; Fe 40 per cent.; S 30 per cent.). On the passage of a current the phenomena occurring are rather complex. As Egli[2] has shown, Cu_2S dissolves anodically as follows:—

$$(a)\quad Cu_2S + 2\oplus \longrightarrow Cu^{\cdot\cdot} + CuS$$
$$(b)\quad CuS + 2\oplus \longrightarrow Cu^{\cdot\cdot} + S.$$

This behaviour appears to be general[3] for metallic sulphide anodes in acid solution. We therefore also have

$$FeS + 2\oplus \longrightarrow Fe^{\cdot\cdot} + S$$
$$PbS + 2\oplus \longrightarrow Pb^{\cdot\cdot} + S.$$

Further, $Fe_2(SO_4)_3$ is present in the electrolyte, and more is formed by

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[1] Cohen, *Zeitsch. Elektrochem.* **1**, 50 (*1894*).
[2] *Zeitsch. Anorg. Chem.* **30**, 18 (*1902*).
[3] Bernfeld, *Zeitsch. Phys. Chem.* **25**, 46 (*1898*).

anodic oxidation of $FeSO_4$. This will act chemically,[1] dissolving both Cu_2S and CuS. Finally, the FeS will be attacked by the H_2SO_4.

Experience showed that the sulphur produced anodically adhered very closely to the electrode. The resistance thus introduced caused increased voltages—sometimes a rise from one volt to five volts. The anodes dissolved unequally, and fragments continually broke off. Low current densities—0·3 amp./dm.^{2}—had to be used. Finally, the electrolyte rapidly deteriorated. Acid was consumed, the iron content increased, and various impurities (Bi, Sb, etc.) dissolved and contaminated the copper deposit.

Mansfeld Experiments.—In view of the ill success of the above process, a recent communication[2] dealing with large scale experimental trials carried out at Mansfeld is of interest. This process is based on a patent[3] of Borchers, Franke, and E. Günther. The copper ore (sulphide) is concentrated by blowing in a Bessemer converter (the SO_2 being worked up to H_2SO_4) until it contains $>$ 72 per cent. Cu, and as nearly as possible 78–80 per cent., which about corresponds to pure Cu_2S. Concentration beyond this limit results in a loss of silver. This rich matte is cast into anodes and refined in an acid $CuSO_4$ solution. In practice the best results are obtained with anode material containing 72–76 per cent. Cu. As, Sb, Bi are almost entirely absent. The chief difficulty is the deposition of sulphur; but using a current density of 0·5 amp./dm.^{2} and agitating the electrolyte, the voltage could be kept steadily below one volt even with a tolerably thick sulphur layer. The best electrolytic copper is produced. These results were given by a plant capable of producing twelve tons of copper per week. If one compares the composition of the anodes employed with those used in the Marchese process, one can well suppose that a pure copper will result and that most of the disturbances of the Marchese process will not be felt. It is not clear, however, in view of the trouble caused before by the layer of sulphur, how this difficulty has been so completely overcome. Probably the anodes, which can be readily cast, are much thinner.

Processes Employing Insoluble Anodes.—To avoid using an impure anode, with the consequent fouling of bath and of cathode deposit, the ore or matte can be lixiviated separately for the preparation of the electrolyte, and an insoluble anode used for the electrolysis. A higher voltage is naturally required than when using a soluble copper-rich anode. This treatment has also been applied to ores too poor in copper to be smelted. The processes[4] of **Keith, Carmichael,** and **Laszczynski** make use of electrolytes obtained by lixiviation of cal-

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[1] Thompson, *Electrochem. Ind.* **2**, 225 (*1904*).

[2] *Metall.* **5**, 27 (*1908*).

[3] D.R.P. 160,046 (*1904*).

[4] *Electrochem. Ind.* **1**, 274 (*1903*); *Metall.* **3**, 820 (*1906*); *Electrochem. Ind.* **5**, 421 (*1907*).

cined copper ores containing up to 5 per cent. copper with dilute (5 per cent.) H_2SO_4. Some iron usually dissolves, however carefully the ore has been roasted. The filtered electrolyte may contain 2–5 per cent. Cu, and some free acid (perhaps 1 per cent.). The anodes are of lead,[1] which soon become coated with PbO_2; the cathodes of graphitised lead or thin copper sheet. A cathodic current density of 0·5–1 amp./dm.^{2} can be used; a higher one gives a spongy deposit. The current efficiency is 90–100 per cent. To keep it to this figure, the copper content of the electrolyte must not fall below 1 per cent.[2] When it reaches this value, the liquors, now containing up to 5 per cent. free H_2SO_4, are withdrawn and used for lixiviating fresh ore. The voltage needed depends on the current density, composition of electrolyte, arrangement of electrodes, etc. It is generally 2·2–2·5 volts.

In the Carmichael process the electrolyte is impregnated with SO_2. The sulphite ion HSO_3' is formed ($OH' + SO_2$), and depolarises, although not rapidly,[3] the OH' discharge at the anode, the reaction

$$HSO_3' + OH' \longrightarrow H^{\cdot} + HSO_4' + 2\ominus$$

taking place. In this way the voltage can be kept at 1·5 volts. The SO_2 also has the advantages of reducing any ferric iron present, thus raising the current efficiency, and of regenerating H_2SO_4 in the bath (according to the above equation). This is necessary, as some is always lost in the lixiviation because of the presence of CaO, etc.

Assuming for these processes an average current efficiency of 95 per cent. and a voltage of 2·4 volts,

1 ton of copper requires

$$\frac{96540 \times 100 \times 1000 \times 1000 \times 2{\cdot}4}{95 \times 31{\cdot}8 \times 1000 \times 3600} \text{ K.W.H.}$$
$$= 2130 \text{ K.W.H.}$$

And one H.P. year would produce 3·1 tons copper. Economically these processes must compete with wet chemical methods (precipitation by iron, etc.), followed by subsequent refining. We cannot further discuss here the conditions for their success or otherwise. The Laszczynski process is at present operated in Poland and in Siberia. The Keith and Carmichael processes are no longer worked.

Siemens-Halske Process.—Two other distinct processes of considerable interest have been proposed for the electrochemical extraction of copper, have received exhaustive trials, but have been abandoned. In

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[1] In the Laszczynski process surrounded by closely fitting diaphragms of flannel or thick cotton cloth, which practically prevent the oxidation of the ferrous iron present in the liquors.

[2] See also Thompson, *Electrochem. Ind.* **2**, 225 (*1904*).

[3] According to Reinartz [*Metall.* **5**, 202 (*1908*)] some 65 per cent. of the total current is thus employed in oxidising the SO_2.

the Siemens and Halske process the calcined ore was lixiviated with (essentially) a $Fe_2(SO_4)_3$ solution containing free acid. The main reaction occurring is

$$Cu_2S + 2Fe_2(SO_4)_3 \longrightarrow 2CuSO_4 + 4FeSO_4 + S.$$

The resulting liquor free from $Fe^{\cdot\cdot\cdot}$ ions entered the cathodic compartment of the cells. There the copper was deposited. It then flowed through a diaphragm into the anode compartment. There, though using an insoluble anode, no gas is evolved, but the reaction $Fe^{\cdot\cdot} + \oplus \longrightarrow Fe^{\cdot\cdot\cdot}$ takes place. $Fe_2(SO_4)_3$ is regenerated, and the liquor is thus ready again for the lixiviation tanks. The total reaction in the cell for the passage of two faradays is

$$CuSO_4 + 2FeSO_4 \longrightarrow Fe_2(SO_4)_3 + Cu \qquad \text{or}$$
$$Cu^{\cdot\cdot} + 2Fe^{\cdot\cdot} \longrightarrow 2Fe^{\cdot\cdot\cdot} + Cu.$$

Electrochemically the process is simple and ingenious, and the actual electrolysis went very smoothly. Copper cathodes were used, taking 0·16 amp./dm.^{2}; the anodes were of lead or of carbon. The electrolyte when entering the cathode chamber contained 3–5 per cent. Cu. About two-thirds were removed before entering the anode compartment. The voltage was 0·7 volt. The decomposition voltage can be calculated thus:—

$$\text{At cathode E.P.}_{Cu^{\cdot\cdot} \rightarrow Cu} + 0{\cdot}33 \text{ volt.}$$
$$\text{At anode E.P.}_{Fe^{\cdot\cdot\cdot} \rightarrow Fe^{\cdot\cdot}} + 0{\cdot}71 \text{ volt.}$$

The copper concentration we will assume 3 per cent., which corresponds to $[Cu] = 0{\cdot}5$ and $[Cu^{\cdot\cdot}]$ about 0·1. Hence

$$\mathcal{E}_{Cu^{\cdot\cdot} \rightarrow Cu} = +0{\cdot}33 + 0{\cdot}029 \log 0{\cdot}1$$
$$= 0{\cdot}30 \text{ volt.}$$

Similarly we may assume $[Fe^{\cdot\cdot}]$ and $[Fe^{\cdot\cdot\cdot}]$ to be approximately equal. In that case $\mathcal{E}_{Fe^{\cdot\cdot\cdot} \rightarrow Fe^{\cdot\cdot}} = \text{E.P.}_{Fe^{\cdot\cdot\cdot} \rightarrow Fe^{\cdot\cdot}} = 0{\cdot}71$ volt, and the decomposition voltage is $0{\cdot}71 - 0{\cdot}30 = 0{\cdot}41$ volt. The difference between this value and the working value is due to the electrolyte and diaphragm.

The difficulties which led to the abandonment of this process were two. No suitable diaphragm could be found—they were not sufficiently durable and offered too great a resistance to the current. Then came the great difficulty of regulating and co-ordinating the calcination and lixiviation of the ore with the electrolysis. The latter demands a regular supply of electrolyte of constant composition, which, with ores of varying composition, undergoing the ill-defined and uncertain operation of roasting, is hard to guarantee. In any case, lixiviation is very slow, and the ore must be exceedingly finely ground and the liquor sometimes filtered. Neither difficulty is perhaps unsurmountable. The question of diaphragms has received much attention during the last few years, whilst, provided that the supply of ore available were of pretty constant composition, one could expect the difficulty of the electrolyte to be overcome. It should be mentioned that the anodes sometimes gave trouble : lead became oxidised with formation of PbO_2 and an increase in voltage, whilst carbon disintegrated and oxidised away. This is closely connected with variations in the electrolyte composition. If the $Fe^{\cdot\cdot}$ concentration becomes too low, then oxygen will be evolved and the disturbances will commence.

Thompson[1] has investigated certain features of this process. He studied the solvent powers of $Fe_2(SO_4)_3$ and H_2SO_4 on various possible products of calcination, and the relations existing during the electrolysis between current density, current efficiency, and concentration.

Hoepfner Process.—This process[2] resembled in some respects the one just described. Finely-ground ore, sometimes unroasted, was lixiviated with a solution containing $CuCl_2$ and an excess of $CaCl_2$ or $NaCl$. The main reaction occurring is the reduction of the $Cu^{\cdot\cdot}$ ions by the Cu_2S in the ore

$$2Cu^{\cdot\cdot} + Cu_2S \longrightarrow 4Cu^{\cdot} + S.$$

Owing to the excess of Cl' ions, the $CuCl$ formed exists in solution as complex anion $CuCl_2'$. When electrolysed, copper is deposited at the cathode, and at the insoluble anode the reaction $Cu^{\cdot} + \oplus \longrightarrow Cu^{\cdot\cdot}$ takes place. Thus no gas is evolved, the voltage is kept down, and the extraction liquor regenerated. The total cell reaction is $2\,Cu^{\cdot} \longrightarrow Cu + Cu^{\cdot\cdot}$ for the passage of one faraday. Hoepfner claimed as advantages over the Siemens-Halske process that (1) the Ag, Au, etc., in the ore were extracted ; (2) far more copper could be dissolved for the same volume of electrolyte ; (3) at the cathode twice as much copper was precipitated for the same number of coulombs passing.

In actual practice the very finely-ground ore was extracted in large wooden drums at about 70° with a liquor containing some 60 grams/litre cupric copper. $PbCl_2$ crystallised on cooling, and silver was removed by passing over copper. To remove As, Sb, and Bi, the product was treated with lime, chalk, or CuO. Iron, the solution of which cannot be entirely avoided, was precipitated at the same time. (If allowed to accumulate, it would lower the amount of cuprous copper which could dissolve: thus $Fe^{\cdot\cdot\cdot} + Cu^{\cdot} \rightleftarrows Cu^{\cdot\cdot} + Fe^{\cdot\cdot}$.) Cu_2O was not precipitated because of the extremely low cupro-*ionic* concentration. The resulting purified liquors, containing about 120 grams/litre cuprous copper, were separated into two streams. One flowed through the cathode system of a number of electrolysis tanks connected in parallel ; the other through the anode system. In each tank the carbon anodes and copper cathodes were separated by a diaphragm. The cathodic and anodic effluents (the former almost copper-free) were mixed on leaving

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[1] *Electrochem. Ind.* **2**, 225 (*1904*).

[2] *Electrochem. Ind.* **1**, 540 (*1903*). *Zeitsch. Angew. Chem.* **4**, 160 (*1891*).

the tanks, and used to extract fresh ore. 0·8 volt was used, and a current efficiency of about 90 per cent. obtained. The deficiency is due to the process $Cu^{\cdot\cdot} \longrightarrow Cu^{\cdot} + \oplus$, which takes place very easily if any $Cu^{\cdot\cdot}$ ions are present, owing to the exceedingly low concentration of $Cu^{\cdot}$ ions in a chloride solution. The cathodic current density was probably about 2 amps./dm.^{2}.[1]

Assuming the above figures, one ton of copper requires

$$\frac{\cancel{96540} \times \cancel{10} \times \cancel{1000} \times 1000 \times \cancel{0{\cdot}8}}{\cancel{9} \times \cancel{63{\cdot}6} \times \cancel{3600} \times 1000} \text{ K.W.H.}$$
$$= 374 \text{ K.W.H.}$$

And 1 H.P. year will produce 17·5 tons copper, nearly six times the quantity[2] furnished by a catholyte containing $Cu^{\cdot\cdot}$ copper and an anolyte from which oxygen is evolved. In spite of this, the Hoepfner process, like the Siemens and Halske, is not in use. And the reasons are the same: difficulties in rapidly and completely extracting the ore and in keeping the composition of the electrolyte constant, the conditions changing every time a fresh ore is treated, and difficulties with regard to the diaphragms.

4. Silver Refining[3]

The raw material of the silver refiner is of several different kinds. It may be crude gold bullion, containing some 30 per cent. Au and 60 per cent. Ag; or the anode slimes from copper refining (freed from copper) or the silver concentrates from the desilverisation of lead (freed from zinc or lead), when it will have 94–98 per cent. silver, and up to 5 per cent. gold. Or it may consist of scrap jewellery, gold and silver plate, etc., containing perhaps 50 per cent. Cu, and large quantities of base metals. To 'part' gold-silver bullion or to extract gold values from crude silver, the old chemical methods consisted in treating with HNO_3 or H_2SO_4, the silver dissolving and leaving behind gold and platinum. These methods have now been almost entirely replaced by electrochemical processes. The advantages gained are considerable. They include: (1) more complete recovery of valuable constituents (Au, Pt), and elimination of harmful ones (Te); (2) far smaller acid consumption; (3) greater cleanliness and ease of working.

As in copper refining, the crude metal is cast into anodes, and the pure product cathodically deposited, the electrolyte being an aqueous silver salt. This procedure is only altered when the anodes contain too great a percentage of metals less noble than silver, which would dissolve, accumulate in the electrolyte, and tend to deposit on the cathode.

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[1] Coehn and Lenz, *Zeitsch. Elektrochem.* **2**, 25 (*1895*).

[2] See p. 262. *Metall. Chem. Engin.* **9**, 443 (*1911*).

The best salt for the electrolyte, easily obtainable and readily soluble, is $AgNO_3$. Its behaviour on electrolysis between pure silver electrodes is simple.[1] At low current densities adherent crystalline silver is quantitatively deposited cathodically. At higher current densities the metal no longer adheres, but forms long loose crystals stretching towards the anode and readily detached. Finally, hydrogen is evolved. At the anode silver is dissolved, again quantitatively. The most accurate coulometer consists of silver electrodes in $AgNO_3$ solution.[2]

The impurities which may occur in crude silver are gold, copper, platinum, lead, zinc, bismuth, cadmium, iron, tellurium, tin, nickel. The Au, Pt, and Te remain unattacked anodically, entering the slimes, which may also contain lead as PbO_2, and Sn and Bi as basic salts. Copper, nickel, iron, zinc, cadmium, and some of the lead, bismuth, and tin will dissolve. Of these copper is the most electro-negative, and hence most likely to deposit cathodically with the silver. $E.P._{Ag^{\cdot}\rightarrow Ag}$ is, however, 0·47 volt more positive than $E.P._{Cu^{\cdot\cdot}\rightarrow Cu}$ (0·80 − 0·33 volt). Copper deposition, therefore, though assisted by the depolarising action of the silver cathode, requires a low $Ag^{\cdot}$ concentration, and a large accumulation of $Cu^{\cdot\cdot}$ ions, helped, moreover, by a fairly high current density with its accompanying increase of the cathodic polarisation or by insufficient mixing of the electrolyte. The chief effect of the soluble anodic impurities is the gradual lowering of the silver content of the electrolyte, as, whatever metal is dissolved anodically, its equivalent of silver is always deposited cathodically.

Moebius Process.[3]—For the treatment of silver residues from the copper or lead refinery, the Moebius process is usually employed. The electrodes are hung vertically in a tank of earthenware or tarred wood (about 12′ × 2′ × 2′), divided into seven compartments. The **anodes** are suspended four or five together from a common bus-bar, each set being surrounded by a stout bag of filter-cloth, stretched over a wooden frame. They have the following average composition: (*a*) from copper refining 95 per cent. Ag, 3 per cent. Au, 2 per cent. Cu, Bi, Pb, Te, Pt; (*b*) from lead refining 98 per cent. Ag, 0·5 per cent. Au, 1·5 per cent. Cu, Bi, Pb. The **cathodes,** suspended in the cell alternately with the anodes, are of thin silver-foil, and of area almost equal to the cross-section of the bath. In each compartment will be perhaps four cathodes and three sets of anodes, some two to three inches apart. Like electrodes are connected in parallel, and the different compartments in series.

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[1] Under certain circumstances, other reactions can take place, but only to an insignificant extent, or else under exceptional conditions. We need not further consider them.

[2] See p. 32.

[3] *Trans. Amer. Electrochem. Soc.* **8,** 125 (*1905*).

The **electrolyte,** because of interest charges, is dilute—containing only 0·5–2·0 grams/litre silver. It is kept slightly acid (0·1–0·5 gram/litre HNO_3), the reasons being to increase the conductivity and to avoid the precipitation of basic salts or hydroxides. Owing to chemical reaction with the silver of both electrodes, $H^{\cdot}$ ions slowly but steadily disappear from the electrolyte during electrolysis, and a neutral solution would soon become alkaline. Although the silver content of the solution is so low, a high current density is used, again to economise interest charges. Because of these two reasons (low $Ag^{\cdot}$ content and high current density), it is impossible to allow copper to accumulate in the electrolyte above a certain limiting concentration, as there would be a risk of its cathodic deposition. Under normal conditions this limiting value is about 4 per cent. A normally working plant will have then an electrolyte containing per litre—

1 gram silver.
40 grams copper.
0·12 gram free HNO_3.

To keep this composition constant, a fraction of the liquors must be periodically drawn off, and replaced by a solution rich in HNO_3 and $AgNO_3$. It is, of course, possible to work with a higher $Cu^{\cdot\cdot}$ concentration, but only by using a lower current density and adding more acid.

The actual current density employed depends on the $Ag^{\cdot}$ and $Cu^{\cdot\cdot}$ concentrations in the bath, on interest charges, etc. With a fresh bath, free from copper, it will be 3·5 amps./dm.², but under normal conditions nearer 2·5 amps./dm.². At this high figure, with such a low $Ag^{\cdot}$ concentration, the silver is deposited in a loose crystalline form which tends to grow out towards the anode. To prevent this, each cathode is provided with a wooden scraper, worked by an eccentric, the deposited metal falling into a tray at the bottom of the tank, which is periodically withdrawn and emptied. The movement of these scrapers also serves to agitate the electrolyte. No other means is used—the liquors are not even circulated. The voltage per compartment is 1·4–1·7 volts, according to the current density. For a refining operation this figure is high, the cause being the comparatively poor conductivity of the electrolyte. The cell polarisation is only 0·15 volt. A higher working temperature would decrease the voltage and allow of heavier current densities, but the chemical action of the acid on the electrodes renders this impossible.

The current efficiency in the Moebius process is 94–95 per cent. A mere trace of copper is deposited (0·02 per cent.), and the deficiency must be ascribed to cathodic reduction of $Cu^{\cdot\cdot}$ to $Cu^{\cdot}$ ions (afterwards re-oxidised by air and agitation), and partly to chemical solution of the silver cathode by the HNO_3. Further, a little HNO_3 is cathodically reduced to ammonia. One kilo of silver requires then

$$\frac{1000 \times 96540 \times 100 \times 1{\cdot}6}{108 \times 95 \times 3600 \times 1000} = 0{\cdot}42 \text{ K.W.H.}$$

The cathodic deposit is 999 fine—very seldom less. The anodes ($\frac{3}{8}''$ thick) remain in the bath for 36–48 hours. The slimes contain Au, Pt, a little Ag and Cu, Te, and PbO_2. After washing and extracting with HNO_3, they are cast into anodes and sent to the gold-refining tanks.

To render his process continuous, Moebius later suggested a modification. The bath was a long shallow tank, through which the cathode, in the form of an endless silver band, almost the width of the bath, constantly moved. At the point where it emerged from the tank, the silver crystals were brushed off. The composition of the electrolyte, cathodic current density, etc., were essentially as before. In practice this process seems to have proved too complicated. The silver crystals did not detach easily, and the band tended to break. It is now stated to be working in one Mexican refinery only.

Balbach-Thum Process.[1]—A further modification of the Moebius process, the Balbach-Thum process, is in operation in two of the great North American refineries, the Raritan and the Balbach works. The cell is particularly simple. It consists of a shallow glazed porcelain trough (Fig. 64), the bottom of which may be horizontal or may partly or wholly slope gently upwards. This surface is lined with Acheson graphite slabs, which form the cathode, of area about eight square feet. The anodes are arranged horizontally on shelves above the cathode, and enclosed in canvas diaphragms. They are kept in the bath until completely dissolved. The electrolyte is the same as already described.

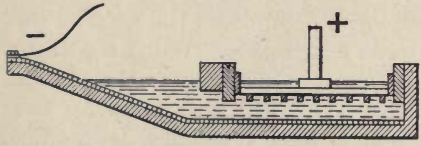

FIG. 64.—Balbach Silver Refining Cell.

The cathodic current density is 2–2·6 amps./dm.^{2}, at the anode twice as great. The voltage is 3·2–3·8 volts. This high value is due to the resistance of the slimes which settle in and on the diaphragm, and also to the distance between the electrodes, which is considerably greater than in the Moebius process. This is necessary, as there is no mechanical arrangement for brushing down the cathodic silver which rapidly grows out towards the anode. The loose deposit must be periodically pressed down and removed. This operation at the same time mixes the electrolyte, the only way in which this happens, as

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[1] *Electrochem. Ind.* **6**, 277 (*1908*).

there is no circulation. If often done, the $Cu^{\cdot\cdot}$ concentration can probably be allowed to rise as high as in the Moebius process ; otherwise it must be kept lower, which necessitates more frequent renewal of the electrolyte. The current efficiency is about 93 per cent. Reckoning the voltage at 3·5 volts, we see that the energy consumption per kilo is twice as great in the Balbach as in the Moebius process. And there is a proportionately larger amount of silver permanently tied up in the bath. Power, however, is a small item in the refining of such a valuable product. And there are the advantages of simplicity and a more complete separation of the silver than the Moebius process allows.

Parting of Bullion.—The electrolytic parting of bullion rich in gold is effected by the same methods. At the Philadelphia mint[1] a modified Moebius process is used. The **anodes** (30 per cent. Au, 60 per cent. Ag, 10 per cent. Cu, Pb, Bi, Zn) are encased in cloth bags and hung alternately with rolled fine silver cathodes in an earthenware trough. The **electrolyte** contains 3–4 per cent. $AgNO_3$ and 1·5 per cent. HNO_3, with certain quantities of dissolved anodic impurities. The current density used is only 0·75 amp./$dm.^2$, and the voltage is low—one volt. A trace of gelatine (1 : 8,000–10,000) is added to the electrolyte. This causes the silver (or nearly all of it) to deposit in a coherent crystalline form, a behaviour rendered easier by the low current density. The metal is exceedingly pure, and the current efficiency approaches 100 per cent. The anodes, after parting, retain their original form owing to the high content of gold. Owing to the large percentage of base metal dissolving, the electrolyte needs frequent renewal.

In the San Francisco mint,[2] the bullion is parted by the Balbach-Thum process, no attempt being made to deposit coherent metal. The anodes have much the same composition as at Philadelphia. The **electrolyte** contains about 4 per cent. silver and 1–2 per cent. free HNO_3, with copper, zinc, bismuth, and lead. The anodic current density is high—5–5·5 amps./$dm.^2$, and 3·5 volts are used. The silver is produced as a coarse sugary deposit 99·95 per cent. pure. 5 per cent. of the electrolyte is daily withdrawn and replaced by liquor very rich in silver. Although the percentage of base metal is considerable and the current density high, the deposits produced are pure by reason of the high $Ag^{\cdot}$ concentration. The advantage of working rapidly probably far outweighs in practice the drawbacks of the high voltage and the non-coherent deposit.

Dietzel Process.[3]—When the percentage of copper in the anode material is very high, the procedure for the recovery of the different values alters essentially. In the Dietzel process the alloy is made anode in a solution containing NO_3' ions. Silver, copper and base metals

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[1] *Electrochem. Ind.* **4**, 306 (*1906*).

[2] *Electrochem. Ind.* **6**, 355 (*1908*).

[3] *Zeitsch. Elektrochem.* **6**, 81 (*1899*).

dissolve, gold and platinum are untouched. The anode liquors are freed from silver chemically outside the electrolysis cell, and then pass to the cathode compartment, where copper is deposited.

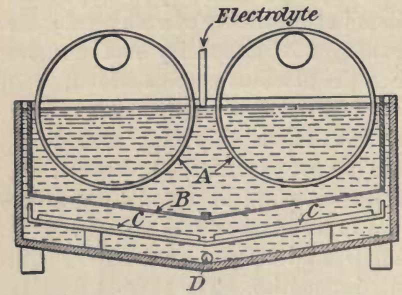

FIG. 65.—Dietzel Refining Process.

Fig. 65 illustrates the electrolysis cell, which is divided into anode and cathode compartments by the canvas diaphragm B. The entering liquor deposits copper on the slowly rotating cylinders AA. It passes through B and arrives at the **anodes** CC. These consist of plates (3–5 mm. thick) of very variable composition, containing perhaps 5–7 per cent. Au, 22–50 per cent. Ag, 40–65 per cent. Cu, 5 per cent. Sn, Zn, Pb, and a little Pt, Cd, Ni, and Fe. They rest on glass or celluloid plates, and are connected with the positive lead by a network of platinum wire. The anode liquors, charged with silver, copper, and various soluble impurities, leave the cell at D and flow through a number of jars containing scrap copper. There the silver is deposited and an equivalent amount of copper dissolved. The desilverised liquors are pumped up into a supply tank, from which they re-enter the cathode chamber.

When the dissolved impurities reach an inconveniently high figure, part of the electrolyte is withdrawn and replaced. Further HNO_3, which is being constantly consumed by the copper in the desilverising vessels, is regularly added. The anodic current density is about 1·5 amps./dm.^{2}, and the average voltage 2·5–3 volts. The anode slimes contain gold with a little silver, platinum, PbO_2, etc. The cathode deposit contains a trace of silver and some oxygen. The electrolyte used is only very faintly acid, and we have seen[1] that this favours the cathodic precipitation of Cu_2O. The current efficiency is somewhat under 100 per cent.: the loss is probably due to the process $Cu^{\cdot\cdot} \longrightarrow Cu^{\cdot} + \oplus$, as the liquors are well saturated with air during their journey outside the cell, and any $Cu^{\cdot}$ ions would be oxidised. At the copper cathode, moreover, an appreciable electrolytic reduction of NO_3' to NH_3 takes place.

Electrolysis as a factor in the **extraction of silver** from its ores is beginning to make an appearance. In Mexico, KCN treatment of silver ores has been introduced; and from the resulting liquors, as in the case of gold,[2] the silver is sometimes precipitated electrolytically.

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[1] P. 247.

[2] P. 276.

5. Gold Refining[1]

The advantages of electrochemical methods for crude bullion refining have been already discussed. In the present case, using a material containing 90–95 per cent. Au, they comprise recovery of platinum and greater ease and cleanliness in working. The actual cost is also less, due to the very low acid consumption. This, however, signifies little, owing to the value of both raw material and product. Interest charges are of primary importance. The process employed is the Wohlwill process, in which the crude anodes are dissolved in an electrolyte consisting of a solution of $HAuCl_4$ with excess of free HCl (KCl or NaCl could equally be used).

Anodic Behaviour of Gold.—The behaviour of pure gold electrodes in a solution containing auric chloride is rather complex. If gold be anodically polarised in a neutral $AuCl_3$ solution, it is found to dissolve nearly quantitatively at an anodic potential $\mathcal{E}_h = +1{\cdot}1$ to $1{\cdot}2$ volts, according to the equation $Au + 3 \oplus \longrightarrow Au^{\cdot\cdot\cdot}$.[2] If the potential be raised to 1·4 volts, the anode quickly becomes passive. Finally, at 1·73 volts, chlorine is evolved. These relations are clearly shown in the accompanying current anode potential curve (Fig. 66). If free HCl be added, the gold begins to dissolve at the same potential, but does not become passive so easily, the potential range over which no electrode action takes place thus becoming smaller. This effect is greater he greater the acid concentration. An electrolyte of pure HCl acts similarly, there being a short potential range over which no gold dissolves and no chlorine is evolved. NaCl acts like HCl—it is the Cl′ which counteracts the passivity, as it does in many similar cases.[3] A rise of temperature has a similar effect. For a given HCl content and for a given temperature, then, there will exist a limiting anodic potential, and consequently a limiting current density, which must not be exceeded if no free chlorine is to be evolved. Thus at

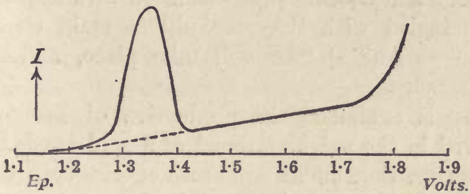

FIG. 66.

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[1] *Metall. Chem. Engin.* **9**, 443 (*1911*); *Electrochem. Ind.* **1**, 157 (*1903*); **6**, 355 (*1908*).

[2] Coehn and Jacobsen, *Zeitsch. Anorg. Chem.* **55**, 321 (*1907*).

[3] See pp. 140, 290, 292, 388.

70°, with 3 per cent. free HCl present, up to 0·3 amp./cm.^{2} can be used.

The gold does not dissolve quite quantitatively as $Au^{\cdot\cdot\cdot}$ ions, but there tends to be set up at the anode the equilibrium $Au^{\cdot\cdot\cdot} + 2\,Au \rightleftarrows 3\,Au^{\cdot}$.[1] The equilibrium constant of this reaction is unknown. For our present purpose this makes no difference, as almost all the gold, whatever its valence, is present as complex anions $AuCl_2'$ and $AuCl_4'$, and the equilibrium constants of the reactions $Au^{\cdot} + 2Cl' \rightleftarrows AuCl_2'$ and $Au^{\cdot\cdot\cdot} + 4Cl' \rightleftarrows AuCl_4'$ would also need to be known before we could calculate in what proportions of aurous and auric salts a gold anode would dissolve in an electrolyte with a given Cl' content. At all events, a certain amount of gold dissolves in the aurous condition, and the loss in weight of the anode will exceed that calculated from Faraday's Law on the assumption that the reaction $Au + 3 \oplus \longrightarrow Au^{\cdot\cdot\cdot}$ is the only one taking place. Further, the concentrated solution leaving the anode will become supersaturated with respect to $Au^{\cdot}$ ions when it has mingled with the more dilute main electrolyte. The reaction $3Au^{\cdot} \longrightarrow Au^{\cdot\cdot\cdot} + 2Au$ will take place, and metallic gold will be precipitated.

In this way is explained the production of finely-divided gold crystals observed in the neighbourhood of a gold anode.[2] The higher the current density, the smaller are these effects, both the excess loss in weight of the anode, and the precipitation of finely-divided gold. This is probably caused by the gold becoming somewhat passive with respect to the production of $Au^{\cdot}$ ions at the higher current densities. Table XXXVII gives some results of Wohlwill. One ampere-hour should dissolve 2·45 grams Au if the sole reaction is $Au + 3 \oplus \longrightarrow Au^{\cdot\cdot\cdot}$.

TABLE XXXVII

Current density	Weight of gold dissolved per ampere-hour
0·049 amp./cm.^{2}	3·35 grams
0·059	3·17–3·26
0·074	2·77–2·84
0·098	2·64
0·15	2·53

Cathodic Behaviour of Gold Solutions.—The cathodic phenomena during the electrolysis of $HAuCl_4$ solutions are no less complex.[3] At room temperature, using a *fresh* solution containing no aurous gold, the first electrode reaction begins at + 1·1 volt. No gold is deposited, but we have the reaction $Au^{\cdot\cdot\cdot} \longrightarrow Au^{\cdot} + 2 \oplus$ (i). With increasing

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[1] Compare p. 245.

[2] Cf. p. 248. A moderate degree of supersaturation of $Au^{\cdot}$ ions will persist for a long time unless the solution be brought into contact with metallic gold.

[3] Coehn and Jacobsen, *loc. cit.*

cathodic polarisation there is another discontinuity at + 0·96 volt, and gold is deposited (ii). Finally, at + 0·90 volt there is a third bend (iii), although the deposition of gold still continues. As the solution is used (i) and (ii) approach one another, until finally, when the equilibrium $2Au + Au^{\cdots} \rightleftarrows 3Au^{\cdot}$ prevails, there are only two decomposition points, at 1·0 and 0·9 volt. At higher temperatures the first decomposition point comes earlier, and the second weakens and finally disappears. Thus, with a fresh solution at 85°, there were only two bends at 1·2 and 0·9 volt.

The reason for the smaller cathodic polarisation required by the process $Au^{\cdots} \longrightarrow Au^{\cdot} + 2 \oplus$ in the hot is that at higher temperatures the equilibrium $Au^{\cdots} + 2\,Au \rightleftarrows 3\,Au^{\cdot}$ moves over in favour of the $Au^{\cdot}$ ions,[1] and, with a given $Au^{\cdot}$ concentration, the driving force of the reaction is thereby increased. The causes of the other phenomena are less clear.

At ordinary temperatures, with a cathode potential between 1·0 (ii) and 0·9 (iii) volt, gold is deposited from auric chloride solutions with an apparent valency of 2·6 to 2·9, the higher the potential the larger being the valency. Whilst with a cathode potential below + 0·9 volt (iii), it is always precipitated quantitatively according to the equation $Au^{\cdots} \longrightarrow Au + 3 \oplus$. As we shall shortly see, gold refining is carried out at about 70°. If we suppose the cathode to be in equilibrium with the electrolyte, the first decomposition point will have disappeared and the second will hardly be noticeable.

Hence the third only need be considered, and this corresponds to a tri-valent deposition of gold. But, under working conditions, the electrolyte leaving the anode is, as we have seen, supersaturated with respect to $Au^{\cdot}$ ions. This supersaturation only slowly disappears unless the liquid is actually in contact with metallic gold, and further, the $Au^{\cdot}$ ions are not oxidised by oxygen to $Au^{\cdots}$ ions as is the case with copper.[2] When the electrolyte arrives at the cathode, this excess is, of course, deposited, and hence, in practice, the increase in weight of the cathode always exceeds the amount calculated from Faraday's Law on the assumption that the sole reaction is $Au^{\cdots} \longrightarrow Au + 3 \oplus$. According to the current density it amounts to 3·02–2·49 $\frac{\text{grams}}{\text{amp. hour}}$ (theory 2·45 grams).

The condition of the deposited metal depends on the gold content of the solution, the temperature and the current density, being more compact the lower the last, the higher the first two factors. Under unfavourable conditions a loose powder results, as deposited in the gold refinery a coarsely crystalline coherent mass.

The gold **anodes** used in the refinery contain generally about 94 per

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[1] Bose, *Zeitsch. Elektrochem.* **14**, 85 (*1908*).

[2] P. 246.

cent. Au, 5 per cent. Ag,[1] and 1 per cent. (Cu, Pb, Pd, Pt), with traces of other platinum metals. Of the impurities, the silver gives AgCl, afterwards found in the slimes. Under ordinary conditions the formation of this insoluble salt limits the permissible percentage of silver in the anodes. If 6 per cent. is exceeded, the layer of AgCl becomes so coherent that it must be mechanically brushed away, or else the gold will not dissolve, chlorine being instead evolved. To avoid this difficulty, Wohlwill has devised a method employing an unsymmetrical alternating current, which we will presently discuss. Lead dissolves as $PbCl_2$, but is continually precipitated by the addition of H_2SO_4. Copper, platinum,[2] and palladium also dissolve, and accumulate in the electrolyte. The platinum content must not exceed 50–60 $\frac{\text{grams}}{\text{litre}}$, that of the palladium 5 $\frac{\text{grams}}{\text{litre}}$, or else cathodic deposition will occur. The copper can be allowed to accumulate considerably.

Because of the impurities, but more so because of the decreasing gold content of the bath, a fraction of the electrolyte must be regularly drawn off, and replaced by a strong $AuCl_3$ solution. The withdrawn portion is freed from gold by SO_2, the platinum precipitated as Am_2PtCl_6, any palladium extracted with ammonia after evaporation to dryness, and copper removed by scrap iron. The slimes contain gold (about 10 per cent. of that cathodically precipitated), AgCl, $PbSO_4$, and the rarer platinum metals. After removal of the $PbSO_4$ by treatment with Na_2CO_3 solution, followed by HNO_3, and the AgCl by fusing and pouring off, the residues are generally recast into fresh anodes.

The electrolysis baths are constructed of glazed porcelain or chemical earthenware, and, as the electrolyte is expensive, are small in size. A number of anodes and cathodes are arranged alternately, ¾″ apart, and connected in parallel, and several baths are placed in series. The anodes are fairly thin (*e.g.* ⅙″), to ensure their only being a short time in the bath. They are either provided with lugs, and hung over the edges of the bath as in copper refining, or are better suspended from platinum hooks and completely submerged. The **cathodes** are of very thin gold foil. All leads are of silver or gold, as copper would be attacked by the traces of chlorine which are continually evolved. In order to consume the anodes rapidly a high current density is necessary. Further, the electrolyte must not contain much of the expensive gold salt. To obtain an adherent deposit under these conditions a high temperature is essential. In practice the **electrolyte** contains 30–40 $\frac{\text{grams}}{\text{litre}}$ Au and 2–3 per cent. free HCl. A

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[1] Can however be greatly exceeded.

[2] Platinum is almost passive in strong HCl (see p. 151), but when alloyed with gold, even up to 10 per cent. and more, readily dissolves.

trace of gelatine may be added to improve the quality of the cathodic deposit. It is circulated through the tanks by propellers or by gravity, the latter system certainly appearing preferable. The temperature varies in different refineries between 50°–70°. The higher value permits of more rapid work and is therefore better. The tanks conveniently rest on a sandbath, heated by steam pipes.

The current densities used with anodes of normal silver content are 10–15 amps./dm.^{2}. Traces only of chlorine are evolved, and the anodes are consumed in 15–20 hours. This rapid rate of work nullifies the last advantage of chemical methods of refining. The electrochemical process formerly required some three days for the consumption of an anode. Higher anodic current densities, up to 30 amps./dm.^{2}, can only be used with anodes very poor in silver and lead. If the silver content is high the current density may drop to 5–7 amps./dm.^{2}. The voltage required is 0·6–1·0 volt, depending on temperature, composition of electrolyte, current density, etc. We have seen that the yield at the cathode is a little higher than that calculated for $Au^{\cdot\cdot\cdot} \longrightarrow Au + 3 \oplus$. Putting it at 103 per cent., and assuming a drop of 0·8 volt per tank, we have that one kilo. of gold requires

$$\frac{1000}{197{\cdot}2} \times \frac{100}{103} \times \frac{96540 \times 3}{3600} \times \frac{0{\cdot}8}{1000} \text{ K.W.H.} = 0{\cdot}32 \text{ K.W.H.}$$

The power cost in gold refining is negligible.

Modified Wohlwill Process.—We have mentioned the modified Wohlwill process[1] for use with anodes of high silver content. Under ordinary circumstances an anode with, for example, 10 per cent. Ag can only carry a current density of 7·5 amps./dm.^{2}, and even then must be regularly scraped every ¾ hour to remove the AgCl layer. Not only is this troublesome in practice, but the low rate of anode consumption means heavy interest charges. To overcome this difficulty Wohlwill employs an unsymmetrical alternating current, consisting of a direct current on which is superposed an alternating current of rather *greater* (*r.m.s.*) value. The quantities of gold dissolved and deposited correspond almost exactly to those given by the direct current alone. But far higher current densities can be employed than are possible in the absence of the alternating current component, and hardly a trace of chlorine is evolved, the gold dissolving quite smoothly.

Thus, for example, the above-mentioned alloy can be refined at a current density of 12·5 amps./dm.^{2}, scraping being unnecessary if an alternating current be employed 1·1 times as great as the direct current flowing; whilst if this ratio be increased to 1·7, a bullion containing 20 per cent. Ag can be refined at a current density of 12 amps./dm.^{2}. With alloys containing normal proportions of silver, far higher current

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[1] *Zeitsch. Elektrochem.* **16**, 25 (*1910*); D.R.P. 207,555 (*1908*).

densities can be employed. Apart from the great saving of interest on the gold stock, the amount of gold entering the slimes, and therefore requiring remelting and retreatment, hardly exceeds 1 per cent. of the amount deposited, instead of 10 per cent. as is otherwise usual. The slimes practically consist of $AgCl$. As we have seen, this non-production of gold slimes is a direct consequence of the higher current densities used.

The way in which this alternating current component acts is not perfectly clear, but is probably as follows. We know that above a certain current density or anode potential gold becomes passive. The effect of the formation of the $AgCl$ layer is to lessen the active area of the anode, and hence the current it can take, without chlorine evolution setting in.[1] According to Foerster,[2] certain metals, such as iron, etc., are *passive* when *pure*, and only become active when charged with hydrogen. It is possible that the case is similar here, that during the short cathodic component of the alternating current the metal is somewhat charged with hydrogen, and thus enabled to dissolve during the succeeding anodic component far more readily than under normal conditions. Only a very small quantity of hydrogen would probably be thus required, as we know the solubility of the gas in gold to be very low.

We may notice in conclusion that the saving in interest, etc., effected by this device far outbalances the extra expense of the alternating current.

6. Gold Extraction

Very large quantities of gold are extracted from the ore by the use of KCN solutions. Two processes are used, the MacArthur-Forest and the Siemens and Halske, and in the latter the gold is precipitated electrochemically from solution. The introduction of cyanide extraction into gold metallurgy has effected a revolution in the industry. Very low-grade ores, down to about $8 \frac{\text{grams}}{\text{ton}}$ gold, can be economically extracted, and the process has found its largest application in the recovery of gold from the tailings and slimes of the amalgamation process. Further, higher grade ores containing the gold too intimately embedded in the pyrites to allow of extraction by the amalgamation process, and which previously were always chlorinated, can also be successfully treated.

KCN solutions can only dissolve gold in presence of air or oxygen. The final result can be expressed thus: $2Au + 4KCN + H_2O + \frac{1}{2}O_2 \longrightarrow 2KAu(CN)_2 + 2KOH$, or $2Au + 4CN' + H_2O + \frac{1}{2}O_2 \longrightarrow 2Au(CN)_2' + 2OH'$. The electrochemical nature of the process is clearly demonstrated by setting up an element of which one electrode

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[1] Cf. pp. 141, 224.

[2] See p. 142.

is gold in air-free KCN solution, the other platinum in a KCN solution through which oxygen is bubbling.[1] Such a combination has an E.M.F of 0·12–0·29 volt, the KCN concentration varying from 0·1 per cent to 1 per cent. On short circuiting, the gold dissolves, giving Au $(CN)_2'$ ions, and at the oxygen electrode OH′ ions result. Bodländer[2] investigated the reaction, and showed that H_2O_2 was sometimes formed as an intermediate product, in which case the first reaction would be $2Au + O_2 + H_2O \longrightarrow Au_2O + H_2O_2$, the Au_2O subsequently dissolving in the KCN, and the H_2O_2 oxidising more gold.

In practice, the crushed and stamped ore, after having as much gold as possible removed by amalgamation, is separated into three fractions by levigation, and then treated with the solution of KCN, or a mixture of KCN with the cheaper NaCN. The heaviest fraction ('concentrates') may contain about 25 $\frac{\text{grams}}{\text{ton}}$ gold, the second and third fractions ('tailings' and 'slimes') 10–15 $\frac{\text{grams}}{\text{ton}}$. In the MacArthur-Forest process the KCN content of the solution used to be 0·3–0·4 per cent., it is now 0·1 per cent. or less. The velocity of solution of the gold depending on the amount of dissolved oxygen in the liquors, air is continually blown in during the lixiviation. When the extraction is finished, the gold content is precipitated by passing the solution over zinc filings or a zinc-lead couple containing 5 per cent. lead.

Siemens and Halske Process.—In this process a 0·1–0·2 per cent. solution is used for the concentrates, the lixiviation taking some weeks. The tailings and slimes only need a 0·01–0·05 per cent. solution, and the extraction is completed far more quickly—in a few days or a few hours, depending on the fineness of division of the gold present. The lixiviation is carried out in huge wooden or iron tanks through which air is blown. Rapidity of work is important. Otherwise Cu_2S dissolves, and iron pyrites is slowly attacked, producing ferric sulphate, and finally causing a loss of cyanide as insoluble Prussian blue. The longer, too, the solution is exposed to air the greater will be the loss of HCN, both by hydrolysis ($CN' + H_2O \longrightarrow HCN + OH'$) with subsequent loss as gas, and by action of atmospheric CO_2 and oxygen. Oxidising agents tend to hasten the solution of the gold, but none has yet found application with the exception of BrCN and ClCN, occasionally used when the gold is present as telluride, which is only very slowly attacked by the dilute KCN solution.

The **liquors,** containing from 3–10 $\frac{\text{grams}}{\text{metre}^3}$ gold, are filtered through sand or carefully decanted, and led to the electrolysis tanks. These

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[1] *Electrochem. Ind.* **7,** 156 (*1909*).

[2] *Zeitsch. Angew. Chem.* **9,** 583 (*1896*).

consist of long wooden vats (perhaps 30′ × 6′ × 5′), divided by means of double-walled divisions into ten or twelve compartments. The electrolyte enters the end compartment at the top, flows through and out at the bottom, up through the double-walled partition, and enters the second division, again at the top. In this way it slowly traverses the whole vat, some 50–80 cubic metres passing through in twenty-four hours. Each compartment contains electrodes.

The **anodes** are of sheet iron, 4–5 mm. thick. They are slowly attacked, giving Prussian blue, for which reason they are enclosed in canvas bags. The addition of some alkali to the electrolyte, beyond that produced by hydrolysis, considerably checks their corrosion and the accompanying loss of cyanide. They last indeed for some years. Other materials have been proposed, notably PbO_2 by Andreoli, but they do not withstand the conditions so well.[1]

As **cathodes** are used spirally wound lead strips, suspended from crossbars of zinced iron. The gold adheres satisfactorily if the electrolyte is kept free from suspended matter and if the current density is not too high. They are removed every one or two months, when they may contain 10 per cent. gold, and cupelled. The resulting crude metal will contain 85–95 per cent. gold, the remainder being chiefly silver and lead. Other cathodes have been used or suggested, for example, tin-foil. A high current density is employed, and the spongy deposit is squeezed off every day or two or falls to the bottom of the tank. These electrodes are thus permanent. Neumann has suggested carbon cathodes. A good deposit can be produced, and they could subsequently be made anodes in a Wohlwill refining bath, and, when the metal had been dissolved, washed and returned to the cyanide tanks.

Like electrodes in the whole bath are connected in parallel and the different baths in series. The current density at both anodes and cathodes is about $0{\cdot}4\ \frac{\text{ampere}}{\text{metre}^2}$. A higher one gives a very loose deposit and attacks the anodes too powerfully. The voltage used is about 1·75–3·0 volts for the more concentrated KCN solutions; for solutions with only 0·01 per cent. KCN it may rise to 4–5 volts. The current efficiency is exceedingly low, averaging less than 1 per cent. Hydrogen is evolved in large quantities. About 80–90 per cent. of the gold is deposited. To precipitate the last traces would be uneconomic. The liquors are either passed over a zinc-lead couple, or, after replenishing the cyanide content, are returned to the lixiviating tanks.

Neumann[2] has made a laboratory study of the influence of varia-

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[1] Neumann, *Electrochem. Ind.* **4,** 297 (*1906*).

[2] *Loc. cit.*

tions of current density and concentration on the yield and the voltage, and the accompanying Table XXXVIII contains some of his results.

TABLE XXXVIII

Concentration Grams Au per metre³	 Per cent. of KCN	Current density in amperes per metre²	Current efficiency	Voltage
10	0·05	0·25	7·5 per cent.	1–1·5 volts
10	0·5	0·5	3·5–4	1·8
10	0·07	2·4	0·1–0·4	2·1
10	0·07	4	0·08–0·25	2·5
10	0·07	9	0·04–0·16	3·0
3	0·05	0·25	3	1·4–1·7
3	0·5	0·5	1·3	2

The current efficiencies are seen to be very low, and to fall off with decreasing gold content or with increasing current density. Power charges are, however, of small account with such a valuable product, and the Siemens-Halske process can be favourably compared with the MacArthur-Forest process on four points: it does not use huge quantities of zinc (the zinc precipitation always demands many times the theoretical quantity); it uses far less KCN—about one-third; the precipitated material is more easily worked up; and a purer product results. Nevertheless the process has recently become of much less importance, and there are reasons to believe it may soon disappear. It requires a larger and more unwieldy plant, and rapid work is impossible. Many modifications of the Siemens-Halske process have been proposed: none have had any success.

Clancy Process.—In conclusion we may briefly mention an electrolytic process described by Clancy[1] for the extraction of gold from very refractory ores, such as tellurides. The crushed ore is contained in an iron tank which acts as cathode. The anodes, which are of magnetite,[2] are cheap, can withstand comparatively high current densities, and have a long life. The dilute electrolyte, which is kept slightly alkaline, contains originally a mixture of KCN, KCNS, and KI, together with $CaCN_2$ (calcium cyanamide[3]). On electrolysis, anodic reactions apparently occur which result in the production of substances capable of attacking the gold tellurides, such as ICN, I_2CN_2 (Clancy). The liberated gold dissolves in the cyanide present. To regenerate the electrolyte, the addition of fresh cyanide is unnecessary. The cheap cyanamide can be added instead, as on electrolysis it is converted

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[1] *Trans. Amer. Electrochem. Soc.* **19**, 137 (*1911*).

[2] See p. 363.

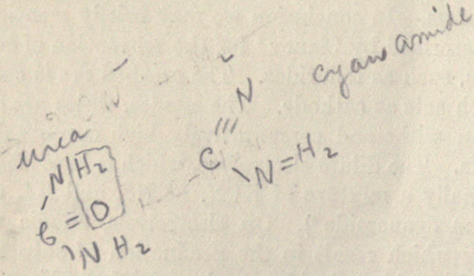
[3] See p. 480.

anodically into $Ca(CN)_2$. If this process gives as good results technically as it seems to have done on an experimental scale, it will undoubtedly find wide application.

Literature

Ulke. *Die elektrolytische Raffination des Kupfers.*
v. Uslar. *Cyanid-Prozesse zur Goldgewinnung.*

$CaCN_2$



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CHAPTER XVIII

ZINC—TIN—NICKEL—IRON—LEAD—VARIOUS

In this chapter we shall discuss the electrometallurgy of metals much less noble than those so far dealt with. The difficulties inherent in their treatment are consequently much greater, and most of the processes considered find small application and are run at a narrow margin of profit. When real economic success has been reached, it has only been after overcoming great obstacles.

1. Electrometallurgy of Zinc

Owing to the great losses of metal (up to 25 per cent.) in zinc metallurgy, and the very considerable wear and tear of the retorts employed, chemists have devoted much attention to the extraction of zinc by roasting the ore, lixiviating, and electrolysing the liquors produced. For several reasons, such processes have only achieved slight success. Such reasons are (*a*) the high power consumption necessary to deposit from aqueous solution a strongly electropositive metal like zinc, using an insoluble anode; (*b*) difficulties encountered in the cathodic deposition; (*c*) difficulties in roasting, lixiviating and purifying the liquors so as to produce an electrolyte of constant and definite composition[1]; (*d*) insufficient demand for the resulting particularly pure product. At present electrolytic zinc seems only to be produced at a plant in Russian Poland and by Brunner, Mond, and Co., Ltd. (at Winnington, Cheshire).

Cathodic Phenomena.—In the cathodic deposition of zinc, two important points must be considered—firstly the conditions under which the metal or hydrogen respectively result, and secondly the nature of the zinc deposit. Zinc is far more electropositive than hydrogen ($\text{Zn} | n.\ \text{Zn}^{\cdot\cdot} = -0{\cdot}76$ volt). One would therefore expect the metal to dissolve freely in acid, and would also expect to find its cathodic deposition impossible with any appreciable amount of free acid in the electrolyte. As a matter of fact, *pure* zinc is not attacked

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[1] Cf. pp. 263, 265, 297.

by acids, and further zinc can be electrolytically deposited from acid solutions with excellent yields if a sufficiently high current density be used. The cause of these contradictions is the very high overvoltage necessary for the discharge of hydrogen at zinc, which is about 0·7 volt, even at very low current densities, the highest value for any common metal except mercury. Consequently, as the hydrogen must be evolved at the zinc surface, the solution of pure zinc in dilute acid does not proceed spontaneously, and from an electrolyte containing both zinc and hydrogen ions, the former are preferentially discharged, unless only present in small amount.

If however the zinc contains metallic impurities at which the hydrogen overvoltage is less than at zinc itself, it will dissolve rapidly in the acid. Such metals are iron, silver, nickel, copper or arsenic, a very small quantity of which will cause the zinc to dissolve. Tin, cadmium, and lead will not act so powerfully. Similarly, if the zinc cathode or the electrolyte is contaminated with one of the above metals (which are all more electronegative than zinc and will therefore deposit more easily) then hydrogen will result instead of zinc. In any case, raising the current density always increases the hydrogen overvoltage and raising the temperature decreases it. A high current density and a low temperature therefore favour a good cathodic current efficiency, which is also assisted by a high zinc and a low acid concentration in the electrolyte.

Nature of Cathodic Deposit.—When the electrolysis is proceeding satisfactorily, the zinc forms a compact greyish white finely crystalline mass, showing a slight tendency to give irregular growths at the edges of the electrode. But very often, without apparent cause, the deposit becomes spongy and dark-coloured, and when this has happened, unless by suddenly raising the current density, or by other means, this zinc sponge is covered over with a layer of coherent metal, it is difficult to prevent zinc subsequently deposited from coming down in the same inconvenient form. Apart from being very voluminous, causing short circuits, enclosing electrolyte, and being difficult to handle, it cannot be melted up without considerable losses as oxide.

Many chemists have investigated the conditions of formation of this zinc sponge, particularly Kiliani,[1] Mylius and Fromm[2] (from $ZnSO_4$ solution), and Foerster and O. Günther[3] (from $ZnCl_2$ solution). Their work has made clear the conditions for the production of satisfactory deposits of zinc, but the cause of the sponge formation is still rather obscure. The view so far generally taken is that the sponge formation is due to the presence of zinc oxide or a basic zinc salt in the electrolyte, which somehow disturbs the crystallisation of the metallic zinc. Any

[1] *Berg-und Hütten. Zeit. 1883*, 251.

[2] *Zeitsch. Anorg. Chem.* **9**, 164 (*1895*).

[3] *Zeitsch. Elektrochem.* **5**, 20 (*1898*), **6**, 301 (*1899*).

cause tending to lower the $H^{\cdot}$ concentration must then tend to favour sponge formation. For example, Foerster points out that if there are irregularities on the surface of the cathode, the current density may fall locally or the electrolyte may fail to be renewed and become depleted of zinc ions, which would cause a further fall in current density. Both these causes, a deficiency in zinc ions and a lower current density, tend to increase the proportionate number of hydrogen ions discharged, and to favour the production of basic salts and the formation of zinc sponge.

Again, if any electronegative metal is present in the electrolyte, it will be deposited, assist hydrogen evolution, and cause the production of zinc sponge. When once the sponge is deposited the discharge of hydrogen ions will increase, as the overvoltage of hydrogen at zinc sponge is much less than at the massive metal. The behaviour of oxidising cathodic depolarisers rather confirms this general view. Depolarisers which oxidise hydrogen to $H^{\cdot}$ ions—*i.e.* which give acids on reduction—usually hinder the sponge formation. Such are the halogens, $HClO$ and $H_2S_2O_8$. Oxidising agents, on the contrary, which give neutral or basic substances on reduction favour the sponge production. Such are H_2O_2 and nitrates. There is further one fact which, at first apparently a contradiction, also confirms this view. When zinc is deposited from alkaline zincate solutions, sponge formation rapidly sets in, though the excess of alkali prevents any precipitation of oxide or basic salt. Hantzsch[1] however has shown that these zincate solutions are more or less strongly hydrolysed, and contain colloidal zinc hydroxide. This will probably affect the zinc deposit.

The conditions for the production of good zinc deposits are as follows :—

(*a*) Moderately strong solutions of zinc salt. 40–60 grams/litre zinc is a suitable concentration.

(*b*) Presence of acid, its amount depending on the efficiency of circulation of the electrolyte. The better this is, the lower the $H^{\cdot}$ concentration can be. Depending on circumstances, the liquors should have a free acid concentration of 0·01–0·1 N. From the point of view of a good cathodic efficiency, the less present the better.

(*c*) Complete absence in the electrolyte of impurities less electropositive than zinc. Copper and arsenic must particularly be avoided. Mylius and Fromm found that, in a 10 per cent. $ZnSO_4$ solution, 0·004 per cent. As almost immediately caused the production of zinc sponge and evolution of hydrogen.

(*d*) Current density must not be low. Suitable limits are 1–2·5 amps. /dm.^{2}

(*e*) Good circulation.

(*f*) Low temperature. Raising the temperature lowers the hydrogen overvoltage and increases the tendency to form basic salts.

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[1] *Zeitsch. Anorg. Chem.* **30**, 298 (*1902*).

Zinc Refining.—The electrolytic refining of zinc can be readily carried out, but generally will be an uneconomic operation. This may be different if the raw material furnishes slimes sufficiently rich in noble metals. The zinc-silver alloy obtained in the Parkes process for desilverising lead is such a raw material, and electrolytic refining processes have been devised by **Hasse** and by **Roesing.** They are not now worked, the older separation by distillation proving simpler to carry out. The crude metal used was the product of the Rössler-Edelmann modification of the Parkes process, and generally contained 11–12 per cent. Ag, 80 per cent. Zn, 6–7 per cent. Cu, smaller quantities of Ni, Pb, and Fe, and traces of As, Sb, and Bi. The anodes were suspended opposite to electrolytic zinc cathodes in a slightly acid normal $ZnSO_4$ solution, the electrolyte being circulated by gravity. At 20°, with a current density of 0·8–0·9 amps./dm.^{2}, 1·25–1·45 volts were used per tank. The zinc produced contained 0·01 per cent. Pb, 0·01 per cent. Fe, 0·004 per cent. Ag. At higher temperatures it was of poorer quality. The slimes consisted of copper, silver, lead, zinc and ZnO. After removing the last two constituents by dilute acid, a little copper also dissolving, they contained about 50 per cent. Ag, 10 per cent. Pb, and 40 per cent. Cu, and were worked up for their separate constituents.

The chief difficulty experienced was in keeping the electrolyte sufficiently free from small amounts of copper and silver dissolved anodically. After passing through a certain number of tanks, it was made to flow in a thin stream over a series of terraces on some of which were placed zinc shavings, on others ZnO. The noble metals were thus precipitated, and, by the combined action of the ZnO and the air, $Fe(HO)_3$ was also deposited. The liquors were finally settled or filtered, treated afresh with acid, and passed again through the cells. Whether this purification was too tedious, or whether it was insufficient, is not known. An arrangement such as used by Dietzel for the separation of silver and copper would have proved more effective. The economic margin of the process in any case was small, and troubles of that kind would easily turn the scale.

Zinc Extraction. Siemens-Halske Process.—Electrochemical processes for the extraction of zinc from its ores can be divided into two classes, using respectively as electrolyte $ZnSO_4$ and $ZnCl_2$ solutions. Of those employing sulphate solutions, we may mention the many Siemens and Halske patents. For the lixiviation of the calcined ores they have recommended at different times acid $Fe_2(SO_4)_3$ liquors, an alum solution, and dilute H_2SO_4. Using the first solution, ZnS and ZnO were dissolved exactly as the corresponding copper compounds in the Siemens and Halske copper process.[1] The electrolysis was also

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[1] See p. 262.

similar—at the cathode deposition of zinc, at the anode oxidation of $Fe^{\cdot\cdot}$ to $Fe^{\cdot\cdot\cdot}$ ions, thus regenerating the lixiviating liquors. But in addition to the difficulties experienced in the corresponding copper process, much iron was precipitated with the zinc, and the deposit was spongy. Using alum liquors, soluble basic aluminium salts were produced; and, on electrolysing, no acid was set free, but the neutral aluminium sulphate regenerated. The zinc deposit under these conditions was probably unsatisfactory.

The best results seem to have been obtained when lixiviating with dilute H_2SO_4,[1] fairly successful large-scale trials having been carried out in Silesia. Careful roasting is necessary, and the liquors must of course be freed from impurities, when good deposits of zinc (99·98–99·99 per cent. pure) result. The presence of alkaline earths in the ore is a disadvantage, causing a loss of H_2SO_4. The question of a suitable anode material at first gave much trouble. Platinum, apart from its high first cost, dissolves too quickly in the technical liquors, which are never free from organic matter. Lead fouled the electrolyte, and Fe_3O_4 proved useless. But Ferchland's anodes[2] of electrolytically deposited PbO_2 have proved to be very stable chemically. Such pure zinc was obtained that it was unattacked by 10 per cent. H_2SO_4. Mechanically, however, they disintegrate after a certain time at the high anodic current densities recommended.[3] The MnO_2 electrodes prepared according to Siemens and Halske's patent do not suffer from this drawback, being unaffected after a year's use. As it was, using the PbO_2 anodes, pure zinc could be produced at an average energy expenditure of 3,900 K.W.H. per ton, this amount falling to 3,300–3,500 K.W.H. per ton when the anodes, which were not uniform, were of good quality. The unrecovered zinc did not exceed one-third of the amount usually lost in the distillation process. The chief difficulties as ever were encountered in the roasting and lixiviation.

Laszczynski Process.—A similar process, due to Laszczynski,[4] is worked with success in Russian Poland. The blende is carefully roasted and systematically extracted with the spent acid liquors from the electrolysis. Dissolved ferrous iron is oxidised by air or by $KMnO_4$ and precipitated by ZnO. Copper, arsenic, and cadmium are removed by H_2S, silver does not dissolve. The electrolysis takes place in lead-lined wooden tanks, each fed with 1,500 amperes at about 4 volts. The current density is about 1 amp./dm.^{2}. The electrolyte is agitated by stirrers. The process of purification has not removed manganese from the liquors. This is easily oxidised anodically to permanganate, and is then capable of attacking the cathodic zinc deposit. This

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[1] Engelhardt and Huth, *Metall.* **7,** 1 (*1910*).

[2] See p. 154.

[3] 30–75 amps./dm.^{2}. The idea is to produce some S_2O_8'' ions, which act against the zinc sponge formation. At the cathode, 1·5–3 amps./dm.^{2} were used.

[4] *Zeitsch. Elektrochem.* **15,** 456 (*1909*). Compare also p. 261.

oxidation is practically entirely prevented by closely surrounding the anodes with a diaphragm of some suitable material.[1] The fresh liquors contain about 10 per cent. zinc; the electrolysis is stopped when this has fallen to 4 per cent. The electrolyte then contains about 9 per cent. free acid. A 94 per cent. current efficiency is said to result, and the zinc produced is 99·97 per cent. pure and unattacked by 12 per cent. H_2SO_4.

Hoepfner Process.—There has also been no lack of proposed processes for zinc extraction involving the electrolysis of aqueous $ZnCl_2$ solutions. The production of these liquors from the ore is less simple: on the other hand their decomposition voltage is lower than that of $ZnSO_4$ solutions. Of these processes, only that due to Hoepfner need be considered. A plant was for some time in operation at Fürfurt, and for years it has been worked in a modified form by Brunner, Mond, and Co. at Winnington. Unfortunately very few details of the working of this latter plant are available.

The calcined zinc ores were formerly stated to be extracted in presence of CO_2 gas with the $CaCl_2$ waste liquors obtained in the ammonia-soda process. $ZnCl_2$ goes into solution as follows:—

$$ZnO + CaCl_2 + CO_2 \longrightarrow CaCO_3 + ZnCl_2.$$

After removal of iron, manganese, and traces of electronegative metals, the solution is electrolysed between graphite anodes and cathodes consisting of large iron discs, revolving on horizontal axes, and only partially immersed in the bath. This renews the electrolyte in the cathode layer, and makes the zinc deposit denser and more even. The graphite anodes are suitably hooded for leading away the chlorine. Judging from the great difficulty introduced in the present case by diaphragms (see below), it is possible that they are here dispensed with, and that the liquors are merely suitably circulated. The cathodic current efficiency is 80 per cent., the losses being chiefly due to chlorine dissolved in the bath. This may either chemically attack the zinc, or depolarise the $H^{\cdot}$ discharge, preventing however any escape of gaseous hydrogen (HCl being regenerated) and thus favouring a good zinc deposit. The anodic current efficiency is 85 per cent., and the gas 60–70 per cent. pure. There are considerable losses due to leakage in the many collecting hoods used. The chlorine is utilised for bleach.

The following description applies to the **Fürfurt** plant.[2] The raw material contained 10–12 per cent. zinc, chiefly as sulphide, and was roasted with 20 per cent. NaCl for 20–22 hours at 600°–650°. The charge was lixiviated hot, and yielded a solution containing 10–11 per cent. zinc, with Na_2SO_4, NaCl, and various impurities. The Na_2SO_4 was removed by crystallisation at $-5°$; iron, manganese, and nickel

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[1] Cf. p. 262.

[2] *Zeitsch. Elektrochem.* **10**, 688 (*1904*).

hydroxides were precipitated by bleach solution and powdered limestone. From the filtered liquors, traces of lead, copper, thallium, arsenic, etc., were removed by zinc dust, and, after a second filtration, a solution was obtained with 9·5 per cent. zinc, 22 per cent. NaCl, a little gypsum, and traces of lead and thallium.

This was acidified with HCl and electrolysed in wooden tanks, V-shaped in end vertical cross-section. Each vat contained several large revolving disc-shaped cathodes, only about one-third immersed in the electrolyte. Between each pair of cathodes was an anode chamber containing a number of hard carbon anodes (graphite was not then available), separated from the cathode compartments by diaphragms, and provided with suitable chlorine exits. The diaphragms caused much difficulty. Nitrated muslin, also muslin with the fibres carefully coated with hydrated silica, were used, but a really resistant material was never obtained. The anodes behaved satisfactorily. The electrolyte circulated through the tanks by gravity. The solution leaving the last tank still contained about 2 per cent. zinc, below which concentration it was uneconomical to reduce it. During the electrolysis a continuous addition of free HCl was necessary, the free-acid content being kept at 0·08–0·1 per cent. (about 0·03 n.).

With a current density of 1 amp./dm.^{2} a tank took 1,000 amperes at 3·3–3·8 volts. The current efficiency was about 95 per cent. Assuming 3·6 volts, one ton of zinc would require about 3,100 K.W.H. The cathode metal was 99·97 per cent. pure, containing 0·01–0·02 per cent. Pb and a trace of iron. The process was given up because of the cost and trouble of calcining and lixiviating ores poor in zinc. Such difficulties are almost invariably the most serious ones encountered when working out electrolytic processes for the extraction of metals from their ores. Of next importance is generally some question of suitable material for diaphragm or anode—in this case diaphragm.

2. Electrometallurgy of Tin

Tin can be extracted from its ores very simply and in a sufficiently pure condition by ordinary metallurgical methods. There is no scope for electrolytic processes in that field. The same statement holds good of tin refining. Crude tin can be readily and economically refined electrolytically in a Na_2S solution, but there is no particular demand for the pure product resulting, and the impurities are not sufficiently valuable for their recovery alone to warrant the process being worked. Thus in one case the anode slimes had Sn 12–15 per cent.; Pb 20–30 per cent.; Sb 20–30 per cent.; Fe 1–2 per cent.; Cu 1 per cent.; Bi 0·5 per cent.; Ag 0·5–1·5 per cent.; Au 0·001 per cent. On the other hand, the recovery of tin from tin-plate scrap and refuse can be readily and economically carried out by electrolytic methods. Such methods have been largely used during recent years, though probably detinning by chlorine gas will become more and more prominent in the future.

The raw material is either tin-plate scrap, produced during the manufacture of tin cans and tinned iron ware, or discarded tin cans from the refuse-heaps of our towns. This second source of material is by no means fully exploited at present. Formerly tin scrap contained about 5 per cent. of its weight of tin—now the deposit is much thinner, and is only 1·5–3 per cent. of the total weight. The electrochemical processes proposed fall into three groups. In those of the first type the tin is dissolved chemically, and deposited electrochemically in another tank. In the second type an acid, in the third an alkaline, electrolyte is used, and in both cases the process is carried out in one operation.

Two examples of the first kind of process are the Bergsoe and Browne-Neil processes, worked in Copenhagen and North America respectively. In the **Bergsoe** process, the tin-scrap is suspended in iron baskets in a cold $SnCl_4$ solution which flows through a series of stripping tanks. The liquors leaving the last tank charged with $SnCl_2$ flow into the electrolysis vats, where they are electrolysed between tin cathodes and graphite anodes. Very pure tin is deposited, and at the anodes $SnCl_4$ is regenerated. The chief advantage of the Bergsoe process is the pure product; its disadvantages are the slow rate of working, and the gradual fouling of the electrolyte with $FeCl_3$. In the **Browne-Neil** process, the tin-plate is stripped by means of a boiling $FeCl_3$ solution, into which the scrap, packed in cages, is lowered. When the tin has dissolved, the cage is rapidly withdrawn, as the uncovered iron is next attacked. Fresh tin scrap is lowered in until all the $FeCl_3$ has been reduced as follows: $2FeCl_3 + Sn \longrightarrow 2FeCl_2 + SnCl_2$. The resulting liquors circulate through concrete tanks containing tin cathodes, the graphite anodes being enclosed in separate chambers of porous clay which are fed with the spent $FeCl_2$ solution leaving the cathode compartment. At the cathodes tin is deposited, whilst at the anodes $FeCl_3$ is regenerated. The chief drawback is the unavoidable solution of much iron by the $FeCl_3$ during the dipping. Neither of these processes has yet been extensively applied.

In processes of the second class mentioned, the proposal is to make the tin-plate anode in an acid solution, whereby it dissolves, and, when sufficient has accumulated in the electrolyte, plates out cathodically. No process of this kind has ever proved practicable, owing to the very rapid deterioration of the electrolyte caused by the iron dissolving.

Goldschmidt Process.—By far the most important process used is that employing NaOH as stripping agent and electrolyte, and first worked out by H. Goldschmidt at Essen. It depends on the facts that tin dissolves anodically in an NaOH solution, whilst iron is passive under similar conditions. From the resulting solution the tin is readily cathodically deposited when its concentration in the electrolyte has reached quite a moderate value.

Anodic Behaviour of Tin.—In practice tin is found to dissolve anodically in the tetravalent form, giving stannate as follows :

$$Sn + 4\oplus \longrightarrow Sn^{\cdot\cdot\cdot\cdot}$$
$$Sn^{\cdot\cdot\cdot\cdot} + 6OH' \longrightarrow SnO_3'' + 3H_2O.$$

This, together with the known fact that alkaline stannite solutions decompose spontaneously, giving metallic tin and stannate, led to the belief that the relations between the $Sn^{\cdot\cdot\cdot\cdot}$ and $Sn^{\cdot\cdot}$ ions and metallic tin were similar to those between $Cu^{\cdot\cdot}$ and $Cu^{\cdot}$ ions and metallic copper—*i.e.* that the equilibrium corresponding to the equation $2Sn^{\cdot\cdot} \rightleftarrows Sn^{\cdot\cdot\cdot\cdot} + Sn$ lies very much over in favour of the right-hand side. Against this was the fact that tin dissolves anodically in acid solution as $Sn^{\cdot\cdot}$ ions. Further, H. Goldschmidt and Eckardt[1] found that pure tin, though readily becoming passive, really dissolves in alkaline solutions also in the stannous condition.

The subject was fully investigated by Foerster and Dolch.[2] They showed that tin is really not analogous to copper in this connection, but that Sn–$Sn^{\cdot\cdot}$, not Sn–$Sn^{\cdot\cdot\cdot\cdot}$, is the stable system. The reason that anodic tin becomes so readily passive in alkaline solution is that, at a certain concentration, a colloidal tin compound is precipitated on the electrode. This prevents the diffusion away of the $Sn^{\cdot\cdot}$ (or SnO_2'') ions, the anode potential being consequently raised to the value necessary for oxygen evolution. The oxygen of course rapidly oxidises the stannite to stannate, the results observed under technical conditions thus being explained. Any insoluble impurities present in the tin assist the setting up of passivity. The higher the temperature and the lower the current density, the more tin can be dissolved before the formation of stannate commences. If the electrode be scraped, it again becomes active. The chemical precipitation of tin from alkaline stannite solution was shown to be preceded by a great diminution of the $Sn^{\cdot\cdot\cdot\cdot}$ (or SnO_3'') concentration, due to a gradual formation of *non-ionised colloidal* meta-stannic acid. It is only when the $Sn^{\cdot\cdot\cdot\cdot}$ concentration in the solution has in this way become very low that the $Sn^{\cdot\cdot}$ concentration exceeds that corresponding to the equation $\frac{[Sn^{\cdot\cdot}]^2}{[Sn^{\cdot\cdot\cdot\cdot}]} = K$, and the reaction $2Sn^{\cdot\cdot} \longrightarrow Sn^{\cdot\cdot\cdot\cdot} + Sn$ sets in.

When the layer of tin has dissolved, a surface of iron is exposed to

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[1] *Zeitsch. Phys. Chem.* **56**, 385 (*1906*).

[2] *Zeitsch. Elektrochem.* **16**, 599 (*1910*). See also Foerster and Yamasaki, *Zeitsch. Elektrochem.* **17**, 361 (*1911*).

the alkali. Iron is more electropositive than tin, and would therefore dissolve, were it not passive. OH' ions are instead discharged, and oxygen liberated. A certain amount of iron does, however, enter and foul the electrolyte. This is probably due to the presence of small quantities of Cl' ions in the liquors, with their well-known effect of removing passivity.

At the cathode we have the discharge of $Sn^{\cdot\cdot\cdot\cdot}$ and $H^{\cdot}$ ions to consider. Insufficient data prevent a discussion as to which takes place preferentially. The discharge of $Sn^{\cdot\cdot\cdot\cdot}$ ions, whether through the intermediate formation of $Sn^{\cdot\cdot}$ ions or directly, is probably rendered difficult by reaction resistances, whilst in the case of $H^{\cdot}$ ions there is the overvoltage to consider, amounting to a minimum of about 0·5 volt at tin and 0·08 volt at iron. (The tin is deposited on an iron cathode.) In practice, current efficiencies of 70–90 per cent., reckoned on tetravalent tin, result. The remaining 10–30 per cent. of the current is carried by $H^{\cdot}$ ions, discharged of course at the iron, not at a tin surface.

In the actual process, the anode material is loosely packed in iron cages. These are suspended within large iron tanks, serving as cathodes. If composed of old tin cans from the refuse-heap, a preliminary treatment is necessary because of the impurities present and the large and inconvenient bulk of the material. The cans are compressed and then lacerated by rollers with sharp cutting points. Fatty matter, enamel, etc., are removed by caustic soda, and, after washing, the material is brought into the electrolysis tanks. (Solder may, if necessary, be removed by heating in a furnace.) If this treatment is omitted, it causes very rapid fouling of the bath. Owing to the necessity of allowing the electrolyte access to all parts of the tin scrap, the anode cages cannot be large or tightly packed. The weight of tin scrap per cage is therefore small—ten to twenty kilos. A tank of three cubic metres capacity may contain six such baskets, which will occupy one-half to three-fourths of the bath volume.

The electrolyte originally contains about 10 per cent. NaOH. This diminishes during the process (CO_2 absorption, etc.), and falls perhaps to 7–8 per cent., at which figure it is kept by constant regeneration. To lower the voltage and improve the nature of the deposited tin, the temperature is kept at 70–80° by a suitable arrangement of circulation and steam coils. The cathodic current density is about 80–100 amps./metre^2, and 1·5–2 volts are used per tank. A cage is three to four hours in the bath. The current efficiency is 70–90 per cent., the deficiency being due to hydrogen evolution. Assuming 1·7 volts and 80 per cent. current efficiency, the recovery of one ton of tin would require

$$\frac{96540 \times 4 \times 1000 \times 1000 \times 100 \times 1{\cdot}7}{119 \times 80 \times 3600 \times 1000} = 1920 \text{ K.W.H.}$$

If the tin recovered be 2 per cent. of the scrap treated, then the treatment of 10,000 tons of scrap per annum would require, assuming 300 twelve-hour working days to the year, an installation capable of furnishing $\frac{1920 \times 10000}{50 \times 12 \times 300} = 110$ K.W. (approximately).

The tin is mostly deposited in spongy form, though a few crystals are obtained. It contains about 2 per cent. each of lead and iron, a little copper, and some stannic hydroxide. The lead is deposited electrochemically, being dissolved from the solder in the anode material. The iron is chiefly mechanically admixed, having dropped from the anode baskets. Tin not immediately under those is materially purer. The product is collected, washed, pressed into briquettes, and melted up with coke and a suitable flux. A metal results containing 99 per cent. Sn with 1 per cent. Pb and small quantities of copper and iron. This is not further purified. The detinned iron still contains at least 0·1–0·2 per cent. Sn. This is partly due to the presence, at the actual surface of contact of tin and iron, of an alloy which is attacked with difficulty by the NaOH. To dissolve the last traces of tin would require too much time, would be wasteful of power, and would result in iron dissolving or becoming loose and falling to the bottom of the bath. There are further bound to be pieces of tin-plate more heavily tinned than the average, or which do not get their fair share of current. Sometimes as much as 0·3–0·5 per cent. Sn remains undissolved on the iron. The detinned material is a valuable product, and is utilised in the open-hearth furnace for steel-making.

An important point is the regeneration of the electrolyte. If the free alkali content becomes too low, stannic hydroxide will settle out; and the NaOH is being continually used up during the process by absorption of CO_2 or by iron oxide dissolving. A fraction of the liquors is regularly withdrawn and replaced by fresh NaOH solution. The foul electrolyte is saturated with CO_2, whereby the tin and iron are precipitated. The resulting solution is then causticised by lime in the ordinary manner and subsequently returned to the tanks. The precipitate of stannic hydroxide is freed from iron by HCl, and can then be worked up in a variety of ways.

It remains to consider the disadvantages of the process. The first is incomplete recovery of the tin, the reasons for which we have discussed. There is also a considerable loss due to the electrolyte which adheres to the detinned iron when it is removed from the bath. Its content of tin cannot be recovered economically by washing. Even more important is the large wages item due to the small units employed, and to the necessity of sorting out the raw material before treatment. These facts make it very probable that in the future the electrolytic detinning process will be replaced by the chlorine detinning process of K. Goldschmidt, in which the treatment is more rapid and the losses considerably less. The pure dry chlorine required can be furnished in practically unlimited quantities by the various electrolytic alkali-chlorine processes at work.

3. Electrometallurgy of Nickel

Nickel, in its sulphide and arsenide ores, is generally accompanied by copper and iron. The iron can be largely removed as oxide and slag by a smelting process which produces a rich copper-nickel matte. This matte can be separated into two parts, one of which, containing little copper and nearly all the nickel, being worked up to a metal containing 98–99 per cent. nickel. For the manufacture of nickel steel this material may suffice. A higher-grade product is, however, often in demand, particularly for anodes in nickel-plating. This purer product can conveniently be prepared by electrolytic methods, which can be applied in two ways. The crude pyrometallurgical nickel can be electrolytically refined. Or the matte obtained at an earlier stage can be suitably lixiviated, the impurities removed chemically or electrochemically, and the purified liquors electrolysed, using an insoluble anode. Processes of both kinds have been or are used.

Anodic Behaviour of Nickel.—We will first consider the behaviour of nickel electrodes in electrolytes containing nickel salts. A nickel anode shows very markedly the phenomena of passivity. The equilibrium potential value[1] of $Ni \mid n.NiSO_4$ at room temperature is about $-0{\cdot}25$ volt. But to bring about the process $Ni + 2 \oplus \longrightarrow Ni^{\cdot\cdot}$ at such an anode, a large excess anodic polarisation is necessary. Thus, for example, Schoch found that in $n.NiSO_4$ at 26°, a nickel anode only dissolves at current densities below 0·036 amp./dm.^{2}. When this value is exceeded, it becomes passive and oxygen is evolved, its potential being about $+ 0{\cdot}28$ volt, and the excess polarisation 0·53 volt. With other electrolytes, or at other concentrations, the results are similar. The passivity of nickel, like that of other metals, decreases with rise of temperature or in the presence of Cl' or $H^{\cdot}$ ions. Hence at a higher temperature, or in a solution of $NiSO_4$ containing acid or NaCl, or in a $NiCl_2$ solution, a nickel anode can be subjected to much greater current densities than the above without passivity setting in. For details the reader is referred to the papers cited.

A further point should be here mentioned, viz. that when subjected to the same anodic current density in the same electrolyte, samples of nickel prepared in different ways dissolve with very different potentials. The reasons for this we have discussed.[2] Electrolytic nickel, unless freshly prepared and thus charged with hydrogen, requires the highest

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[1] Schoch, *Amer. Chem. Jour.* **41**, 208, 232 (*1909*); Schweitzer, *Zeitsch. Elektrochem.* **15**, 602 (*1909*).

[2] P. 135.

anodic polarisation. Rolled nickel sheet dissolves more easily, cast nickel more easily still. Best of all is cast nickel the surface of which has been roughened in some way, perhaps by acid.[1] If the current density is sufficiently high for passivity complications to enter, these potential differences may even rise in some cases to one volt.[2] Wrought or cast nickel anodes of uneven structure often therefore yield a large proportion of undissolved slimes,[3] which is very inconvenient in electroplating.

Cathodic Behaviour of Nickel.—In connection with the cathodic deposition of nickel, there are several questions to be discussed. The equilibrium potential for Ni | n. $NiSO_4$ is about – 0·26 volt, and hence, unlike copper, nickel cannot be quantitatively deposited out of solutions containing moderate quantities of free acid. The hydrogen overvoltage at nickel amounts to a minimum of 0·2 volt at room temperature, but this is nullified by the fact that, just as the small velocity of the process $Ni + 2 \oplus \longrightarrow Ni^{\cdot\cdot}$ causes passivity at a nickel anode, so does the low velocity of the converse process $Ni^{\cdot\cdot} \longrightarrow Ni + 2 \oplus$ necessitate a considerably higher cathodic polarisation than corresponds to the equilibrium value for nickel deposition.[4] This has been made clear by the work of Schoch[5] and Schweitzer.[5] At moderate current densities (0·3–1·0 amp./dm.^{2}) and at room temperature the excess cathodic polarisation necessary is 0·3–0·4 volt. Thus, Schweitzer found the following cathodic potentials necessary for nickel deposition from n. $NiCl_2$ solution at 16° in a hydrogen atmosphere:

TABLE XXXIX

Current density	Cathode potential
0·0 (equilibrium potential)	– 0·31 volt (about)
0·01 amp./dm.^{2}	– 0·462
0·03	– 0·486
0·06	– 0·51
0·11	– 0·535
0·9	– 0·645

This excess polarisation increases with the current density, but decreases with rise of temperature. Above 90° it is only about 0·1 volt. The hydrogen overvoltage, of course, behaves similarly.

Whatever the temperature, then, the $H^{\cdot}$ concentration must be kept down or else the current efficiency of nickel deposition will be low. At the same time there is a lower limit set to the acidity of the electrolyte, as otherwise basic salts would separate out, foul the bath, and affect the quality of the nickel deposit.

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[1] In that case it is charged with hydrogen, which helps its solution. Cf. p. 142.

[2] Brown, *Trans. Amer. Electrochem. Soc.* **4**, 83 (*1903*).

[3] See p. 295.

[4] See p. 121.

[5] *Loc. cit.*

Another point to be noticed is the difficulty of obtaining at room temperature *thick* cathodic deposits of the metal. Unless exceedingly low current densities are employed, the deposit peels off in thin flakes and shavings, and a coherent thick plate cannot be made. In the case of iron,[1] a similar phenomenon has been traced to the simultaneous deposition of hydrogen, which distributes itself unequally in the metal, thus producing strains and causing the flaking. It would seem natural to attribute the flaking in the present case to the same cause. According to Engemann,[2] however, this is not so, the amounts of hydrogen dissolved in the deposited metal being too low. The phenomenon is rather due to the presence of traces of iron in the electrolyte. This metal is discharged from solution more easily than nickel, and the first layers of the deposit therefore contain a higher proportion of it than do subsequent layers. Strains are in this way set up, and result in the flaking. If electrolyte and anode are perfectly free from iron there is no difficulty in getting a satisfactory deposit. Low temperature, low $H^{\cdot}$ concentration in the electrolyte, and high current density, all of which favour an irregular deposition of iron, also favour the flaking of the cathodic deposit. At higher temperatures (50°–90°) there is no difficulty in getting good deposits, even at current densities of 2·5 amps./dm.^{2}.[3]

Laboratory work on the electro-deposition of nickel has been carried out by Foerster [4] and by Kern and Fabian.[5] As we have seen, Foerster showed the necessity with ordinary electrolytes of working above room temperature if thick deposits are to result. Generally the higher the temperature and the nickel content of the electrolyte, the better the deposit. Any iron and cobalt present in the nickel anode are deposited cathodically. Very little separation can be effected, owing to the chemical and electrochemical similarity of the metals concerned and their tendency to form solid solutions with one another. Kern and Fabian worked with different electrolytes, and varied the concentration of free acid, temperature, and current density. They observed the cathodic current efficiency and the bath voltage. In all their experiments the anodes were of crude cast nickel, containing 92 per cent. Ni, 5 per cent. Fe, some copper and carbon, and were placed 1″ from the cathodes. The following table contains a selection of their results. The heavy deposits given by neutral $NiSO_4$ solutions were due to the formation of basic salts. This tendency was much less marked with $NiCl_2$ solutions.

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[1] See p. 300.

[2] *Zeitsch. Elektrochem.* **17**, 910 (*1911*).

[3] Foerster, *Zeitsch. Elektrochem.* **4**, 160 (*1897*).

[4] *Loc. cit.*

[5] *Electrochem. Ind.* **6**, 365 (*1908*).

TABLE XL

Electrolyte	θ	Current density	$NiCl_2$		$NiSO_4$	
			Voltage	Current efficiency	Voltage	Current efficiency
			Volt	Per cent.	Volt	Per cent.
8 per cent. Ni + 0·5 mol. equiv. of free acid	20° C.	10 amp. foot^2	0·49	3·20	0·89	0·86
	40°		0·36	1·25	0·65	0·62
	60°		0·21	1·01	0·42	0·39
8 per cent. Ni + 0·1 mol. equiv. of free acid	20°	10	0·73	62·6	0·91	1·50
	40°		0·52	79·0	0·78	1·60
	60°		0·35	71·0	0·51	1·50
8 per cent. Ni + 0·05–0·04 mol. equiv. of free acid	20°	12	0·86	67·2	0·97	0·0
	40°		0·53	75·7	0·79	0·7
	60°		0·44	80·7	0·61	2·8
8 per cent. Ni; neutral	20°	10	0·78	96·6	1·50	102·2
	40°		0·59	99·4	1·35	106·9
	60°		0·44	99·2	0·88	101·1
8 per cent. Ni; neutral	20°	20	1·06	91·2	3·45	—
	40°		0·73	94·7	2·30	—
	60°		0·64	88·3	1·40	—

In the electrolytic refining of nickel the **impurities** to be considered are copper, cobalt, iron, carbon, and sulphur. Of these, only the last two can be eliminated if the process be carried out in one operation, using crude soluble anodes; for copper is precipitated more readily than nickel, and, as we have seen, Foerster showed that no separation of iron and cobalt is possible in this way. The only nickel refining process of this type of which the author knows was that worked by the Balbach Smelting and Refining Co. (U.S.A.) some years back.[1] The anodes contained 94–97 per cent. Ni; 0·75 per cent. Fe; 0·2–0·6 per cent. Cu; 0·25 per cent. Si; 2–3 per cent. C. The electrolyte was a hot (50°–60°) $NiSO_4$ solution, the current density being 1·5 amps./dm.^{2} and a bath taking 1·7–1·8 volts. A H.P. year is said to have produced 2–4 tons nickel, which corresponds to an expenditure of 1,600–3,300 K.W.H. per ton. The metal was of excellent quality, containing 99·5–99·7 per cent. Ni + Co, 0·1–0·2 per cent. Cu, 0·25 per cent. Fe, with traces of carbon, sulphur, arsenic, and silicon. This process has now been discontinued for some years. The cause is stated to have been the large quantities of anode residues produced in the electrolysis. The crude metal contained a large percentage of carbon, gave brittle unhomogeneous castings,

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[1] *Electrochem. Ind.* **1,** 208 (*1903*); *Zeitsch Elektrochem.* **10,** 821 (*1904*).

and, when once the outer layer had been dissolved, crumbled away very readily. Its high melting-point rendered this a particularly heavy drawback. Patents, in fact, were taken out for the use of frames packed with powdered nickel as anodes.

Most other electrometallurgical nickel processes have employed insoluble anodes for the final electrolysis, previously removing impurities from the electrolyte in various ways. Thus electrolytic means have been applied to the removal of copper from the liquors, and this electrolysis of solutions containing copper and nickel has been studied by Neumann[1] and by E. Günther.[2] Neumann used anodes containing 48·9 per cent. Ni, 50·1 per cent. Cu, 0·63 per cent. Fe, with some carbon and silicon, in an electrolyte (circulated) of initial composition —$CuSO_4, 5H_2O$, 180 $\frac{\text{grams}}{\text{litre}}$; H_2SO_4, 85 c.c. per litre. He found that the anode dissolved readily and copper was cathodically deposited, the electrolyte growing continually poorer in copper, and richer in nickel and iron. Finally, the quality of the deposit began to deteriorate, hydrogen being evolved. This happened at a current density of 1·5 amps./dm.^{2}, when the electrolyte still contained 20 $\frac{\text{grams}}{\text{litre}}$ of copper. No nickel was deposited.

Günther used anodes containing Cu 26·4 per cent., Ni 50·2 per cent., Fe 21·2 per cent., with some sulphur and carbon. The electrolyte was acid $CuSO_4$ with 38·4 $\frac{\text{grams}}{\text{litre}}$ copper and 62·7 $\frac{\text{grams}}{\text{litre}}$ H_2SO_4. With electrodes 5 cm. apart, and a current density of 2 amps./dm.^{2}, the cathodic current efficiency was 95–97 per cent., and the bath voltage 0·56, rising to 1·16 volts. The copper produced was 99·97 per cent. pure. At the start the electrolyte was stirred by blowing in air. When the copper content had fallen to 1 per cent. circulation was commenced. By this means the copper concentration was lowered to 0·5 per cent. before the deposit became spongy. It is, however, better, working with 2 amps./dm.^{2}, not to allow the copper content to fall below 1 per cent. The electrolysis should then be discontinued, and the remainder of the copper removed by H_2S.

Hoepfner Process.—Of technical processes, that of Hoepfner should first be noticed. It received very extended trials, and underwent many modifications, but never became really successful. In one form which it assumed, the nickel ore, containing copper and iron, was partially roasted to render most of the iron insoluble, and then extracted with a $CaCl_2$ solution containing $CuCl_2$, the anode liquors

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[1] *Zeitsch. Elektrochem.* **4**, 316 (*1898*).
[2] *Ibid.* **9**, 240 (*1903*).

of the subsequent electrolysis. Copper and nickel sulphides dissolved as follows:

$$Cu_2S + 2CuCl_2 \longrightarrow 2Cu_2Cl_2 + S$$
$$CuS + CuCl_2 \longrightarrow Cu_2Cl_2 + S$$
$$NiS + 2CuCl_2 \longrightarrow Cu_2Cl_2 + NiCl_2 + S$$

After removing silver and iron chemically, the purified electrolyte charged with NiCl and Cu_2Cl_2 was electrolysed as described on p. 264. The greater part of the copper in the cathodic compartment was thus removed electrolytically, and the last portions chemically. The purified solution containing $CaCl_2$ and $NiCl_2$ was then electrolysed, using a nickel sheet cathode and a graphite anode. Nickel of excellent quality resulted, whilst, at the anode, either chlorine was evolved and utilised in lixiviating the roasted ore, or else, as in the copper electrolysis, the anode compartment was fed with the solution of Cu_2Cl_2 and $NiCl_2$ resulting from the lixiviation of the ore, and $CuCl_2$ was regenerated.

Savelsberg-Wannschaff Process.—The circumstances which caused the abandonment of the Hoepfner copper process—difficulties connected with diaphragms and lixiviation of the calcined ore—affected the nickel process adversely also. It was worked for some years in Papenburg, but was later replaced there by a process devised by Savelsberg and Wannschaff.[1] A matte with 65–70 per cent. Ni, containing iron, but very free from copper, is finely ground with water or $CaCl_2$ solution and treated with chlorine. Nickel and iron dissolve, sulphur is liberated and partially oxidised to H_2SO_4, whilst the excess of HCl produced is neutralised by adding Fe_2O_3. The solution, after filtration from $CaSO_4$, sulphur, silica, Fe_2O_3, etc., contains chlorides of nickel and iron. It is heated to 60°–70°, treated with fresh powdered ore, and air is blown in. The iron in solution is thus replaced by nickel, and $Fe(HO)_3$ is precipitated. After decantation and filtration, the liquors, containing $NiCl_2$, are electrolysed between sheet-metal cathodes and graphite anodes, the latter being hooded to collect the chlorine. The electrolyte contains initially 100 $\frac{\text{grams}}{\text{litre}}$ nickel, and leaves the bath with 30 $\frac{\text{grams}}{\text{litre}}$. The cathodic current density is 1–1·2 amps./dm.². The working temperature is not stated; 4–4·5 volts per bath are used, and the average current efficiency is 93 per cent., though 99 per cent. is sometimes reached. The product is perfectly compact, though of a somewhat warty appearance, due to bubbles of hydrogen adhering to the electrode and becoming gradually covered with metal. It contains 99·9 per cent. Ni + Co; 0·06 per cent. Fe; 0·02 per cent. Cu; 0·02 per cent. SiO_2;

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[1] *Zeitsch. Elektrochem.* **10**, 821 (*1904*). Also Billiter, *Die Elektrochemischen Verfahren*, etc., vol. i., p. 282 (1909).

sulphur, carbon, arsenic, antimony, etc., etc., traces or absent. Assuming 93 per cent. current efficiency and 4·3 volts, we have

1 ton nickel requires

$$\frac{100 \times 2 \times 96540 \times 1000 \times 1000 \times 4{\cdot}3}{93 \times 58{\cdot}7 \times 3600 \times 1000} = 4200 \text{ K.W.H.}$$

Browne Process.—The next process which will be considered is that of Browne,[1] carried out successfully for years by the Canadian Copper Co. at Brooklyn, and now again in operation elsewhere by the same company. A copper-nickel-iron matte, containing about equal quantities of copper and nickel, is desulphurised, half of the product cast into anodes, the other half granulated. This granulated material is treated with chlorine in presence of a brine solution, and yields the electrolyte for use with the anodes just mentioned, containing $NiCl_2$, Cu_2Cl_2, $FeCl_2$, and NaCl. The anodes (in Brooklyn) had 54·3 per cent. Cu and 43·1 per cent. Ni, the remainder being iron and sulphur. The electrolysis took place in cement tanks, using thin electrolytic copper cathodes. A coherent, but rather crystalline, copper deposit resulted.

The current efficiency was about 90 per cent. (copper deposited from the cuprous state), the deficiency being due to the presence of $Cu^{\cdot\cdot}$ ions ; 0·3–0·35 volts were used. On leaving this series of tanks, the ratio Ni : Cu in the liquors was about 80 : 1. The rest of the copper was precipitated by Na_2S, the iron oxidised and removed as hydroxide, and, after concentration, practically all the NaCl crystallised out. In the final electrolysis the cathodes were of nickel strip, the graphite anodes being provided with porous clay diaphragms and hoods. A cathodic current efficiency of 93·5 per cent. resulted, 3·5–3·6 volts being required per tank. The nickel deposit was of excellent quality, analysing Ni 99·85 per cent., Cu 0·014 per cent., Fe 0·085 per cent.

Before finally leaving this subject, it should be mentioned that the statement has been made that electrolytic nickel is at present also produced by the Orford Copper Co., New Jersey, using anodes of nickel matte in a $NiCl_2$ solution as electrolyte, and getting cathodic deposits of excellent quality. Sulphur will, of course, remain undissolved at the anode, and in view of the difficulties experienced in working the Marchese copper process technically one is inclined to doubt the reliability of the information.[2] E. Günther,[3] working on a small scale, studied the behaviour of nickel matte anodes in $NiSO_4$ solution. They dissolved with surprising ease, and the cathodic nickel deposits

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[1] *Zeitsch. Elektrochem.* **9**, 392 (*1903*).

[2] *Cf.*, however, p. 261.

[3] *Metall.* **1**, 77 (*1904*).

were of good quality. He experienced, however, some trouble with the anodes (owing to their brittleness, irregular structure, etc.), and these difficulties would undoubtedly be far greater on a technical scale.

4. Electrolytic Refining of Iron

In recent years this subject has been much studied, chiefly from the point of view of preparing pure iron for experimental alloy work. Lately, however, the well-known firm of Langbein and Pfanhauser, of Leipzig, using the process of Fischer, has commenced to electrolytically refine iron for use in transformer cores, etc. The pure product has very favourable magnetic properties.

We already know that an iron anode markedly exhibits the phenomena of passivity. The conditions for its ready solution are high temperature, low current density, and presence of Cl' and $H^{\cdot}$ ions in the electrolyte. It is particularly from a study of the behaviour of this metal that Foerster has based his views on passivity.[1]

Cathodic Deposition.—Most attention has, however, been devoted to the cathodic deposition of iron. We may particularly mention the work of Burgess and Hambuechen,[2] Foerster, Mustad and Lee,[3] and Pfaff.[4] There are several points to be considered. Firstly, iron is much more electropositive than hydrogen. The equilibrium potential $Fe \mid n.\ FeSO_4$ is about $-0{\cdot}46$ volt, whilst even in neutral solution the potential of the hydrogen electrode is $-0{\cdot}41$ volt. The reversible deposition of hydrogen from such a solution should therefore take place rather more easily than that of iron, and the small hydrogen overvoltage at that metal barely equalises matters. But we have seen[5] that iron, like nickel, is one of those metals whose cathodic deposition encounters strong irreversible reaction resistances. This fact, of course, favours the preferential discharge of $H^{\cdot}$ ions, and if satisfactory current efficiencies are to be obtained the ratio $\frac{Fe^{\cdot\cdot}}{H^{\cdot}}$ must be as high as possible. It is limited by the solubility of the iron salt employed, and by the fact that at low $H^{\cdot}$ concentrations basic salts are liable to precipitate, affecting the quality of the cathodic deposit. A rise in temperature, however, decreases the reaction resistance, and should therefore increase the current efficiency. The same should result from an increase in current density, which is known to largely increase the overvoltage effect.

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[1] See p. 142.

[2] *Electrochem. Ind.* **2**, 184 (*1904*). *Trans. Amer. Electrochem. Soc.* **19**, 181 (*1911*).

[3] *Abhand. Bunsen Ges.* **2**, 34 (*1909*).

[4] *Zeitsch. Elektrochem.* **16**, 217 (*1910*).

[5] P. 121.

The figures of Tables XLI and XLII show these deductions to be true.

TABLE XLI

Electrolyte $2{\cdot}3\ n\ .\ FeSO_4$

θ	Current efficiency.				
	Cathodic current density 1·6 amps./dm.^{2}		3·2 amps./dm.^{2}		
	Acidity 0·05 *n*.	0·1 *n*.	0·01 *n*.	0·05 *n*.	0·1 *n*.
	Per cent.				
18°	30–33	4·8	86·8	61·6	21·4
37°	40–45	6·7	89·0	52·0	19·6
55°	58–64	13·2	90·8	60·0	26
75°	80–85	34·8	94·8	72·0	48·7
95°	—	58·8	—	—	78·8

TABLE XLII

Electrolyte $FeCl_2 + 0{\cdot}05\ n\ .\ HCl$. Current density 1·6 amps./dm.^{2}

θ	Current efficiency		
	$4{\cdot}6\ n\ .\ FeCl_2$	$2{\cdot}3\ n\ .\ FeCl_2$	$0{\cdot}8\ n\ .\ FeCl_2$
	Per cent.		
18°	49·6	21·0	9·0
37°	46·3	30·4	12·7
55°	62·7	46·0	21·1
75°	81·7	64·6	34·0

The best results for a good current efficiency are therefore : (*a*) high $Fe^{\cdot\cdot}$ concentration ; (*b*) $H^{\cdot}$ concentration only high enough to prevent precipitation of basic salts ; (*c*) high temperature ; (*d*) high current density.

Nature of Deposit.—There are two further points connected with the character of the cathodic deposit. By varying the conditions the iron can be produced either exceedingly hard and brittle or else ductile. Also the tendency for any but very thin deposits to flake off is very marked, as in the case of nickel. Both these facts have been shown to result from the presence or otherwise of hydrogen in the metal. If it be present, the deposit is hard and brittle, and moreover readily rusts; if absent, a soft ductile iron results.[1] If it is unequally and irregularly dissolved it sets up strains, and causes the metal to flake off, as Lee has clearly shown. He found the percentage of dissolved hydrogen to

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[1] The nature of the deposit also appears to depend on the iron salt used : sometimes it is crystalline ; sometimes, as when produced at high temperatures and high current densities from a $FeCl_2$ solution, it is smooth and dark grey in colour. Engemann (*Zeitsch. Elektrochem.* **17**, 910, *1911*) has shown electrolytic nickel deposition to be somewhat similarly affected.

increase somewhat with *decrease* of acid in the electrolyte, with increase of iron in the electrolyte, and with increase of current density. Far greater, however, was the effect of increased temperature, which caused the hydrogen content to rapidly diminish. Thus, under certain conditions, iron deposited at 18° contained 0·085 per cent. hydrogen, at 37° 0·039 per cent., at 55° 0·024 per cent., at 75° 0·0096 per cent. At high temperatures, then, iron can be electrolytically deposited using large current densities, and yet contain little hydrogen and be ductile. Moreover, the rapid diffusion possible under those conditions equalises the concentration of the dissolved gas, and thus removes the tendency to flake off.

Burgess and Hambuechen, using anodes of wrought iron, employ a bath of ferrous ammonium sulphate with 40 $\frac{\text{grams}}{\text{litre}}$ iron. It is not circulated. They work at 30° with a cathodic current density of 0·6–1 amp./dm.^{2}, the bath taking about 1 volt. (This value, high compared with the voltage of the copper refining tank, is of course due to the irreversibility at both anode and cathode.) The current efficiency is practically 100 per cent., the very uniform product 99·97 per cent. pure (free from C, Si, Mn), hard and brittle. One kilo of refined iron is produced per K.W.H.

Pfaff recommends a $FeSO_4$ bath not less than twice normal, and acidified with H_2SO_4 (0·01 normal). He works at 70°, using a cathodic current density of 2 amps./dm.^{2}, and obtains a perfectly homogeneous, dense, finely crystalline product. The current efficiency is about 87 per cent., and the bath voltage 0·7 volt. In order to remove hydrogen bubbles adhering to the cathode surface, he blows in air.

The two processes more or less worked technically employ $FeCl_2$ solutions. Merck[1] works at 70°, with a solution containing 100 grams $FeCl_2$ to 100 grams H_2O. (NH_4Cl is also said to be added.) The electrolyte is circulated, and the current density is 3–4 amps./dm.^{2}. Experiments of Pfaff indicate that $FeSO_4$ solutions behave more satisfactorily. Fischer uses a bath containing 450 grams $FeCl_2$ + 500 grams anhydrous $CaCl_2$ + 750 grams water. The working temperature is at least 90°, and the current density 10 amps./dm.^{2} (according to one account 20 amps./dm.^{2}). Ductile iron deposits of any thickness, and at least 99·95 per cent. pure, result.

5. Electrometallurgy of Lead

The refining of crude lead has so far been mainly carried out for the recovery of the silver. Of the two processes used, the Pattinson and the Parkes processes, the latter has in recent years become the more

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[1] D.R.P. 126,839.

important. Both involve a considerable fuel consumption, and cannot be economically worked on a small scale. In the Parkes process there is a further continual loss of zinc. In neither case is the bismuth eliminated, and the resulting product is not as suitable for the manufacture of lead colours—white lead, chrome yellow—as a bismuth-free lead would be. A simple and efficient electrolytic refining process, taking into account the high electrochemical equivalent of lead, would seem to be offered an excellent field.

There are two difficulties to be overcome. Firstly, electrolytes containing the anions commonly used in electrolytic refining—Cl', NO_3', SO_4''—cannot be employed. $PbCl_2$ and $PbSO_4$ are too insoluble. NO_3' ions would bring any anode silver into solution unless the current density were exceedingly low, and this would be subsequently cathodically deposited; further, metallic lead chemically reduces NO_3' to NO_2', the solution becoming yellow, and under certain conditions complex nitrites settling out. Secondly, lead is not readily deposited cathodically in compact form, but gives crystalline growths which—apart from the inconvenience of handling—spread towards the anode and cause short circuits.[1] Only by using exceedingly concentrated $Pb(NO_3)_2$ or $PbAc_2$ solutions could Glaser[2] get a coherent lead deposit. The only early process which ever promised anything was that of **Keith,** whose electrolyte was a solution of $PbSO_4$ in NaAc. The cathodic lead was practically pure except for bismuth, but was crystalline, and tended to continually form short circuits. The process proved unable to compete with the Parkes process.

Betts Process.[3]—In 1902 Betts proposed the use of a $PbSiF_6$ solution as electrolyte, with the addition of a trace of gelatine. The resulting lead is compact, there is little or no trouble from crystalline growths, and all impurities present in appreciable quantity enter the slimes. The power cost is low, and certain difficulties encountered in working up the slimes have now been partly overcome. This process has been working on a large scale for years in America and England, and must be regarded as a serious competitor of the older methods of refining.

Senn[4] has made a laboratory study of the process. He first showed that the nature of the electrolyte is essentially important.[5] Using a solution containing 8·3 per cent. lead and 11·7 per cent. H_2SiF_6, and

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[1] *Cf.* p. 267.

[2] *Zeitsch. Elektrochem.* **7**, 365 (*1900*).

[3] *Electrochem. Ind.* **1**, 407 (*1903*); *Metall.* **6**, 233 (*1909*).

[4] *Zeitsch. Elektrochem.* **11**, 229 (*1905*).

[5] Mathers (*Trans. Amer. Electrochem. Soc.* **17**, 261 (*1910*), has shown an acid solution of $Pb(ClO_4)_2$ to be also a very suitable electrolyte. It has, moreover, a higher conductivity than has the acid $PbSiF_6$. There is a prospect that it will also shortly come into technical use.

a current density of 1·07 amps./dm.^{2}, a good coherent lead deposit, tending merely to crystal formation at the edges, resulted. With 1·72 amps./dm.^{2} the product was highly crystalline. On adding gelatine ($0·1 \frac{\text{gram}}{\text{litre}}$ gave the maximum effect), the higher current density furnished a coherent though crystalline deposit with a few needles at the edges only; and with 1·07 amps./dm.^{2}, a fine silky deposit with no trace of crystalline growths resulted. Using $Pb(NO_3)_2$ or $PbAc_2$, coherent, crystalline and very brittle deposits were given after adding gelatine, but the latter salt required far more. Both electrolyte and gelatine, therefore, assist in the favourable results. Temperature seemed of little influence. And, provided that the total SiF_6 content of the electrolyte remained constant, the lead concentration could be considerably lowered without affecting the results. The cathodic current efficiency was about 98 per cent., and the anode dissolved quantitatively as $Pb^{\cdot\cdot}$ ions.[1] The anodic loss, indeed, exceeded 100 per cent., on account of chemical solution of the lead in the free acid.

Senn finally showed that a lead anode, saturated with copper or containing 20 per cent. Bi, could be dissolved at 0·5–1·5 amps./dm.^{2}, these metals remaining in the slimes. With 10 per cent. Sb present, 1 amp./dm.^{2} could be safely used. At 1·5 amp./dm.^{2} the antimony dissolves and is cathodically deposited. With a normal anodic content of any of these metals no appreciable quantity should be found in the cathodic lead.

Technically the electrolysis takes place in large tanks of tarred wood or cement. Anodes and cathodes are suspended alternately and connected as in the multiple system of copper refining. The anodes are wedge-shaped, thicker at the top than at the bottom. Their average composition (mean of ten analyses) is Pb 98·1; Ag 0·61; Sb 0·7; Cu 0·23; As 0·19; Bi 0·1; Sn 0·03; Fe 0·01; Au 0·007. They are provided with lugs which rest on the positive busbars. The cathodes (formerly prepared by electrolysis in a separate tank) are now made by pouring out a thin sheet of refined molten lead on to an iron plate. They are wrapped round copper rods which hang on the negative busbars. The composition of the electrolyte can vary considerably. An average liquor initially contains 70–80 grams lead (as $PbSiF_6$) and 100–110 grams free H_2SiF_6 per litre. It is prepared by acting on fluor-spar and silica with H_2SO_4, and adding white lead to the H_2SiF_6 solution produced. The free acid keeps back the hydrolysis of the SiF_6'' ions and increases the conductivity; 0·1–0·2 per cent. gelatine or glue is present. The specific resistance is 3·6 ohms/cm.^{3}. The liquor is circulated by gravity. The fall in level per tank is slight, and contact

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[1] See also Elbs and Nübling, *Zeitsch. Elektrochem.* **9**, 781 (*1903*).

with air during circulation is avoided as far as possible, as dissolved oxygen attacks the antimony in the slimes, and when that metal is once in solution it is cathodically deposited.

During the electrolysis the electrolyte deteriorates. The two most important changes are the disappearance of free acid and of glue. The former change is caused by (*a*) the discharge of $H^{\cdot}$ ions at the cathode, and (*b*) the lead dissolving chemically, whereby its concentration in the electrolyte rises. Regular addition of fresh H_2SiF_6 (6–12 lbs. per ton of lead produced) is necessary. Glue is consumed at the rate of $\frac{1}{2}$–1 lb. per ton of cathodic lead, and must also be continually renewed. Most of it is cathodically precipitated with the metal or adsorbed in the slimes. Other changes are the production of HF by the hydrolysis of SiF_6'' ions with formation of hydrated silica, and the slow accumulation of iron, zinc, antimony, etc.

The current density is 17–20 amps./dm.^{2} The working voltage (including that lost in leads) is about 0·28 volt with fresh anodes, but gradually rises to 0·40 volt, owing to the increasing resistance of the slimes. The actual polarisation voltage is only about 0·02 volt per tank. The working temperature, kept up by the current, is 30°–35°. Anodes and cathodes are in the bath for about eight days. At the end of that time the anodes still contain about 25 per cent. of unattacked material (including lugs). This proportion is greater than in the case of copper refining (10–15 per cent.). Their remelting is, however, easy, and further electrolysis means constantly rising voltage, due to the increasing thickness of slimes. During the electrolysis, any anodic zinc, nickel, or cobalt, together with some of the iron and tin, dissolve. None of these accumulates sufficiently to deposit appreciably on the cathode. We have also seen that dissolved oxygen can cause antimony from the slimes to enter the electrolyte and appear in the cathodic deposit.

The refined lead is very pure. An average analysis of eight samples gives Pb 99·996 ; Fe 0·0013 ; Sb 0·0006 ; Cu 0·0005 ; Ag 0·0001 ; Sn 0·0001 ; As trace ; Zn, Bi, Ni, etc., absent. The cathodic current efficiency averages about 90 per cent. at the current densities quoted. By altering the latter, it can easily rise to 95 per cent. or fall to 85 per cent. The loss is due to slow $H^{\cdot}$ discharge and to chemical solution of the lead. Taking the average cell voltage as 0·34, we find that one ton of lead requires

$$\frac{96540 \times 2 \times 1000 \times 1000 \times 100 \times 0{\cdot}34}{207{\cdot}1 \times 90 \times 3600 \times 1000} = 98 \text{ K.W.H.}$$

Treatment of Slimes.—The greatest difficulty in the Betts process has been the treatment of the slimes. An efficient treatment is essential in the refining of a material like lead, where the demand for the particularly pure cathode product is limited. An average sample of the slimes (which do not fall off, but retain the form of the anode) contains perhaps 25 per cent. Sb, 20 per cent. As, 10 per cent. Pb, 10 per cent. Cu, 25 per cent. Ag, 5 per cent. Sn, 3 per cent. Bi, 1 per cent. Fe, 0·1 per cent. Au. But besides metallic constituents, hydrated silica, PbF_2, and large quantities of admixed fluo-silicate solution are present. The silica and PbF_2 result from the hydrolysis of the SiF_6'' ions in the electrolyte, and this in its turn is caused by the low $H^{\cdot}$ concentration in the immediate regions of the anode (due to the migration away of positive ions) and by chemical action of the lead on the dissolved acid. The deficiency of $H^{\cdot}$ ions and the resulting precipitation of non-conducting substances both contribute towards the high resistance of the slimes which we have already noticed.

The slimes are first carefully washed on the counter-current principle, and the resulting liquors returned to the electrolysis tanks. The subsequent treatment does not yet appear quite settled. Of the many methods suggested, we will briefly note the two following. The slimes, now free from H_2SiF_6, are washed with alkali and boiled with a 6 per cent. Na_2S solution containing free sulphur. The antimony dissolves, but only a little of the arsenic, and is precipitated electrochemically.[1] The filtered slimes are roasted. Arsenic is driven off and the lead enters the slags. The product is then extracted with hot H_2SO_4 in presence of air. Silver and copper dissolve, the silver is precipitated on copper strips, and copper sulphate subsequently crystallised out. Further treatment of the residue with H_2SO_4 will finally leave any gold undissolved. Another method is to cupel the slimes, after washing and drying, in a basic hearth with the addition of soda. As_2O_3 and some Sb_2O_3 are driven off, and PbO and Sb_2O_3 are found in the slag and worked up to antimonial lead. Ag, Bi, Au, Cu and Pb remain in the metallic mass, which is apparently treated with H_2SO_4 as in the first process given.

The chief advantages of the Betts process do not consist in its relative cheapness—there is little difference here between it and the Parkes process—but in the fact that it gives a lead free from bismuth and antimony, allows of the recovery of these substances, and involves a smaller loss in lead and noble metals. On a small scale, as has been mentioned, the Betts process can be quite easily worked, while the older processes fail.

Electrolytic Extraction of Lead.—Whilst, however, electrolytic methods can be successfully applied to lead refining, it is very doubtful whether they can be economically used for the extraction of the metal from its ores. The pyrometallurgy of lead is simple and inexpensive, and recent improvements have reduced the silver losses to a very low figure.

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[1] P. 307.

The **Salom Process**[1] for the electrolytic reduction of galena was nevertheless worked for some years on a large scale at Niagara. In the final form it took, the finely-powdered galena, which must be of high quality, was fed continuously into a ring-shaped cell of antimonial lead containing a 10 per cent. H_2SO_4 solution as electrolyte. The base and sides of the cell slowly revolved and constituted the cathode, whilst the anode was stationary and insulated by rubber rings. The cathodic reaction is $PbS + 2H^{\cdot} \longrightarrow Pb + H_2S + 2 \oplus$, and *not* chemical reduction by liberated nascent hydrogen.[2] The lead sponge formed was scraped out regularly at a later stage in the revolution of the cathode, and H_2S passed off through suitable exits. 2·5–2·9 volts were required per cell, and with well-ground material a current efficiency of 70 per cent. was obtainable. The power expenditure per ton of lead sponge was thus only about 1,000 K.W.H. The lead sponge was chiefly calcined to litharge, and it also was intended to use it for accumulators, though for this purpose it would doubtless be too impure. The disadvantages of the process which led to its abandonment were: (*a*) the necessity of using a very pure galena; (*b*) the fine preliminary grinding required; (*c*) the incomplete reduction obtained, usually only 95 per cent.; (*d*) difficulties connected with leakage of the H_2S; (*e*) the fineness of division of the product rendering it impossible to melt it up without losses. The first is particularly vital.

6. Bismuth and Antimony

In conclusion certain processes proposed for the electrolytic refining or production of bismuth and antimony will be briefly noted. Mohn[3] has described experiments on the refining of crude **bismuth** anodes of the following composition—94 per cent. Bi, 2·2 per cent. Pb, 3·1 per cent. Ag, 0·5 per cent. Cu, 0·1 per cent. Sb, 0·1 per cent. Au. The electrolyte contained 7 per cent. Bi as $BiCl_3$ and 9–10 per cent. free HCl. Anodic and cathodic current density were about 2 amps./dm.^{2} and 6 amps./dm.^{2} respectively. The bath took 1·2 volts. The results were not very satisfactory. Lead, antimony and copper, and, unless care was taken, some silver also, dissolved. Of these, silver at once enters the cathodic deposit, and copper and antimony can only be allowed to accumulate in the electrolyte to a small extent. After melting up with nitre and soda to remove any arsenic or antimony, a 99·8 per cent. pure product, containing otherwise only silver, resulted. According to Foerster and Schwabe,[4] an electrolyte of bismuth fluosilicate promises much better results. The single potentials shown

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[1] *Electrochem. Ind.* **1**, 18 (*1902*); *Zeitsch. Elektrochem.* **9**, 380 (*1903*).

[2] Bernfeld, *Zeitsch. Phys. Chem.* **25**, 46 (*1898*).

[3] *Electrochem. Ind.* **5**, 314 (*1907*).

[4] *Zeitsch. Elektrochem.* **16**, 279 (*1910*).

by silver, lead and bismuth against solutions of their fluosilicates are far apart, and a good separation of these metals should thus be possible. Using, in fact, a crude bismuth anode containing silver and lead, it was found that the silver remained undissolved in the slimes, the lead accumulated in the electrolyte, and a very pure cathodic bismuth resulted. The character of the deposit was also compact and dense.

Antimony has been prepared by Siemens and Halske by electrolytic deposition from alkaline sulphantimonite solutions. The product is very pure. Such a liquor with 3·5 per cent. Sb also results from one method of working up the slimes of the Betts lead-refining process. It is electrolysed until its content has sunk to 1 per cent., a current efficiency of 45 per cent. being obtained. Betts[1] has also experimented with acid solutions of $SbCl_3 + FeCl_2$ and of $SbF_3 + FeSO_4$. At the anode ferric salts were regenerated, which could be subsequently used, for example, to dissolve up more antimony or antimony compounds. At the cathode a pure deposit of antimony of good quality resulted, provided that copper and arsenic were absent.

Literature

E. Günther. *Die Darstellung des Zinks auf elektrolytischem Wege.*
Betts. *Lead Refining by Electrolysis.*

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[1] *Trans. Amer. Electrochem. Soc.* **8**, 187 (1905).

CHAPTER XIX

ELECTROPLATING AND ELECTROTYPING

Electroplating is the art of covering a metallic surface by electro-deposition with an adherent coating of some other metal, the form of the original surface being fully retained. The second metal may be deposited for decorative purposes, or because of its superior resistance to chemical and atmospheric influences. **Electrotyping** is the art of reproducing the form of an object by electro-deposition on a cast or negative.

Electroplating—General Considerations.—The conditions governing the cathodic deposition of metals, the nature of the deposit, and related phenomena, have been already considered,[1] and to these discussions the reader is referred. Special attention should be paid to the paragraphs dealing with irreversible effects, hydrogen overvoltage, concentration polarisation, depolarisation by deposition as alloy, effect of $H^{\cdot}$ and metallion concentration, presence of organic addition agents, current density, deposition from complex salts, etc., etc.

Certain points should be particularly emphasised here. The first essential in an electrogalvanic deposit is that it should be continuous, regular, and should adhere perfectly to the object plated. The latter is therefore always first very thoroughly cleaned by methods presently described. But another condition must be satisfied. If the metal to be plated and the deposited metal do not cohere well, or if their coefficients of expansion are somewhat different, then the deposit will not adhere to the plated object, but will easily flake off.

This, however, is not so if the metals have any tendency to alloy together. Under such circumstances the electro-deposition of the plating metal is depolarised by the plated metal, and the first thin layer of the former is deposited, not as pure metal, but as an alloy with the material of the object treated. As electro-deposition continues the alloy becomes gradually richer in the deposited metal, until it finally contains no admixture of the other constituent. This layer of alloy is

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[1] Pp. 115, 118–126. Various points have also been considered in the last two chapters.

extremely thin, but nevertheless the increase in cohesion is sufficiently great and the change of coefficient of expansion sufficiently gradual to result in a strong and adhesive deposit.[1] Haber[2] has suggested that this alloying is essential if the deposit is to adhere. Nickel does not deposit satisfactorily on either tin, zinc, or lead unless a preliminary coating of copper or brass is plated on, and the very frequent use of intermediate coatings of these substances in electroplating is accounted for by their strong alloying tendencies.

Another point is that non-adhesive deposits often result if, when the object is placed in the bath, the process is not immediately started, or if the electrolysis is interrupted before its completion. The cause is the formation of a thin oxide layer on the clean surface. This phenomenon is, of course, only noticeable with metals more electropositive than hydrogen. In the case of aluminium, it renders electroplating exceedingly difficult.

As a galvanic deposit must be continuous, and usually capable of a high polish, its crystalline structure should be as fine as possible. This explains the frequent use of baths containing the plating metal as complex anion. We have seen[3] how such solutions generally furnish compact finely-grained deposits.

Technical.[4]—The first process in electroplating is the cleaning of the surface to be treated. If coated with rust or oxide, and if of a convenient size, a preliminary cleaning is given by a sandblast, wire brushes, or other suitable arrangement. Grease is carefully removed by dipping into a hot alkaline solution. Then the last traces of oxide are dissolved and a bright metallic surface produced by means of a 'pickling' solution, naturally varying with the metal treated. Acid solutions—HCl, HNO_3, H_2SO_4—are usually employed. The details we need not consider. Occasionally the article (particularly if of iron or steel) is cleaned by making it cathode in a bath containing H_2SO_4 or HCl. In both the chemical and electrochemical treatment with acid, the gas evolution removes much of the scale or oxide mechanically. The object is finally thoroughly washed with water, and introduced into the plating bath, the current being usually immediately switched in (see above).

The plating tanks are generally wooden lead-lined vessels of convenient size, though the smaller ones are often constructed of glazed earthenware. As the objects are continually removed and replaced, an arrangement of the different tanks in series would prove very inconvenient. They are therefore connected in parallel, and fed by

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[1] This can be otherwise when two metals are deposited together irregularly. See p. 294.

[2] *Grundriss der technischen Elektrochemie*, p. 280 (1898).

[3] P. 125.

[4] *Metall. Chem. Engin.* **8**, 274 (*1910*); Pfanhauser, *Metall.* **1**, 313 (*1904*).

a low-voltage dynamo capable of giving a large current. Each tank should be independently provided with ammeter, voltmeter, and regulating resistance. The objects under treatment (cathodes) are usually suspended by hooks from copper rods laid across the top of the tank, these being in turn connected with the negative pole of the source of current. The anodes are of purest sheet metal, if necessary enclosed in linen or parchment bags to retain the slimes. Occasionally, where the employment of an anode of the plating metal (*e.g.* of gold) would prove too expensive, an insoluble anode is used.

Anodes and cathodes are as far as possible arranged symmetrically, and so as to occupy the whole cross-section of the bath. To ensure a uniform deposit on an article of irregular shape, auxiliary anodes placed in special positions are sometimes employed. Small objects, such as nails, etc., are filled into suitable baskets or drums, which are immersed in the bath. In other cases—*e.g.* the galvanising of wire—special arrangements are adopted.

The current density is as high as is consistent with the furnishing of a satisfactory deposit. It varies (with the plating bath and the temperature) between 0·1–2·0 amps./dm.^{2}. The thickness of deposit given is usually very small, thousandths of a mm. for cheap articles, and rarely exceeds a few tenths of a mm. At the end of the operation the articles are removed from the bath, dried, and in most cases finally polished. The utmost cleanliness is necessary throughout all the operations.

Zinc-plating (Wet Galvanising).—As is known, many iron objects are coated with zinc to protect them against rust—*e.g.* roofing, fencing, wire, etc. This is at present effected either by dipping the cleaned article in a molten zinc bath, or by electro-deposition. The former method (*hot galvanising*) gives a more brilliant coat, but possesses several disadvantages. It is wasteful, forming deposits of high-melting iron-zinc alloy in the bath; it gives a coat the thickness of which is not easily controllable and which is often irregular, and its mechanical and resistive properties fall short of those of the electro-deposit.[1] As a consequence, the method of electro-, cold, or wet galvanising wins more and more favour.

The conditions favouring the formation of a good zinc deposit at high current efficiency are set out on p. 283. In accordance with these conditions, we find that Langbein recommends a bath containing per hundred litres :—

20 kilos. $ZnSO_4$, $7H_2O$,
4 kilos. Na_2SO_4, $10H_2O$,
1 kilo. $ZnCl_2$,
0·5 kilo. boric acid crystals.

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[1] Burgess, *Electrochem. Ind.* 3, 17 (*1905*).

This can be taken as typical of other solutions. The sodium sulphate increases the conductivity; the boric acid gives the required acidity, which is kept constant by the continuous regulated addition of dilute H_2SO_4. The current density used is generally about 50–100 $\frac{\text{amps.}}{\text{metre}^2}$, as the electrolyte is not very efficiently circulated. Sometimes it rises to 200 $\frac{\text{amps.}}{\text{metre}^2}$. The bath is worked at room temperature or at 40°–50° (particularly with objects of a highly-developed surface). 3–6 volts are used, depending on the conductivity of the electrolyte (always rather low), temperature, and current density.

Nickel-plating.—The mechanical strength and chemical resistivity of this metal, together with its capability of taking a high polish, have resulted in an enormous application in the electroplating industry. It can be used for coating practically all the cheaper metals. Except with iron and steel, to which nickel adheres if the object is thoroughly clean, a preliminary copper coating is first deposited.

The cathodic and anodic behaviour of nickel has been discussed on pp. 292–294. A *thin* deposit of nickel which does not flake off is obtainable at room temperature if the nickel content of the solution is high, the acid content low, and the current density not too great. To get satisfactory thicker deposits under ordinary conditions, the temperature must be raised to about 70°, when higher current densities can be employed. Nickel anodes readily become passive in most electrolytes (not when chlorides are present) unless the current density is kept very low. But their behaviour also depends largely on their method of preparation. Both rolled and electrolytic nickel, particularly the latter, dissolve much less readily—*i.e.* become passive sooner—than cast nickel.

As most nickel electro-deposits are thin, the nickel-plating bath is generally run at room temperature. The nickel, about 10 $\frac{\text{grams}}{\text{litre}}$, is present as sulphate. A large quantity of $(NH_4)_2SO_4$ is usually added to increase the conductivity, and the bath is acidified with citric acid and kept acid with H_2SO_4 just as is the case with zinc. The cathodic current density is generally low, 0·3–0·6 amp./dm.^{2}. In some cases 1 amp./dm.^{2} can be used. At the anode the figure is still lower. The voltage varies between 1·8–3·5 volt. For thicker deposits, although special electrolytes have been suggested for use at ordinary temperatures, it is better to work at higher temperatures. The bath must be much richer in nickel, but large current densities can be employed. The current efficiency[1] of cathodic nickel deposition seldom exceeds 90 per cent., owing to hydrogen evolution. For the same reason, both the acid and nickel concentrations of the electrolyte alter.

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[1] Brown, *Trans. Amer. Electrochem. Soc.* **4**, 83 (*1903*).

Langbein has overcome this difficulty by utilising the above-mentioned differences in ease of solution of different varieties of nickel anodes. If all anodes are of cast nickel, which does not readily become passive, then the nickel concentration of the bath will steadily increase, and the acid concentration decrease. If all consist of rolled nickel, only a small fraction of metal will dissolve anodically, large quantities of acid being formed instead with liberation of oxygen. By using suitable numbers of cast and rolled anodes the composition of the bath can be regulated, and the continual addition of acid or nickel salts avoided.

Copper-plating.—This process is usually only an intermediate stage prior to the electro-deposition of other metals. Occasionally it is carried out for its own sake, in which case the article is subsequently dipped into an alkaline polysulphide bath, in order to produce the film of Cu_2S known as 'oxidised copper.' A bath of potassium cuprocyanide is almost invariably used. It is prepared from KCN and some cupric salt, Na_2SO_3 being added to reduce the copper to the cuprous condition, and to avoid the production of poisonous cyanogen gas which otherwise occurs.

Spitzer[1] has investigated the electro-deposition of copper from cyanide solutions at room temperature. He showed that an irreversible effect (probably connected with a slow rate of the reaction $Cu(CN)_2' \longrightarrow 2CN' + Cu^{\cdot}$)[2] is present, the polarisation needed for copper deposition considerably exceeding the equilibrium value. Thus, with a solution of 0·1 n. CuCN + 0·2 n. KCN (which corresponds closely with the technical electrolyte), whilst the equilibrium value for a copper electrode was − 0·61 volt, the potential was − 0·77 volt at a current density of 0·001 amp./cm.^{2} and − 1·12 volts at 0·003 amp./cm.^{2}. The hydrogen equilibrium potential in such a solution is − 0·7 volt, and the hydrogen overvoltage at a copper surface at these low current densities about 0·2–0·3 volt. We see therefore that even at low current densities large quantities of hydrogen must be evolved simultaneously with the copper deposition. In fact, Spitzer found that as the current density rose from 0·001 to 0·02 amp./cm.^{2}, the current efficiency fell from 58 per cent. to 10·6 per cent. With excess of KCN still worse results were obtained, in respect both to voltage and current efficiency. The experience of the electroplater corresponds fully with these results. Although the current density is low (0·3 amp./dm.^{2}), yet the deposition of copper is accompanied by a violent gas evolution, and the voltage necessary is 3 volts.

Brass-plating.—This operation also is chiefly carried out to provide a surface to which other electro-deposited metals can firmly adhere. A number of motor-car fittings are, however, electrolytically brassed.

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[1] *Zeitsch. Elektrochem.* 11, 345 (*1905*).

[2] See p. 120.

The electrolyte contains a mixture of $K_2Zn(CN)_4$ and $KCu(CN)_2$. As the deposit contains about 20 per cent. Zn : 80 per cent. Cu, the brass anode used should have the same composition. In sulphate solutions the potentials of zinc and copper are far apart, a fact on which the E.M.F. of the Daniell cell depends. But in cyanide solutions they lie far closer together,[1] and, if a considerable excess of cyanide be present, the zinc becomes nobler than the copper. In practice this last factor does not come into play, as a large excess of cyanide is avoided.

But two other circumstances bring the zinc and copper discharge potentials near to one another, and thus render possible the cathodic deposition of brass. The first is that the irreversible polarisation[2] necessary for the discharge of these metals from cyanide solution increases with current density far more rapidly with copper than with zinc, and even at quite low current densities (0·003 amp./cm.^{2}) the potentials are already very close together. Secondly, $Zn^{\cdot\cdot}$ discharge is depolarised by the copper content of the cathode in virtue of the mutual tendency to alloy formation, and zinc is therefore deposited at a polarisation below that necessary in the absence of copper. With a normal current density of 0·003 amp./cm.^{2}, with an equal number of gram-atoms of copper and zinc in solution, and with no great excess of KCN, the brass produced contains 20 per cent. Zn. Excess of KCN causes a greater hydrogen evolution and a decreased current efficiency. Too little KCN increases the distance between the zinc and copper potentials, and diminishes the proportion of the former metal deposited.

The electro-deposition of brass has also been studied by Field,[3] who paid particular attention to current efficiency and the composition of the cathodic deposit, investigating the influence of such factors as excess of KCN and temperature.

Silver-plating.—We have already[4] seen in what form silver usually deposits from its simple salts. As a silver electro-deposit must essentially be capable of polish, a cyanide bath is always used in electroplating. This gives a fine deposit, sometimes already brilliant, sometimes milk-white, which can easily be polished. The electrolyte contains 8–20 $\frac{\text{grams}}{\text{litre}}$ silver, and is usually prepared from AgCl and KCN in the ratio 1[AgCl] : 3–4[KCN]. The fine silver anodes readily dissolve. The current density is 0·1–0·25 amp./dm.^{2}, and the voltage 0·5–1·0 volt, depending on the resistance of the bath and the current density. Very little hydrogen is evolved, the current efficiency being about 99 per cent. Like all cyanide baths exposed to air,[5] the electrolyte gradually

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[1] See p. 120.

[2] See p. 120.

[3] *Trans. Farad. Soc.* **5**, 172 (*1909*).

[4] P. 266.

[5] *Cf.* p. 277.

deteriorates, forming carbonate, ammonia, etc., and must be regularly renewed. The deposition of silver from cyanide solutions has been studied by Foerster and Brunner.[1] The discharge potentials of silver and hydrogen ions lie so far apart that, even with a solution low in silver, the formation of hydrogen is only to be feared at comparatively high current densities. The usual small deficit in the cathodic silver deposit is essentially due to the depolarisation of $H^{\cdot}$ discharge by dissolved air. If the electrolyte be agitated, the loss increases. On the other hand, excess of KCN, by increasing the alkalinity, makes $H^{\cdot}$ discharge so difficult that in a solution containing 1[AgCN] : 40[KCN], in presence of air and with stirring, a current density of 2 amps./dm.^{2} can be used without appreciable cathodic loss due to hydrogen.

Gold-plating.—A cyanide bath is also used here, prepared by the addition of KCN to some suitable gold salt. If used at low temperatures (for the gilding of large objects), it may contain up to ten $\frac{\text{grams}}{\text{litre}}$ gold as $KAu(CN)_2$; at temperatures of about 70° (for the gilding of smaller objects), when diffusion is much greater, a concentration of one $\frac{\text{gram}}{\text{litre}}$ gold suffices. The KCN added is about five to six times the quantity necessary to convert the gold into AuCN. The anodes are generally of fine gold, but graphite can also be used. At a current density of 0·001 amp./cm.^{2}, or a little higher, a fine, uniform, well-coloured deposit results. The voltage varies considerably, depending on the arrangement of the bath and the exact composition of the electrolyte. Average values, using a gold anode, are one volt for a hot and four volts for a cold bath. With a graphite anode they are naturally higher. The gold anode is sometimes observed to become passive.

Coehn and Jacobsen[2] have studied the anodic and cathodic processes at gold electrodes in a gold cyanide bath. With a saturated (14 per cent.) $KAu(CN)_2$ solution, gold deposition took place at a potential 0·2 volt positive to that of hydrogen in the same solution. As technical current densities are very small, and as gold cyanide solutions show no abnormal cathodic behaviour like cuprous cyanide solutions, this explains the fact that little or no hydrogen evolution takes place in the plating bath. At the anode, passivity phenomena were observed, depending in a curious manner on current density and KCN concentration, and fully explaining the variations noticed in practice. With a solution containing 1–2 per cent. free KCN and a current density of 0·0004–0·002 amp./cm.^{2}, the gold dissolved quantitatively as AuCN.

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[1] *Zeitsch. Elektrochem.* **13**, 561 (*1907*).

[2] *Zeitsch. Anorg. Chem.* **55**, 321 (*1907*).

If the amount of KCN were decreased, passivity set in, accompanied by gas evolution. If it were increased above the 1–2 per cent., brown or yellow colorations due to polymerised cyanogen compounds were produced at the anode, which again became passive, necessitating an increased anodic polarisation of 0·7–0·8 volt. A still further concentration increase resulted again in solution of the gold.

Platinum-plating.—Up to now platinum-plating has been little practised, owing to the difficulty of producing satisfactory deposits, but the possibility of making platinum-coated anodes, crucibles, etc., etc., justifies a brief mention here. Langbein recommends a $(NH_4)_2PtCl_6$ bath, containing about 7 $\frac{\text{grams}}{\text{litre}}$ platinum, together with a considerable quantity of sodium citrate. A certain excess of NH_4Cl can be added to diminish the resistance. Other baths are prepared by adding ammonium or sodium phosphates to an H_2PtCl_6 solution. Instead of citrates or phosphates, Jordis recommends the use of lactates. The electrolysis is best carried out at 80°–90°, the current density being 0·01 amp./dm.^{2}. As the anode (whether platinum or not) is insoluble, the voltage is high—three to six volts. McCaughey and Patten[1] have studied platinum deposition from solutions containing citrates. Their work makes it clear that the problem is a somewhat complex one. The use of alkaline platinite solutions might perhaps give satisfactory results.

Electrotyping.—Practically all electrotypes consist of copper, though sometimes, when the surface is liable to much wear, they are coated with a thin layer of iron. An acid $CuSO_4$ bath is used, similar to that employed in refining. The first step is the preparation of a negative cast of the original. This usually consists of plaster of Paris or of wax of suitable mechanical properties, and great care must naturally be taken that it is in all respects an absolutely true one. Its surface is then well brushed over with graphite to render it conducting, it is attached at its edge to a copper lead connected with the negative current pole, and placed in the bath. This contains 200 grams $CuSO_4$, $5H_2O$ and 30 grams H_2SO_4 per litre, and is kept at room temperature. The anodes, sheets of electrolytic copper, are enclosed in linen bags to retain traces of slimes. The current density is about 2 amps./dm.^{2}, and the bath voltage about one volt. For more rapid working, the temperature is raised and the electrolyte stirred by vigorously blowing in air. In that way current densities of 5–8 amps./dm.^{2} can be employed, at the cost of a considerably increased bath voltage. When the copper positive is sufficiently thick and rigid, the whole is taken from the bath, the negative cast detached, and the electrotype backed with some low-melting lead alloy to provide the necessary strength.

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[1] *Trans. Amer. Electrochem. Soc.* **15**, 523 (*1909*); **17**, 275 (*1910*).

An electrolytic iron coating, if applied, is deposited on account of its hardness, due, as we have seen, to dissolved hydrogen. Suitable conditions are those under which Burgess and Hambuechen worked.[1]

Elmore Process.—We must, in conclusion, describe certain electrotyping processes applied to a particular purpose—viz. the production of seamless copper tubes. The best known is that of Elmore,[2] worked in Leeds, France, and Germany. The electrolyte consists of acid $CuSO_4$ solution, the anodes are of cast copper, at least 98 per cent. pure. The cathode is a drum, cylinder, or rod of the required diameter, usually of brass or of coppered cast iron, slowly revolving horizontally partly within and partly without the electrolyte. To facilitate the removal of the tube subsequently formed, it is covered with a thin layer of oil and graphite. Contact with the negative current pole is made by brushes. The bar anodes are arranged symmetrically in a curved wooden frame under the lower surface of the revolving cathode (Fig. 67). The baths are run at room temperature. No figures have been published on the current density. It and the bath voltage will probably be similar to those used in the ordinary copper electrotyping process (2 amps./dm.^{2} at the cathode, and 1–1·5 volts).

The particular feature of the process is the means used to produce a dense and even cathodic deposit. This is effected by causing pieces of agate, pressed on the cathode surface by springs, to travel continuously from one end of the cathode to the other and back again. This movement, combined with the rotation of the cathode, leads to all parts of the surface of the latter being regularly and frequently subjected to pressure, and effectually prevents any formation of irregular or uneven growths on the same. To subsequently detach the tubes from their cores, they are gently heated, and worked loose by pressure. Their great tensile strength allows them to be easily drawn; consequently a few standard sizes only are directly made in the bath. Tubes up to five feet in diameter and sixteen feet in length have been produced.

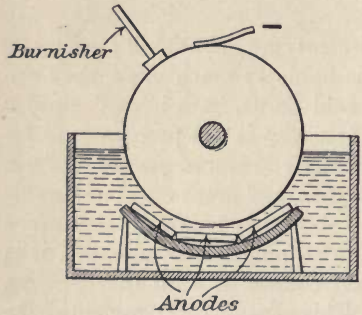

FIG. 67.—Elmore Process.

A modification of this process due to **Jullien and Dessolle**[3] is successfully at work in France. Besides the longitudinal motion, the burnisher is provided with a superposed alternating movement in another plane, and better effects are said to result.

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[1] See p. 301.

[2] *Electrochem. and Metall.* 3, 150 (*1903*).

[3] French Patent 369,746 (*1906*).

Cowper-Coles[1] proposes the use of very rapidly revolving cathodes and higher temperatures. Working in this way, far higher current densities can be employed, and the friction between electrolyte and cathode nevertheless ensures an excellent deposit. Although 50–60 amps./dm.^{2} can be used, this renders the voltage too high. 20 amps./dm.^{2} is a convenient figure, and with a strongly acid, well-conducting electrolyte, the bath voltage is then only 0·8 volt. Cowper-Coles has also worked out a very ingenious method of producing copper wire from the cylinders and tubes which result.

Literature.

Schlötter. *Galvanostegie*, vol. i.

[1] *Electr.* **61,** 680 (*1908*).

CHAPTER XX

HYPOCHLORITES AND CHLORATES

1. General Theory

When aqueous NaCl is electrolysed between platinum electrodes, the primary electrode reactions are perfectly simple. E.P. $Na^{\cdot} \longrightarrow Na$ is $- 2{\cdot}72$ volts. If therefore $Na^{\cdot}$ ions are to be discharged cathodically and reversibly at room temperature from a given solution, $\log[Na^{\cdot}]$ must be $\frac{2{\cdot}72}{0{\cdot}058}$ (about 47) times as great as $\log[H^{\cdot}]$. Putting $[H^{\cdot}]$ in a neutral aqueous solution at $0{\cdot}8 \times 10^{-7}$, we have $[Na^{\cdot}] = 10^{40}$. It is therefore obvious that $H^{\cdot}$ ions are preferentially discharged even from a very strongly alkaline solution, and, although requiring a certain overvoltage, the cathodic hydrogen production is primary, and not secondary, as is often assumed.[1]

At the anode the possible processes are the discharge of OH' and Cl' ions. For the oxygen electrode we have $O_2 \mid n.OH' = + 0{\cdot}41$ volt. Hence reversible oxygen discharge from a neutral aqueous solution will commence at an anodic potential of $0{\cdot}41 - 0{\cdot}058 \log 0{\cdot}8 \times 10^{-7} = + 0{\cdot}82$ volt. Anodic oxygen evolution, however, is subject to a very high overvoltage, which, even at platinised platinum, rises to nearly one volt at moderate current densities, corresponding to a final anodic potential of $+ 1{\cdot}8$ volts. The equilibrium value $Cl_2 \mid n.Cl'$ is $+ 1{\cdot}36$ volts at 25°. For $Cl_2 \mid n.NaCl$ it will be about $+ 1{\cdot}37$ volts. At platinised platinum, Cl' discharge is almost reversible, and consequently, at such an electrode, chlorine and not oxygen will be more easily liberated. At polished platinum the relations remain unaltered, increased overvoltage causing in each case an increased polarisation of about $0{\cdot}6$ volt.

The electrolysis will thus yield hydrogen and, as $H^{\cdot}$ ions disappear, an alkaline solution at the cathode, and chlorine at the anode. If it be carried out so that the different products are kept separate as far

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[1] If the $Na^{\cdot}$ discharge is depolarised, the results can of course be different. See pp. 121, 342.

as possible, we have an electrolytic alkali-chlorine cell. Such cells will be discussed in the next chapter. If, on the other hand, the products be allowed to mix and react, there result, according to the conditions, NaClO solutions—bleaching liquors—or $NaClO_3$ solutions (KClO or $KClO_3$ if KCl be the starting material). The study of these conditions is the subject of the present chapter. It may be remarked at the outset that it is chiefly due to the exhaustive work of Foerster and his pupils that our knowledge is in its present satisfactory state.

As a necessary preliminary we must consider the rather complex chemical reactions involved. When a halogen reacts with a solution containing OH′ ions, with the exception of fluorine, which directly decomposes the water, liberating oxygen, the following equilibrium is set up:

$$\underset{\text{Halogen}}{X_2} + OH' \rightleftarrows X' + \underset{\substack{\text{Halogen}\\\text{oxy-acid}}}{HXO} \qquad \text{(i)}$$

Thus chlorine gives Cl′ ions and HClO. The reaction goes more completely from left to right the more reactive the halogen—*i.e.* the greater its ionising tendency. For example, a saturated aqueous chlorine solution is about 30 per cent. hydrolysed at 0°, and more so at higher temperatures, the reaction being endothermic. At 25° the equilibrium constant $K = \frac{[Cl_2] . [OH']}{[HClO] . [Cl']}$ is $1{\cdot}5 \times 10^{-11}$.[1] But bromine water only contains traces of HBrO, and in an iodine solution there is no perceptible hydrolysis. If an equivalent of alkali be present per molecule of chlorine, the reaction is pretty complete in dilute solutions. In more concentrated solutions free chlorine and alkali can be detected. With bromine or iodine the hydrolysis is far less, and considerable quantities of either halogen can exist in presence of free alkali.

Now, as one of the resultants of the above equation is an *acid*, the reaction will proceed further if sufficient OH′ ions are present. We shall have

$$HXO + OH' \longrightarrow XO' + H_2O, \qquad \text{(ii)}$$

taking place the more completely the stronger the acid. If the latter is a so-called ' strong ' acid, the neutralisation will be almost complete, and, as reaction (i) will progress in consequence of the removal of the HXO, the final result of the interaction of a molecule of halogen and two of alkali can be written

$$X_2 + 2ROH \longrightarrow RXO + RX + H_2O \qquad \text{(iii)}$$

corresponding to the well-known equation $Cl_2 + 2NaOH \longrightarrow NaClO + NaCl + H_2O$. This last equation, in fact, nearly represents the truth. The amount of free HClO resulting from the action of two equivalents of alkali on one molecule of chlorine is quite small. With bromine

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[1] Jakowkin, *Zeitsch. Phys. Chem.* **29**, 613 (*1899*).

and iodine the case is very different. Both free acid and free halogen are present, in greater quantity with iodine than with bromine.[1] HIO is so weak that it is believed it can also ionise to $I^{\cdot} + OH'$ [2]—*i.e.* that it is a so-called *amphoteric electrolyte.*

Further reactions are, however, possible. A hypohalogenite-halide mixture does not represent the stablest system which the action of halogen on alkali can furnish. The stablest, as a matter of fact, is oxygen + halide. We accordingly find that hypochlorite solutions slowly decompose thus:

$$2ClO' \longrightarrow 2Cl' + O_2 \qquad \text{(iv)}$$

This reaction under ordinary conditions is exceedingly slow, but is greatly accelerated by small quantities of cobalt or nickel salts. A well-known method of preparing oxygen depends on this fact. More interesting and important is the mechanism of production of RO_3' ions in hypohalogenite solutions. This takes place as follows[3]:

$$2HXO + XO' \longrightarrow XO_3' + 2X' + 2H^{\cdot} \qquad \text{(v)}$$

Solutions containing ClO' or BrO' ions alone are stable, as also are solutions containing free HClO or HBrO only. When mixed they react as above. The $H^{\cdot}$ ions liberated produce more undissociated HXO from the XO' ions present. The HXO concentration thus remains fairly constant throughout, whilst that of the XO' decreases. The velocity constant of this reaction (k in the equation $\frac{dx}{dt} = k[HXO]^2[XO']$) is 0·0023 at 25° for $X = Cl$. For bromine it is far greater, about 0·25, and for iodine greater still.

If we also notice that the reaction velocity depends on the *square* of the free acid concentration, but only varies directly as the XO' concentration, we see that a solution prepared from definite molar concentrations of bromine and alkali will give bromate far more rapidly than a solution containing the same original molar concentrations of chlorine and alkali will give chlorate. Not only is the velocity constant greater in the first case, but HBrO, being weaker, is neutralised to a lesser extent than HClO by the alkali. With iodine and alkali, the tendency to give halogenate is still stronger. HIO solutions are only stable when exceedingly dilute. Otherwise the reaction $2HIO + IO' \longrightarrow IO_3' + 2I' + 2H^{\cdot}$ commences at once, the very small IO' concen-

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[1] Foerster and Gyr, *Zeitsch. Elektrochem.* **9**, 1 (*1903*).

[2] Le Blanc has shown that iodine can dissolve anodically in acid solution to give HIO_3, a far stronger acid than HIO. The primary formation of $I^{\cdot\cdot\cdot\cdot\cdot}$ ions is to be assumed here.

[3] Foerster and Jorre, *Jour. Prakt. Chem.* **59**, 53 (*1899*). Foerster, *loc. cit.* **63**, 141 (*1901*). Kretzschmar, *Zeitsch. Elektrochem.* **10**, 789 (*1904*). Foerster and Gyr, *loc. cit.* **9**, 6 (*1903*).

tration produced by the OH' ions of the water ($HIO + OH' \longrightarrow IO' + H_2O$) sufficing. At the same time the I' ions liberated react with the HIO ($I' + HIO \longrightarrow I_2 + OH'$), the equation being the reverse of equation (i). Thus, except when very dilute or in presence of a large excess of alkali, an HIO solution rapidly decomposes, giving iodine and HIO_3.

Returning to the case of chlorine, it has been seen that if one molecule only of halogen reacts with two equivalents of alkali the rate of formation of chlorate is very slow, partly owing to the prevailing low HClO concentration. The equation $Cl_2 + 2ROH \longrightarrow RCl + RClO + H_2O$ represents pretty closely the final stage. If now a small extra amount only of HClO be added, the rate of production of chlorate will be very greatly increased, for this small addition may mean a very large *relative* increase in the HClO concentration, on which the reaction velocity essentially depends. In practice this addition can be effected by using rather more than one molecule of chlorine to two equivalents of alkali. Fresh HClO is formed according to equation (i), there is no alkali to neutralise it, and reaction (v) will therefore commence. This explains the fact, long known (Gay Lussac), that an excess of chlorine over and above the amount demanded by the usual equation

$$6KOH + 3Cl_2 \longrightarrow KClO_3 + 5KCl + 3H_2O$$

is necessary for the formation of chlorate from chlorine and alkali. For the thorough comprehension of this series of reactions, and of the differences shown by the different halogens, this equation indeed is quite inadequate.

There is one other way in which hypochlorite solutions may decompose, giving rise to chlorate. The reaction $3ClO' \longrightarrow ClO_3' + 2Cl'$ takes place with very low velocity at ordinary temperatures, rather more rapidly with increased alkali content of the solution. As a factor in the reaction producing chlorate under technical conditions, it hardly needs mention. Even at higher temperatures it is quite dwarfed by other reactions.

2. Hypochlorites—Theory

It has been shown that the primary products of the electrolysis of a pure neutral NaCl solution are hydrogen and NaOH at the cathode, chlorine at the anode. For every molecule of halogen evolved, we obtain two equivalents of alkali. If the anodic and cathodic liquors be continually mixed, the chlorine will react on the OH' ions according to equations (i) and (ii)[1] thus:—

$$\begin{aligned} Cl_2 + OH' &\rightleftarrows Cl' + HClO \\ HClO + OH' &\rightleftarrows ClO' + H_2O. \end{aligned}$$

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[1] P. 319.

When conditions have become constant, the actual concentrations of the substances involved in these equilibria will, of course, differ at the two electrodes. At the anode, owing to the excess of chlorine, there will be a high $HClO$ concentration; at the cathode this will be very low. Hence at the anode, or near it, the direct chemical formation of $NaClO_3$ according to the equation $2HClO + ClO' \longrightarrow ClO_3' + 2Cl' + 2H^{\cdot}$ is possible. The better the circulation of the liquid, the less will this reaction take place, and in any case it amounts to little if the working temperature be low. Under favourable conditions, very little chlorine should escape, and the electrolysis should produce $NaClO$ almost quantitatively according to the total equation—

$$NaCl + H_2O \longrightarrow NaClO + H_2,$$

this representing the result of the passage of two faradays through the cell.

As the chemical decomposition of neutral hypochlorite solutions is very slow, this process could proceed to the formation of a saturated solution but for the cathodic and anodic behaviour of the ClO'. At the cathode, whatever the electrode material, it is very readily reduced by the nascent hydrogen ($2ClO' + H_2 \longrightarrow 2Cl' + H_2O$). Failing steps to prevent this reduction, a hypochlorite concentration will finally be reached at which as much is reduced as is simultaneously re-formed from chlorine and alkali. Its yield will thus fall to zero. This reduction can be avoided by adding a little K_2CrO_4 to the electrolyte. This important point was first discovered by Imhoff, and the mechanism of its reaction recognised by Müller.[1] It is to be ascribed to the reduction of CrO_4'' ions to $Cr^{\cdots}$ ions and the formation of a thin diaphragm of insoluble chromium chromate around the cathode. This prevents contact of the bulk of the solution with the electrode, and thus with the nascent hydrogen. If the electrolyte be made strongly acid or alkaline, when in either case such a film would be dissolved, the addition no longer works, or its action is weakened.

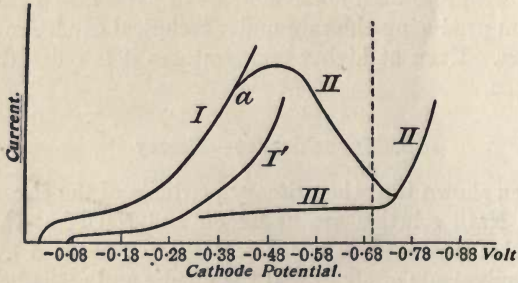

FIG. 68.

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[1] *Zeitsch. Elektrochem.* **5**, 469 (*1899*); **7**, 398 (*1901*); **8**, 909 (*1902*).

The current potential diagram (Fig. 68) clearly shows its influence on the cathode potential. Curves I and I′ are taken without the addition of chromate. Hydrogen evolution is depolarised and considerable currents pass at a lower cathodic polarisation than the normal one for hydrogen discharge (the dotted line). If, when the point *a* is reached on curve I, some chromate be added, the reduction ceases, the current immediately drops, and curve II is followed. Another rise in the curve only commences when the hydrogen discharge potential is exceeded. If now the polarisation be gradually lessened, curve III is followed continuously, showing that depolarisation effects no longer enter. As typical of the effect produced by the chromate addition on the yield we may take a result of Müller's. Working with neutral 30 per cent. NaCl at 45°–50° and using smooth platinum electrodes, the yield of active oxygen was only 32·8 per cent., the reduction being 54·5 per cent. With the addition of 0·18 per cent. K_2CrO_4, these figures became 69·6 per cent. and 3·6 per cent. respectively. Other addition agents have been recommended. Vanadium salts and sodium resinate may be mentioned. Important is the addition of high-molecular non-aromatic sulphur organic compounds in presence of calcium salts, patented by Thiele.[1] The mode of action appears to be similar.

At the anode, the disturbing reaction which limits the possible concentration of electrolytic hypochlorite solutions is ClO' discharge. Instead of this, according to most analogies, proceeding thus, $2ClO' + H_2O \longrightarrow 2HClO + \frac{1}{2}O_2 + 2\ominus$, ClO_3' ions are produced. Cl' ions are simultaneously formed, and the whole has been shown[2] to take place probably as follows :—

$$6ClO' + 3H_2O \longrightarrow 6H^{\cdot} + 2ClO_3' + 4Cl' + 1\tfrac{1}{2}O_2 + 6\ominus \qquad \text{(vi)}$$

The Cl' ions are subsequently discharged and the $H^{\cdot}$ ions neutralised by the six OH' ions simultaneously formed cathodically. ($HClO$ behaves similarly, forming $HClO_3$, and evolving oxygen and chlorine.) When a stationary state has been reached, with a constant NaClO concentration, the ClO' ions formed in a given time, minus the number cathodically reduced, will equal the number discharged according to the above equation.

Now the production of six ClO' ions [(*a*) $2Cl' \longrightarrow Cl_2 + 2\ominus$; (*b*) $Cl_2 + OH' \longrightarrow ClO' + Cl' + H^{\cdot}$] necessitates the passage of *twelve* coulombs through the cell. Hence, at the stationary state, two-thirds of the current will be spent in producing chlorine which reacts with the alkali, giving ClO' ions, and one-third in the discharge of these ClO' ions. As the former reaction produces *available* oxygen, ultimately as $NaClO_3$, whereas the second reaction furnishes *free* oxygen, we shall finally have a system in which the hypochlorite concentration is constant, in which

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[1] D.R.P. 141372 (*1902*), 205087 (*1906*). See also p. 333.

[2] Foerster and Müller, *Zeitsch. Elektrochem.* **8**, 665 (*1902*).

$NaClO_3$ is produced with a 66·6 per cent. current efficiency and in continually increasing concentration, and in which the remaining 33·3 per cent. of the current gives oxygen. Hydrogen, of course, is continually discharged at the cathode.

This has been experimentally proved over a considerable range of temperature, current density, and NaCl concentration. We are here, however, chiefly concerned with the constant NaClO concentration which can finally be reached. This will depend on several factors, anode material, NaCl concentration, current density and temperature being the chief. Fig. 69 gives the current—anode potential curves for the electrolysis of NaCl and NaClO solutions. Curve 1 was taken with a platinised platinum anode, 2 and 3 with smooth platinum, the difference between 1 and 3 being due to the increased overvoltage at the latter. We see that ClO′ discharge takes place far more easily than Cl′ discharge, and for a given initial strength of NaCl and a given anode potential ClO′ ions will soon accumulate in the electrolyte sufficiently to take part in the electrolysis. With a platinised platinum anode (the hypochlorite curve is not given) the distance between the two curves is not so great. Therefore a larger accumulation of hypochlorite is necessary before the ClO′ ions are discharged, and the final equilibrium concentration is also higher.

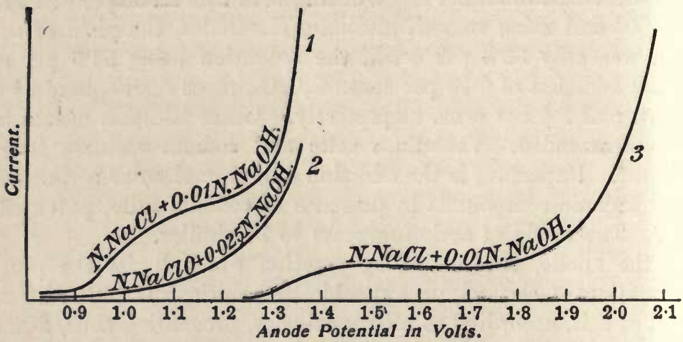

FIG. 69.

The whole course of the electrolysis of a neutral brine solution at smooth and platinised platinum anodes is shown in Fig. 70. The electrolyte initially consisted of 220 c.c. of 5·1 *n.* NaCl, containing 0·2 per cent. K_2CrO_4. It was electrolysed at 12–13° with 2 amperes at an anodic current density of 0·067 amps./cm.^{2}. The full curves are for a platinised platinum anode, the dotted curves for smooth platinum. The difference between the final hypochlorite concentrations is clearly shown, and we see how chlorate formation and oxygen evolution commence sooner at the polished than at the platinised electrode.

The higher the NaCl concentration, the more easily Cl′ ions are discharged, and the greater must be the ClO′ concentration for *their* discharge to commence. A high NaCl concentration favours a high NaClO concentration. A high current density causes efficient mixing, owing to the rapid gas evolution. This prevents local concentration of ClO′ ions at the anode, and makes a higher concentration in the whole

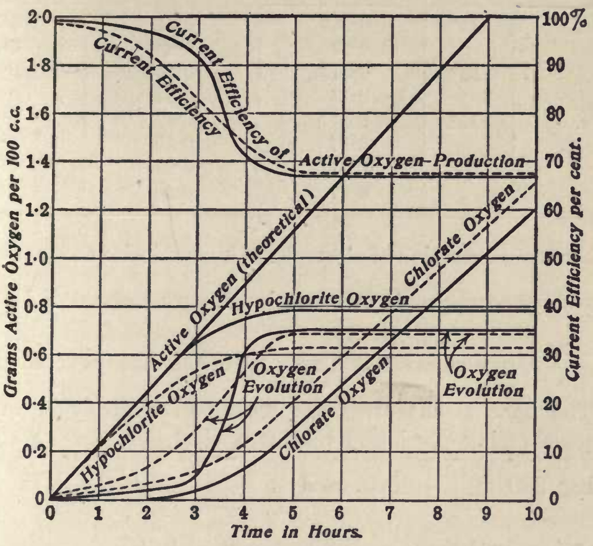

FIG. 70.

electrolyte a necessary condition for their discharge. It is found in practice that a high current density favours a high hypochlorite content. The temperature finally should be kept low, not so much to lower the rate of chemical decomposition of the hypochlorite as for the following reason. The ClO′ concentration necessary for anodic chlorate formation, and therefore the corresponding final stationary state, is only slightly dependent on the temperature. On the other hand, the equilibrium

$$Cl_2 + 2OH' \rightleftarrows H_2O + Cl' + ClO'$$

moves strongly in favour of the *left-hand side* with *fall* of temperature. If, therefore, a solution which has reached the stationary state at a high temperature be cooled, a considerable re-formation of chlorine and alkali will take place, and the cooled liquors will contain less hypochlorite than if they had been prepared at room temperature. The accompanying Table XLIII[1] clearly shows the effect of these different influences on the final equilibrium NaClO concentration.

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[1] Foerster and Müller, *Zeitsch. Elektrochem.* **9**, 196 (*1903*).

TABLE XLIII

Concentration of NaCl	Temperature	Anodic current density in amps./cm.^{2}	Grams of hypochlorite oxygen per 100 c.c.	
			Platinised platinum anode	Polished platinum anode
4·8*n*.	13°	0·017	0·61	0·34
		0·17	0·89	0·68
	50°	0·017	0·31	0·17
		0·17	0·64	0·42
1·7*n*.	13°	0·017	0·48	0·28
		0·17	0·65	0·47
	50°	0·017	0·23	0·15
		0·17	0·40	0·35

The highest concentration of electrolytic hypochlorite so far prepared in the laboratory corresponds to an active oxygen content of 10·56 $\frac{\text{grams}}{\text{litre}}$ (46·8 $\frac{\text{grams}}{\text{litre}}$ active chlorine). This figure has been exceeded technically. The next table[1] gives the results of electrolysis on a laboratory scale (using platinised platinum electrodes) of an electrolyte containing 280 $\frac{\text{grams}}{\text{litre}}$ NaCl and 2 $\frac{\text{grams}}{\text{litre}}$ K_2CrO_4. (In the last experiment only 100 $\frac{\text{grams}}{\text{litre}}$ NaCl were used.)

TABLE XLIV

θ	Anodic current density in amps./cm.^{2}	Voltage	Grams hypochlorite oxygen per litre	Grams bleaching chlorine per litre	Current efficiency	One gram hypochlorite oxygen requires in watt-hours
					per cent.	
13°	0·017	2·4	4·20	18·6	96	8·4
13°	0·017	2·4	5·24	23·2	90	8·95
10°	0·07	3·1	6·8	30·1	96	10·84
13°	0·17	3·6	5·28	23·4	99	12·2
13°	0·17	3·6	8·7	38·5	87	13·5
14°	0·17	4·7	5·20	23·0	95	16·6

From the preceding discussion it will be seen that the most favourable conditions for the electrochemical production of hypochlorite solutions are:

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[1] Foerster and Müller, *Zeitsch. Elektrochem.* **8**, 8 (*1902*).

(1) Strong NaCl solution, both to lower the resistance and to permit the production of stronger hypochlorite solutions.

(2) Low temperature.

(3) High anodic current density.

(4) Presence of K_2CrO_4.

(5) Use of platinised platinum electrodes.

In practice these conditions are modified for other reasons. The use of concentrated brine means a high salt consumption and also larger shunt current losses.[1] A low temperature involves artificial cooling. Platinised platinum electrodes are too fragile—the deposit easily drops away. Even platinum electrodes, unless of particular construction, mean a large initial outlay. Then there are other points. The circulation must be adequate, or free chlorine will escape. If the crude brine contains a large proportion of calcium or magnesium salts, particularly if the bleaching liquor is to be stored before use, a preliminary purification is necessary, otherwise difficultly soluble calcium and magnesium hydroxides are precipitated at the cathode. The solution thereby becomes acid, and can decompose as follows:

$$2HClO + ClO' \longrightarrow ClO_3' + 2Cl' + 2H^{\cdot} \qquad \text{(v)}$$

Often these salts are not completely removed, and the cathode becomes gradually covered with a crust which raises the cell voltage. This can be readily removed by reversing the current for a little while. Again, the energy efficiency diminishes rapidly as the hypochlorite concentration rises. It is often cheaper to make dilute solutions than concentrated solutions which are diluted before use. A point to be considered in designing the apparatus is its freedom from exposed metal (copper or nickel) parts which are liable to attack by the spray given off during the electrolysis. If this happens, the liquors will become contaminated with copper or nickel salts, and the decomposition

$$2ClO' \longrightarrow 2Cl' + O_2 \qquad \text{(iv)}$$

will be accelerated.

3. Hypochlorites—Technical

A large number of different electrolysers have been designed, and the most successful will here be described. They mostly use bi-polar electrodes. These are advantageous because they allow of very compact apparatus, and also because exposed metallic connections and bus-bars are dispensed with. A considerable drawback is the liability to shunt current losses and consequent decreased current efficiencies. We have already encountered such losses in the series system of copper refining.[2] But here the danger is considerably greater; for whereas in the Hayden process the voltage drop between adjacent electrodes is

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[1] See pp. 258, 392.

[2] See p. 258.

only about 0·13 volt, in a hypochlorite electrolyser it rarely falls below four and can exceed six volts. There is thus a correspondingly greater inducement for the current to pass directly from one end electrode to the other through the electrolyte.

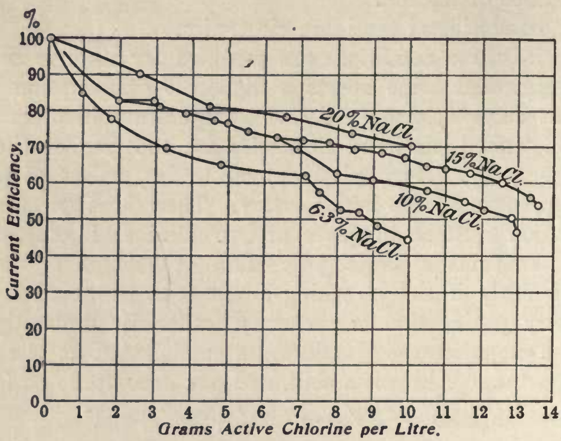

FIG. 71.

Kellner Cell : Vertical Type.—The Kellner apparatus in one form consists of a tall rectangular earthenware trough, divided into a

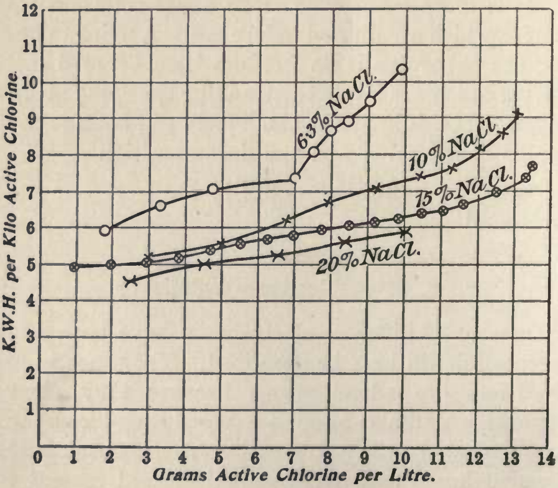

FIG. 72.

number of vertical chambers by a series of glass plates. These plates are wound round with Pt-Ir wire or partly covered on both sides with a continuous network of the same, and constitute the bi-polar electrodes.

The winding or network does not extend over the whole length of the plates—only about half is covered, and both ends are left free. This is done to diminish the shunt current losses by increasing the electrolyte resistance which has to be overcome. The end electrodes are of stouter network, and are provided with platinum-coated leads. The brine enters a chamber in the bottom of the cell, and, ascending, distributes itself amongst the different compartments, where it is electrolysed. It leaves the cell by spouts with which each compartment is separately provided, and falls back into the main supply tank placed underneath. There it is cooled by means of a coil, and pumped back into the electrolyser until the required strength has been reached. An electrolyser with twenty compartments (nineteen bi-polar and two end electrodes) takes 110 volts, therefore 5·5 volts to each compartment. This high figure is due to the very heavy current density (under normal working conditions 0·5–0·75 amps./cm.^{2}) and to the high overvoltages involved.

Figs. 71[1] and 72 show the relations existing between current efficiency, energy expenditure, and available chlorine concentration, using brine solutions of different strengths. Table XLV indicates the results with different quantities of added Na_2CrO_4, and also gives the expenditure of salt per kilo. of active chlorine. A 10 per cent. NaCl solution was used.

TABLE XLV

Grams of active chlorine per litre	With 0·08 per cent. Na_2CrO_4			With 0·12 per cent. Na_2CrO_4		
	Current efficiency	K.W.H. per kilo. Cl_2	Kilos. NaCl per kilo. Cl_2	Current efficiency	K.W.H. per kilo. Cl_2	Kilos. NaCl per kilo. Cl_2
	per cent.			per cent.		
3·8	79·0	5·1	26·3			
4·0				88·3	4·5	25·0
6·8	70·9	5·6	14·7			
6·9				76·3	5·2	14·5
9·0				66·2	6·0	11·1
9·4	65·0	6·2	10·6			

It is customary in practice to use 10 per cent. brine with 0·1–0·5 per cent. added Na_2CrO_4, and to work at 12°–15°. An apparatus such as is described, carrying 100 amperes and yielding liquors with $10\,\frac{\text{grams}}{\text{litre}}$ available chlorine at a 63 per cent. current efficiency, will produce in twenty-four hours nearly forty kilos. of active chlorine.

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[1] Engelhardt, *Hypochlorite und elektrische Bleiche* (Technisch-konstruktiver Teil), p. 160.

Haas and Oettel Cell.—This apparatus employs bi-polar carbon electrodes. Its latest construction is shown diagrammatically in Figs. 73 and 74. An earthenware trough, open above, is divided into narrow vertical compartments by plates of Acheson graphite *a a a*, securely cemented into position. From both sides of the top of the trough projects out a series of open earthenware channels *d d d*, separated from one another by earthenware ribs, and serving as outlets for the different electrolysis chambers. The base of the trough is provided with an opening (*C*) common to all the different compartments. Current is led in and out at the two end electrodes. The electrolyser stands in a tank containing brine, the normal level of which is rather below the level of the above-mentioned earthenware channels.

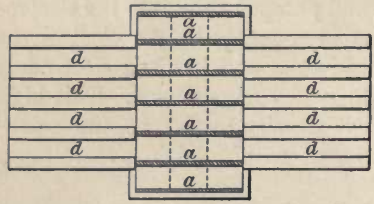

FIG. 73.—Haas and Oettel Cell. Plan.

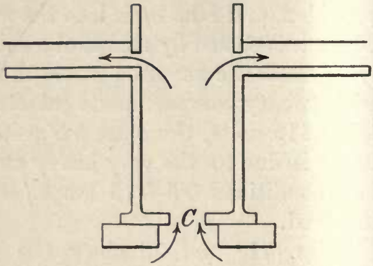

FIG. 74.—Haas and Oettel Cell. End Elevation.

When the current is switched in, the strong gas evolution raises the level of the cell liquid to the point where it can enter these channels, through which it flows, and out into the supply tank, whilst fresh brine is continually sucked in below. Thus the circulation is automatically effected by the electrolysis and, moreover, controlled by it. For the higher the current density the greater is the heat developed, and the more rapidly are the liquors carried through to the main tank which contains cooling coils. The discharge channels serve to increase the liquid ohmic resistance between adjacent compartments, and thus diminish shunt current losses. In earlier types of the electrolyser (still in use) this was more effectually done by a system of longer and narrower closed channels, but in practice these were liable to choke up and cause disturbances.

Oettel[1] gives the following details for an apparatus of the older type, using 17 per cent. NaCl. It contained 28 compartments and took 116·5 volts and 61·5 amperes, corresponding to 4·16 volts per compartment and a current density of about 10 amps./dm.^{2}. The temperature was 22·5°.

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[1] *Zeitsch. Elektrochem.* **7**, 319 (*1901*).

TABLE XLVI

Grams active chlorine per litre	Current efficiency	K.W.H. per kilo. of active chlorine	Kilos. salt per kilo. of active chlorine
	Per cent.		
2·55	95·0	3·31	66·6
4·59	82·4	3·82	37·0
5·90	72·1	4·36	28·8
7·41	68·2	4·61	22·9
8·82	64·8	4·85	19·3
10·50	61·9	5·08	16·2
11·22	59·1	5·32	15·1
12·30	56·7	5·54	13·8
13·35	54·8	5·74	12·7
14·31	52·8	5·96	11·9

With the newer electrolysers the results are rather less favourable. One kilo. of active chlorine requires about 6·4 K.W.H. with a salt consumption of 14 kilos., the concentration being about 12 $\frac{\text{grams}}{\text{litre}}$ active chlorine. The reason is the increased shunt current losses, the current efficiency dropping to 46 per cent.

The Haas-Oettel apparatus uses brine without the addition of chromate or other substances. It is enabled to do this probably because, owing to the porosity of the carbon,[1] a considerable fraction of the $H^{\cdot}$ discharge actually takes place within the electrode material, and the nascent gas does not thus come into contact with the ClO' ions in the bulk of the electrolyte. The carbon electrodes, however, also exert another influence. The formation of a small quantity of CO_2, resulting from oxygen discharge at the porous anodes, is inevitable. This produces free HClO, accelerates the chemical production of $NaClO_3$, and lowers the hypochlorite current efficiency. Finally, although the substitution of carbon for platinum means a considerable initial saving, repairs and renewals are more expensive. The electrodes deteriorate owing to both chemical attack and mechanical disintegration.

Schuckert Cell.—This electrolyser does not employ bi-polar electrodes, and, in its most usual form, is so constructed that the liquors reach the required concentration by flowing once through the apparatus. By means of vertical partitions, alternately reaching from the top nearly to the bottom of the cell, and from the bottom nearly to the top, a trough of suitable length is divided into a number of compartments which contain alternately electrodes and cooling coils. Each electrode chamber has two graphite plate cathodes, and an anode of thin Pt-Ir foil, the electrode connections with the next compartment being carefully protected by being

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[1] P. 345.

covered over with earthenware and cement. Current is led in and out at the two end electrodes, and hence, although the cell does not strictly consist of a series of bi-polar electrodes, it nevertheless suffers from the shunt current losses inherent in such a system. Each separate compartment absorbs about 6 volts. Through this series of cells the brine flows in a zigzag course, the solution leaving the electrolyser having a NaClO concentration depending on the current, the size of the unit, the brine concentration, and its velocity of flow. To counteract cathodic reduction, a little sodium resinate is added to the brine.

Table XLVII shows the results the apparatus can furnish.

TABLE XLVII

Strength of brine used	Grams active chlorine per litre	K.W.H. per kilo. active chlorine	Kilos. of salt used per kilo. active chlorine.
10 per cent.	10–12	5	10–10·5
10	20	7	5–5·3
15	10–12	4·5	15–16
15	20	6	7·5–8

Solutions containing 20 $\frac{\text{grams}}{\text{litre}}$ active chlorine are generally prepared, but liquors with 30 or even 50 $\frac{\text{grams}}{\text{litre}}$ can be economically produced if power is relatively cheap compared with salt. Electrolysers are now also made fitted with bi-polar electrodes.

Kellner Cell: Horizontal Type.—The most efficient electrolytic hypochlorite apparatus is, however, probably that devised by Kellner, using horizontal electrodes. It is shown diagrammatically in Figs. 75 and 76. A long cement trough is divided by glass walls into a number of electrolysis chambers. These are usually arranged terrace-wise, so that the brine, entering at the uppermost, circulates through the series by gravity, passing from one compartment to the next by the channels shown. The electrodes, as in the Kellner electrolyser already described,

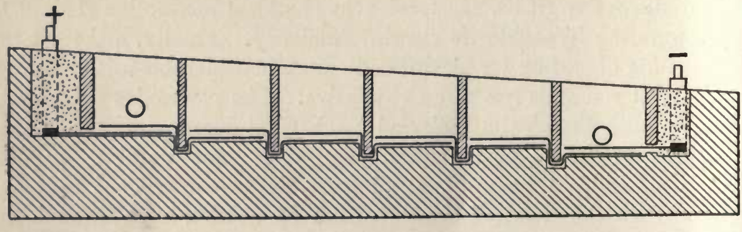

FIG. 75.—Kellner Cell. Side Elevation.

are of Pt-Ir network, and bi-polar. The anodic half lies very close to the bottom of the cell, the cathodic half (where gas is liberated) some 5 mm. *above* its anode. Connection between the two halves of the same electrode is made beneath the separating glass plates. A 220-volt 60-ampere unit will have 36 compartments, each requiring 21 grams platinum. 15 per cent. brine is usually employed, with the addition of an organic sulphur compound[1] (and if necessary some $CaCl_2$), to counteract cathodic reduction. It passes several times through the apparatus until of the required strength, cooling and circulation being effected as with the earlier type of Kellner electrolyser. The temperature is kept at about 21°.

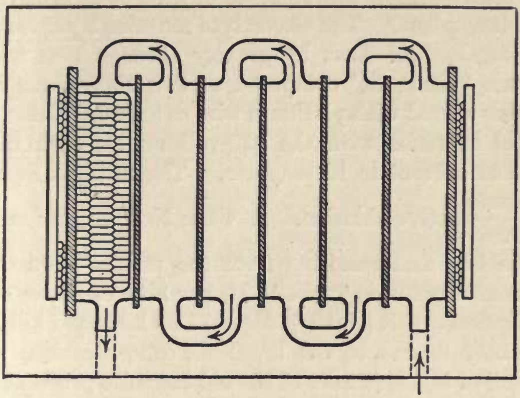

FIG. 76.—Kellner Cell. Plan.

This cell yields very favourable results. A liquor containing 25–30 $\frac{\text{grams}}{\text{litre}}$ active chlorine can be produced with an energy expenditure of 6–6·3 K.W.H. per kilo., the salt used being only 4–6 kilos. per kilo. of active chlorine. And solutions with 50 $\frac{\text{grams}}{\text{litre}}$ active chlorine can be produced at 9·3 K.W.H. per kilo. Even without the addition of the membrane-forming substance, the results are good. Thus a liquor with 20 $\frac{\text{grams}}{\text{litre}}$ active chlorine can be produced with salt and energy consumption of 5 kilos. and 7 K.W.H. respectively per kilo. of active chlorine. Kellner assumes, to account for these results, that the alkaline solution formed at the cathode falls away from it, on account of its greater specific gravity, and meets with an ascending layer of brine saturated with chlorine. The production of hypochlorite thus takes place in a

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[1] See p. 323.

more or less well-defined region some way removed from the cathode, and, with the stirring due to the hydrogen also largely eliminated by the electrode arrangement, the cathodic reduction of ClO′ ions is much lessened. This explanation is not improbable, and may be accepted in default of a more certain one.

Finally, brief mention will be made of the Poplar municipal electrolytic disinfectant plant.[1] The electrolyte contains 5 per cent. NaCl and 1 per cent. $MgCl_2$, and flows by gravity through four troughs, each containing ten 'elements,' composed of two zinc plates as cathodes and a slate slab wound with platinum wire as anode. These 'elements' are connected in series with the 230-volt mains, each taking about 5·6 volts. The current is 16 amperes. The finished liquors contain about 4·5 $\frac{\text{grams}}{\text{litre}}$ active chlorine. A little NaOH solution is added to neutralise the free acid resulting from the precipitation of magnesia. The power consumption is 7·2 K.W.H. per kilo. of active chlorine, the total consumption of salt ($NaCl + MgCl_2$) 13·5 kilos. per kilo. The poor energy efficiency is due to the low NaCl concentration, to the irrational addition of $MgCl_2$ (a relic of the old Hermite process), to the high working temperature (30°–35°), to the absence of chromate, etc.

Comparative.—The following Table (XLVIII) contains typical results yielded by the above electrolysers. They cannot be very closely compared, owing to the varying conditions, but nevertheless give an idea of the relative capabilities of the different types.

TABLE XLVIII

Type	Brine used	Grams active chlorine per litre	K.W.H. per kilo. active chlorine	Kilos. of salt per kilo. active chlorine	Addition
	Per cent.				
Kellner (vertical electrodes)	15	12	6·5	—	K_2CrO_4
Haas-Oettel	17	12·3	6·4	14	—
Schuckert	15	20	6	7·8–8	Sodium resinate
Kellner (horizontal electrodes)	15	25	6	4–6	Sulphur compound

The great advance represented by the later Kellner type is at all events clear. That the Haas-Oettel apparatus works without any addition agent should be noted, and its cheaper first cost must not be forgotten. Of course, if dilute bleaching liquors only are needed, then the difference

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[1] *Trans. Farad. Soc.* **2**, 182 (*1906*).

between the various types largely disappears, and particularly the use of the Haas-Oettel apparatus, with its lower cell voltage, becomes increasingly advantageous. Its electrodes are also less attacked under those conditions than usually.

The reversible voltage needed to convert a brine solution into a hypochlorite liquor of given strength has been calculated.[1] If we assume as a final product a 2·5 n. $NaCl + 0{\cdot}25$ n. $NaClO$ solution (14·6 per cent. NaCl; 17·7 $\frac{\text{grams}}{\text{litre}}$ active chlorine), this reversible decomposition voltage works out at 1·68 volts. (Thomson's Rule gives 2·3 volts.) The production of one kilo. of active chlorine needs therefore a minimum of

$$\frac{96540 \times 1000 \times 1{\cdot}68}{35{\cdot}5 \times 3600 \times 1000} = 1{\cdot}27 \text{ K.W.H.},$$

and the efficiencies obtained in practice amount to only about 20–25 per cent. High overvoltages and low current efficiencies are jointly responsible.

Electrolytic bleaching liquors have considerable advantages over bleaching powder solutions for certain kinds of work. Cost of production is not one. There is very little difference for dilute solutions; and for stronger solutions bleaching powder has the advantage. Thus, for paper-pulp bleaching or for sewage treatment, electrolytic liquors can seldom be economically employed. But for laundry work, fine textile bleaching, and other purposes for which dilute liquors suffice, the reverse is true. Owing to the presence of the HClO they bleach more quickly. Subsequent dipping in acid is hardly necessary, as there are no insoluble lime salts to remove. The fabric is exposed to the action of neither acid nor alkali. And the electrolytic liquors can be relied on far more for constancy of composition and regularity of action. The extreme simplicity and ease of working of the process are also of importance—for those reasons even the Poplar installation has commended itself, in spite of its low electrochemical efficiency.

4. Chlorates.—Theory

We have seen that in electrolysing a neutral alkaline chloride solution the primary products are chlorine and alkali, and that from them results hypochlorite, together with a little free HClO produced by hydrolysis. From such a solution chlorate formation is possible in two ways, chemically through oxidation of ClO' ions by free HClO, and electrochemically through ClO' discharge. Under the conditions so far considered, the former reaction is very slow, and the latter furnishes

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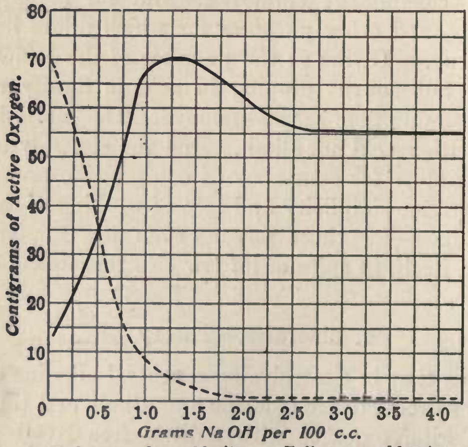
[1] Luther, *Zeitsch. Elektrochem.* **8**, 601 (*1902*); also Abel, *Hypochlorite und Elektrische Bleiche.*

a maximum current efficiency of only 66 per cent., together with a solution containing much available chlorine as hypochlorite. Nevertheless these two reactions are fundamental in technical chlorate production, and we must discuss how they can be modified so as to yield satisfactory commercial results.

A consideration of the phenomena of electrolysis of alkaline chlorides containing free alkali or acid is first necessary. The electrolysis of a halide solution containing free alkali is qualitatively identical with the electrolysis of a neutral solution, but quantitatively very different. The presence of the alkali increases the ClO′ concentration—*particularly at the anode*—at the expense of the HClO otherwise present, and causes it to discharge more easily than in a neutral solution. Consequently the formation of chlorate and the evolution of oxygen commence sooner and at a lower hypochlorite concentration than in a neutral solution. If more alkali be added the effect becomes greater, and finally the whole current is engaged in producing chlorate and liberating oxygen, the NaClO concentration sinking to a very low figure indeed. (The current efficiency of the chlorate production does not, of course, exceed 66 per cent.) With still further rising alkali content, the oxygen evolution increases and the rate of chlorate falls. This is due to direct OH′ discharge.

Fig. 77 expresses the relations existing between the alkali concentration and the quantities of hypochlorite and chlorate produced by the passage of a given quantity of electricity through a 20 per cent. NaCl solution at 5°.[1] Strongly alkaline solutions commence by giving oxygen only, particularly with a platinised platinum anode; but, because of



Dotted curve—hypochlorite. Full curve—chlorate.

FIG. 77.

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[1] Foerster and Müller, *Zeitsch. Anorg. Chem.* 22, 72 (1899).

the progressive increase in the oxygen overvoltage, the anodic potential soon rises to the value at which depolarised Cl' ions are discharged. A low anode potential, in fact, always means a larger fraction of the current used in evolving oxygen, and a lower chlorate yield. The equilibrium hypochlorite content, on the other hand, is greater, a larger concentration being necessary for discharge at the low polarisation. It is accordingly found that better chlorate yields and lower hypochlorite concentrations are obtained at a polished than at a platinised platinum electrode. For the same reason an increase in current density lowers the hypochlorite concentration. These points are illustrated by Table XLIX.[1]

TABLE XLIX

Anode	Anodic current density	Current evolving oxygen	Grams of chlorate oxygen	Grams of hypochlorite oxygen
	Amp./cm.^{2}	Per cent.		
Platinised	0·067	75	1·049	0·087
Smooth	0·067	58	1·639	0·0012
Smooth	0·017	58	1·586	0·0032

The electrolyte consisted of 200 c.c. of n. NaOH + 3·6 n. NaCl at 17°. A rise in temperature, on the other hand, increases the hypochlorite concentration, owing to the lessened oxygen overvoltage and the resulting fall of anode potential. The yield of chlorate simultaneously decreases. (See Fig. 78.) We see then that electrolysis at a low temperature of a brine solution containing 1–1·5 per cent. NaOH (Fig. 77), using a smooth platinum anode and a fairly high current density, will yield chlorate with a 66 per cent. current efficiency and with very little formation of hypochlorite.

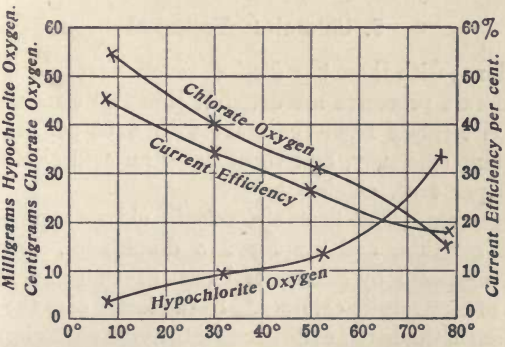

Fig. 78.

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[1] Foerster and Müller, *Zeitsch. Elektrochem.* **9**, 203, 204 (*1903*).

The electrolysis of an alkaline chloride solution which contains a little free *acid* is a quite different process. In absence of acid, the first product of mixing anolyte and catholyte is a hypochlorite solution containing a little free HClO. If now a little free mineral acid be added, the concentration of this HClO is proportionately very much increased. And hence also the velocity of the reaction

$$2HClO + ClO' \longrightarrow ClO_3' + 2Cl' + 2H^{\cdot} \qquad \text{(v)}$$

The hydrogen ions liberated give more HClO, and the process continues, chlorate being formed in all parts of the electrolyte. This reaction is not very rapid at room temperatures. But if the electrolysis be carried out at 70°, its velocity is enormously increased, and under those circumstances will play a far larger part in the formation of chlorate than does the ClO′ discharge. If cathodic reduction is avoided by addition of chromate, and if ClO′ discharge does not take place, then a 100 per cent. current efficiency should be possible, as at no stage of the process is oxygen evolved.

In practice, 85–95 per cent. current efficiencies can be obtained using smooth platinum anodes, and up to 99 per cent. using platinised platinum. The deficiency is due to ClO′ discharge, with its accompanying free oxygen production. Reference to Fig. 69 will explain the difference shown by the two kinds of anode, resulting from the higher potential at the smooth platinum. The free HClO necessary can be produced by the addition of $NaHCO_3$, $Na_2Cr_2O_7$ (instead of Na_2CrO_4) or HF. In this last case Foerster and Müller[1] have shown that no specific effect of the F′ is involved as the patentee asserted. Best of all is the regulated addition of dilute HCl.

5. Chlorates—Technical

In accordance with these two distinct reactions resulting in chlorates, technical chlorate processes are divisible into two classes—those using an alkaline electrolyte from the start with a 66 per cent. maximum possible current efficiency, and those using an acid electrolyte with a possible 100 per cent. efficiency.

Early Processes.—The first electrolytic chlorate processes used a neutral KCl solution, and employed a diaphragm. Such were the original one proposed by **Hurter** and that of **Gall** and **Montlaur,** the first makers of electrolytic chlorate. In the latter case the liquors were circulated from cathode to anode in order to avoid reduction. Although the current efficiency was only 25 per cent., the process paid well, due to its extreme simplicity and the cheap power available. Diaphragm cells have now fallen entirely into disuse, cathodic reduction being to a great extent prevented by a suitable addition to the electrolyte. Most

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[1] *Zeitsch. Elektrochem.* **10,** 781 (*1904*).

plants also have recently stopped working the **alkali (Oettel)** process, its slightly simpler character not compensating for its low electrochemical efficiency.

Later Processes.—Our knowledge of the actual arrangement and working of a chlorate plant is very meagre, but the main outlines are probably as follows. The cells used (of cement or some similar material) are rectangular in shape, carefully insulated, and arranged in terraces so that the electrolyte circulates by gravity. Every anode is placed between two cathodes and similar electrodes are connected in parallel. The largest units will take 1000–1500 amperes. The anodes are of smooth platinum or platinum-iridium foil. Platinised platinum would be better if its use were possible—the voltage would be reduced and the yield increased.[1] Unfortunately, the platinum black deposit is too loose. It has been shown,[2] however, that if platinised platinum be carefully heated and converted into coherent 'grey' platinum, it still largely retains the properties of the original platinum black, and the more so the lower the temperature to which it has been heated. Thus under certain conditions the voltages using different electrodes were :—

Smooth platinum 3·45 volts.
Platinised platinum 2·88 volts.
Grey platinum 2·95 volts.

And the following comparable yields of chlorate were obtained :—

TABLE L

Black	Grey	Smooth
59·2	60·3	58·4
60·5	59·0	58·8
69·6	69·0	64·0
77·6	77·6	74·3
74·2	78·0	75·2
72·2	72·2	65·4

Using such electrodes (though it is doubtful for how long they would retain their special qualities), it would seem possible both to considerably reduce the voltage and to get rather higher yields. It should be mentioned that, whereas platinum black is slightly attacked by anodic chlorine, grey platinum, like smooth platinum, is comparatively unaffected.

As cathode material, Acheson graphite can be used with advantage, and, in working the acid process, nickel, copper, brass, etc. (With the alkaline process such cathodes should not be employed. The small quantities of copper or nickel salts which would undoubtedly enter the

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[1] Magnetite would behave similarly to smooth platinum.

[2] Geibel, *Zeitsch. Elektrochem.* **12**, 817 (*1906*).

electrolyte would catalyse the decomposition $2\,ClO' \longrightarrow 2\,Cl' + O_2$. In the acid process the ClO' concentration is always very small.) Iron can also be employed, if chromate or some other efficient agent be used for preventing cathodic reduction. ClO_3' ions are reducible by hydrogen at an iron cathode. With the alkaline process, zinc can be employed.

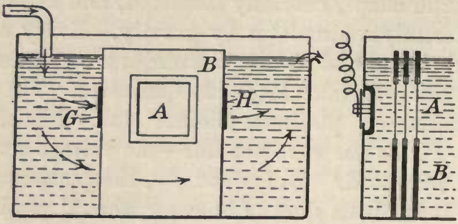

Fig. 79.—Bi-polar Electrode for Chlorate Cell.

Bi-polar electrode systems have also been used. Corbin's electrodes (Fig. 79) consisted of thin platinum foil (A) in the middle of large ebonite frames (B). These were placed about 15 mm. apart in a long trough, and kept exactly parallel by suitable guides (GH). The position of the electrode surface in the middle of the ebonite frames largely prevented shunt current losses. Current was led in and out at the ends of the trough by platinum-covered metal discs.

The electrolyte initially contains about 25 per cent. of KCl or NaCl. Small quantities of lime or magnesia salts are no drawback—rather an advantage.[1] The insoluble bases which are precipitated leave acid behind which accelerates the process. Normally the electrolyte is continually treated with small quantities of dilute HCl. The chromate used is added as K_2CrO_4 $\left(1\ \frac{\text{gram}}{\text{litre}}\right)$ or $K_2Cr_2O_7$. Even though acid is being continually added, the solution is always yellow, as no marked quantity of the red Cr_2O_7'' can exist at the $H^{\cdot}$ concentration of the HClO present. The anodic current density averages 10–20 amps./dm.^{2}. This high value and the close proximity of the electrodes keep the liquors at a working temperature of 70°, at which the reaction producing chlorate proceeds very rapidly. The voltage, despite the hot electrolyte, is 4·5–5·5 volts.

If $KClO_3$ is being prepared, the liquors are circulated through the cells until saturated at the working temperature, drawn off, and allowed to crystallise. The product is recrystallised and is then very pure. The mother liquor is re-saturated with KCl and returned to the cells. If $NaClO_3$ is being produced, the treatment is different, owing to its great solubility. Fresh salt is continually added until the chlorate content

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[1] Compare their effect on the preparation of bleaching liquors (p. 327).

has reached about 750 $\frac{\text{grams}}{\text{litre}}$, when the greater part will crystallise out on cooling. Or the liquors are withdrawn when containing 500–600 $\frac{\text{grams}}{\text{litre}}$ $NaClO_3$ and 120 $\frac{\text{grams}}{\text{litre}}$ NaCl and evaporated. The NaCl precipitates, and the chlorate crystallises on cooling. There is no fear of perchlorate formation in this long-continued electrolysis, provided that the NaCl concentration is kept up.

The current efficiency for either $KClO_3$ or $NaClO_3$ by this process is about 90 per cent. Assuming 5·0 volts to be required, we calculate that 1 ton $KClO_3$ requires

$$\frac{96540 \times 6 \times 10 \times 1000 \times 1000 \times 5}{9 \times 123 \times 3600 \times 1000} = 7300 \text{ K.W.H.}$$

Taking Luther and Abel's figure of 1·43 volts[1] as the theoretical voltage required to produce chlorate from chloride, one ton $KClO_3$ requires a minimum of

$$\frac{96540 \times 6 \times 1000 \times 1000 \times 1{\cdot}43}{123 \times 3600 \times 1000} = 1870 \text{ K.W.H.}$$

Technically, therefore, an energy efficiency of only about 25 per cent. is obtained, a result due to the high voltage needed. The success of these electrolytic methods, which have very largely displaced the older chemical processes, is essentially due to their great simplicity. One main raw material only is necessary, and the operation is completed in a few stages.

Literature

Abel. *Hypochlorite und Elektrische Bleiche.* Theoretischer Teil.

Engelhardt. *Hypochlorite und Elektrische Bleiche.* Technisch-konstruktiver Teil.

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[1] *Zeitsch. Elektrochem,* **8,** 601 (*1902*). *Hypochlorite und Elektrische Bleiche.*

CHAPTER XXI

ALKALI-CHLORINE CELLS

1. General Theory

It has been shown above that, when an aqueous alkaline chloride solution is electrolysed, the chief products are hydrogen and an alkaline hydroxide at the cathode, chlorine at the anode. When cathode and anode products are allowed to freely intermix, we obtain, depending on the conditions, hypochlorite or chlorate. In this chapter will be considered the methods by which these products—the alkaline solution and the chlorine—can be kept apart and worked up separately.

We will first discuss the various electrode reactions involved and the other substances which can thereby arise, and how the formation of these various products is affected by changes in electrode material, temperature, concentration of electrolyte, current density, etc.

Cathodic Processes.—An aqueous brine solution will be taken for consideration. At the cathode the two possible primary electrode reactions are $H^{\cdot}$ and $Na^{\cdot}$ discharge, and we have already seen that normally $H^{\cdot}$ ions are discharged far more easily. For example, from a neutral aqueous solution normal with respect to $Na^{\cdot}$ ions, their discharge requires a cathodic potential of $-2{\cdot}71$ volts, that of $H^{\cdot}$ ions only $-0{\cdot}4$ volt. Under certain conditions these relations can be reversed. If the electrolytic solution pressure of sodium is lowered by its being discharged, not as pure metal, but as an alloy with the cathode material, or if the cathode metal has a high hydrogen overvoltage, then cathodic sodium deposition is no longer impossible.

In agreement with this, it is found [1] that at cathodes of tin, platinum, lead, etc., using high current densities (with correspondingly high hydrogen overvoltages), sodium alloys result. These subsequently react with the water of the electrolyte and the escaping gas disintegrates the surface of the cathode. With mercury, a sodium amalgam is obtained, and the fact of its being liquid (when unsaturated) renders possible the various 'mercury' alkali-chlorine cells, in which the amalgam, after removal from the brine solution, is decomposed by water. If again the

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[1] See p. 122.

electrolyte, instead of being a neutral brine, has a very high value for the ionic ratio $\frac{Na^{\cdot}}{H^{\cdot}}$, primary cathodic sodium formation is rendered possible. For example, metallic sodium can be directly deposited in globules from an exceedingly concentrated NaOH solution at room temperature.

Except, however, in the mercury cells, hydrogen, not sodium, is liberated, and it is important that the cathode used should have a low hydrogen overvoltage. Amongst the commoner metals, the overvoltage at lead is particularly high, very near the figure for mercury. The values for copper and nickel are less, but for iron still lower, and this metal, with its further advantage of cheapness, is the one most frequently employed. At technical current densities (1–10 amps./dm.^{2}) and temperatures (30°–90°), the overvoltage apparently varies between 0·3–0·55 volt.[1]

The strength of the brine used is important in the mercury processes. If the $Na^{\cdot}$ content becomes low, hydrogen discharge is facilitated, and the current efficiency falls. In other cells, the most important factor is the alkali concentration at which the catholyte is drawn off, a higher polarisation being necessary to liberate hydrogen from strong alkali solutions than from weak. The last important factor is the temperature. Raising it lowers the hydrogen overvoltage. Thus, with iron, Sacerdoti found a decrease of 0·05–0·1 volt on increasing the temperature from 24° to 97°. A high temperature is therefore favourable when hydrogen is the primary cathode product, but unfavourable when the object is to deposit sodium, as in the mercury processes. There it will also hasten the rate of decomposition of the amalgam.

Anodic Processes.—At the anode there have to be considered very similar reactions to those already discussed in the previous chapter, but as the cathodic OH′ ions are as far as possible kept away from the electrode, these reactions are here much less important. As before, the equilibrium

$$Cl_2 + H_2O \rightleftarrows H^{\cdot} + Cl' + HClO$$

tends to be set up, and from the HClO formed ClO′ ions result. These can discharge as follows:

$$6ClO' + 3H_2O + 6\oplus \longrightarrow 2ClO_3' + 4Cl' + 6H^{\cdot} + \tfrac{3}{2}O_2$$

It has also been shown that free HClO can react anodically thus:

$$6HClO + 3H_2O + 6\oplus \longrightarrow 2ClO_3' + 4Cl' + 12H^{\cdot} + \tfrac{3}{2}O_2.$$

In both cases oxygen and chlorate are produced, and the solution becomes acid. Another possible reaction is OH′ discharge. This will occur less easily the more acid the solution.

Let us now consider the anode processes during the electrolysis of a brine solution with constant current, all cathode products being

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[1] Sacerdoti, *Zeitsch. Elektrochem.* **17**, 473 (*1911*).

kept apart, and no further salt being added to keep up the concentration. At first chlorine will be evolved and the equilibrium $Cl_2 + H_2O \rightleftarrows H^{\cdot} + Cl' + HClO$ will set in. Gradually the Cl' concentration will fall. As that of the dissolved chlorine remains constant, the HClO concentration will increase according to the above equation and the mass-action law; and further, to keep the current constant, a higher anodic polarisation will be required. As a result of these two factors, anodic chlorate formation will slowly commence, the solution will become more acid, and oxygen will be evolved. The lower the Cl' content falls, the larger will be the fraction of the current so employed. As the very mobile $H^{\cdot}$ ions will rapidly migrate away from the anode, there will never be a large accumulation of acid.

Now, as the concentration of dissolved chlorine in the electrolyte is in equilibrium with the atmosphere above it, the increasing percentage of oxygen in the anode gases will effect a continuous decrease in the chlorine, and hence in the HClO concentration in the electrolyte. Gradually this effect will overpower the opposing one due to the decreasing Cl' concentration. The HClO concentration, and hence the fraction of the current engaged in chlorate formation, will reach a maximum, and, as the electrolyte becomes more and more dilute, this fraction will steadily decrease. This critical maximum point will be reached the more quickly because, as the anode potential rises, OH' discharge will begin to be appreciable, and the chlorine partial pressure will thus fall off more quickly than would otherwise be the case. As the electrolysis proceeds, this last process will become increasingly important, and we have as follows:

(*a*) Chlorine evolution—diminishes continually throughout.

(*b*) Chlorate formation—increases to a maximum and then falls off.

(*c*) Oxygen evolution due to OH' discharge—increases continually throughout.

The following Tables, LI and LII[1] show the progressive results of halide electrolysis at platinum anodes. The first holds for the electrolysis of aqueous KCl, the second for HCl. The two sets of figures are further not strictly comparable, owing to differences in current density, etc.

TABLE LI

Concentration of KCl	Percentage of current giving oxygen	Concentration of free acid at the anode after the experiment
3·16–3·04	0·09 per cent.	0·0001 N.
1·96–1·92	0·20	0·0007
1·47–1·42	0·43	0·0014
0·98–0·92	1·20	0·0024
0·48–0·43	3·15	0·005
0·30–0·22	6·3	0·01

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[1] Foerster and Sonneborn. *Zeitsch. Elektrochem.* **6**, 597 (*1900*). Haber and Grinberg. *Zeitsch. Anorg. Chem.* **16**, 221 (*1898*).

TABLE LII

Concentration of HCl	Percentage of current giving chlorate oxygen	Percentage of current giving oxygen gas
1·0 *n.*	1·04 per cent.	0·9 per cent.
0·33	6·54	9·7
0·1	34·62	34·41
0·033	26·50	53·6

Anodes.—The nature of the anode can exert a two-fold influence on these processes. The overvoltage required for chlorine or oxygen discharge may vary, and secondly it is very important as to whether the anode is porous or not. In practice the materials employed are platinum, carbon, and magnetite. Platinum is always used smooth, never platinised, the platinum black deposit being very easily rubbed off. Carbon anodes at present in use are almost invariably of artificial graphite. Both magnetite and platinum need a considerable over-polarisation for Cl′ or OH′ discharge, graphite electrodes a far lesser one. Consequently the formation of chlorate will commence later at graphite than at the other electrodes under otherwise equal conditions. On the other hand, OH′ discharge will commence earlier, and will take a larger fraction of the total current.

Considerably more important is the influence exerted by the porous structure of the carbon, from which magnetite and platinum are free. The electrolyte penetrates inside at the beginning of the operation, and Cl′ ions are discharged in the ordinary way. But whereas the Cl′ content at the boundary of contact of electrolyte and electrode can continually be renewed, this is much more difficult for the solution in the pores, which therefore becomes depleted far more quickly than the main bulk of the electrolyte. Oxygen evolution commences sooner, and, except with a very non-porous electrode, the oxygen percentage in the gases and the acid content of the anolyte are very sensibly increased. But this oxygen does not entirely appear in the free state. It attacks the carbon electrodes and burns them to CO_2, which partly dissolves in the electrolyte, and partly enters the anode gases. The destruction of the electrode is often not confined to loss as CO_2. If of poor quality carbon it will partly disintegrate, and the dust produced will be found in the anode liquors. Graphite also, which burns away much less readily,[1] has a tendency to 'dust.'

An increase of *temperature* lowers the solubility of the chlorine in the solution, but increases its degree of hydrolysis, these two actions affecting the hypochlorite concentration in opposite senses. Experimentally it is found that the fraction of current producing chlorate decreases. But, on the other hand, the OH′ discharge overvoltage decreases. At a carbon electrode there is the further disadvantage that

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[1] *Cf.*, however, p. 152.

the production of CO_2 is much facilitated. To get a good yield of chlorine, therefore, the temperature should be low.

Current density is the last point to be considered. Using platinum, the high cost practically necessitates the use of high current densities, though these of course involve high bath voltages. With Fe_3O_4 the case is otherwise, and low current densities are advantageously employed. With a porous carbon anode, on the other hand, the current density is best kept high, as by far the greater part of the electrolysis will then necessarily take place on the surface of the electrode. The electrolysis of the dilute solution in the interior of the carbon will thus be largely avoided, and a purer anode gas will result. The less porous the anode and the lower the temperature, the lower the current density can be.

The best conditions for the production of a pure anode gas are then: (1) anode of platinum or good quality carbon; (2) strong brine; (3) high current density; (4) low temperature. In practice, of course, it is often impossible to entirely keep away cathodic alkali from the anode. The discharge of OH' and ClO' ions thus takes place more readily, and the formation of chlorate, oxygen, and CO_2 becomes more important.

The importance of carbon anodes in brine electrolysis makes some rapid method of testing their efficiency desirable. A determination of their porosity might be thought to be a suitable test. In fact, porosity and liability to attack do run very roughly parallel, as the following figures show:

Porosity per cent. by volume	Relative losses in weight
11	13
13	24
21	27
22	37
28	41

The test, however, is insufficiently conclusive, and a direct one is better. We have seen that the anodic processes in chlorate and in alkali-chlorine cells are essentially similar, the difference being quantitative only. It follows that a good test for an anode intended for the latter purpose is to use it for the electrolysis of a brine solution without a diaphragm and with addition of K_2CrO_4. The more nearly it behaves like one of platinum, in respect to both electrolytic products and evolved gases, the better it will serve its purpose.[1] A porous carbon anode intended for working at low temperatures is materially improved by soaking in wax. This treatment is more harmful than otherwise at higher temperatures, as the chlorine will attack the wax.

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[1] Sprösser, *Zeitsch. Elektrochem.* **7**, 1092 (*1901*).

Classification of Cells.—The first problem in the design of alkali-chlorine cells is the keeping apart of cathodic alkali and anodic chlorine. As the solubility of chlorine in the strong brine used is low, the extent of its diffusion to the cathode compartment will also be low. On the other hand, the alkali produced completely dissolves, and its passage towards the anode is determined not only by diffusion, but also by migration of the negative OH' ions. The problem, therefore, practically reduces to one of preventing the alkali from reaching the anolyte, and the means adopted for this purpose afford us a convenient method of classifying the different kinds of cells. The usual method of dividing them into diaphragm, gravity, and mercury cells is somewhat empirical and arbitrary, and the following classification is preferable :

(1) Cells in which the OH' ions are not liberated inside the electrolysis chamber. *E.g.* all mercury processes.

(2) Cells in which the OH' ions liberated at the cathode are prevented from being carried to the anode by convection or mechanical causes, but in which no attempt is made to counteract their electrical migration. *E.g.* Griesheim process.

(3) Cells in which *all* the causes tending to carry the OH' ions formed at the cathode towards the anode are more or less counteracted. *E.g.* Bell-jar process and most diaphragm cells.

2. Mercury Cells.

In these cells the cathodic process is not $H^{\cdot}$, but alkali metallion discharge. The liberated metal dissolves in the mercury cathode, and the amalgam is removed and decomposed elsewhere. At the anode chlorine is evolved, and, as the OH' concentration is very low, a pure gas results, provided that the anodes (if carbon) are of good quality, and that the concentration of the alkaline halide in the electrolyte is kept up. The theory is therefore simple.

Reversible hydrogen evolution from a neutral aqueous solution requires a cathodic potential of $-0{\cdot}4$ volt. With a low current density—*e.g.* 0·1 amp./$dm.^2$—at a mercury cathode, the overvoltage is about 1·0 volt. The deposition of metallic sodium from a $n.Na^{\cdot}$ solution would require a cathodic potential of $-2{\cdot}7$ volts, and the formation of a saturated sodium amalgam a potential of at least $-1{\cdot}8$ volts. (The figures for potassium and potassium amalgam are very similar.) Under these conditions, hydrogen, not sodium, would be liberated. But if the current density is raised, and with it the hydrogen overvoltage, making $H^{\cdot}$ discharge less easy, and if $Na^{\cdot}$ discharge is facilitated by quickly removing the mercury and producing a *dilute* and not a *concentrated* amalgam, sodium is the substance chiefly deposited, small quantities only of hydrogen being liberated.

In practice, at the current density and temperature used, the hydrogen overvoltage is about 1·25 volts, corresponding to a necessary potential of − 1·65 volts. At the same time, by producing an amalgam with only 0·02 per cent. sodium instead of a saturated one, the sodium potential is lowered to perhaps about − 1·5 volts. Electrolysis, therefore, must furnish sodium, not hydrogen. Using KCl, the necessary polarisation is probably a little higher.

At the anode, Cl′ discharge determines the potential. If smooth platinum anodes are used, there is a high chlorine overvoltage. With technical current densities, the anodic potential is probably about + 2·1 volts, making the total drop at the two electrodes 3·6 volts.[1] To this must be added the voltage drop in the electrolyte, determined by the brine concentration, the distance apart of the electrodes, the temperature, and the current density.[2] Current density must be high for reasons already discussed, and it is advantageous to place the electrodes close to one another (which raises the temperature) and to use strong brine. In practice this extra voltage amounts to perhaps 1·4 volts, making a total bath voltage of about five volts. With carbon anodes, owing to the lower overvoltage, this total seldom exceeds 4·3–4·5 volts, except with exceptionally high current densities.

Sources of Loss.—Although no alkali is supposed to form in the electrolyser, nevertheless the current efficiencies of the different cells do not reach 100 per cent., but generally vary round about 95 per cent. There are several reasons for this. If the current density falls too low, if the brine circulation is too slow, or if the amalgam becomes too concentrated, H˙ discharge will become important. In good practice this does not exceed 1 per cent. of the total current, but nevertheless does take place. It becomes far greater if carbon anodes (arranged above the cathodes) are used. Firstly, small quantities of acid are produced at them which facilitate cathodic H˙ discharge; and secondly, small particles of carbon, falling on to the mercury, permit of hydrogen evolution at a lower overvoltage. The same effect will result if the electrolyte contains metallic impurities which are easily reduced at the cathode to a form which will not amalgamate with the mercury.[3]

Besides the electrochemical evolution of hydrogen, there is its chemical production by interaction between the amalgam and the aqueous brine. This reaction, which is slow at room temperature, goes quickly at higher temperatures, and the electrolyser must be kept

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[1] Taussig [*Trans. Farad. Soc.* **5**, 258 (*1909*)] found the back E.M.F. for brine electrolysis between a mercury cathode and a platinum anode to increase from 3·0 to 3·2 volts as the sodium concentration in the amalgam increased from 0·002 per cent. to 0·02 per cent.

[2] Taussig (*loc. cit.*) has made a detailed investigation of the relations which hold for brine electrolysis between voltage, current density, concentration of amalgam, rate of brine and mercury circulation, electrode distance, and temperature. The reader is referred to the original paper for his interesting results.

[3] Compare pp. 201, 209, 227, 282, 402.

below 60° in consequence. Particles of carbon or metallic substances floating on the mercury greatly accelerate the change by facilitating the evolution of hydrogen. Cells with carbon anodes usually give, therefore, a lower cathodic current efficiency and more hydrogen than cells using platinum. A high current density proportionately reduces these chemical losses,[1] as also does rapid removal of the amalgam from the cell. These sources of loss all involve formation of hydrogen instead of sodium, and further produce an impure anode gas. Dangerous explosions have occurred as a result of this hydrogen content, and in any case there is always the possibility of subsequent formation of HCl, which will give trouble in the bleach chambers. The average hydrogen content in the anode gases from cells with carbon anodes is 2–3 per cent., but may rise to 5 per cent. with bad management. The danger of explosions is then considerable. With platinum anodes the amount is much less, seldom exceeding 0·5 per cent.

Another source of loss in mercury processes is *cathodic ionisation of dissolved chlorine* as follows: $\frac{1}{2}Cl_2 + \ominus \longrightarrow Cl'$. This reaction takes place more easily than either $Na^{\cdot}$ or $H^{\cdot}$ discharge, and, as anodes are close to cathodes and there is no diaphragm, will proceed just as rapidly as chlorine can diffuse from the anode. This source of loss affects both anode and cathode current efficiencies, and amounts to perhaps 3 per cent. We can therefore say that the average current efficiency in a mercury cell using platinum anodes will be about 96–97 per cent. at both electrodes. The anode gases will contain a small quantity of hydrogen and oxygen. With carbon anodes 95 per cent. will be obtained. The anode gases will contain 2–3 per cent. of both CO_2 and hydrogen.

In actual practice the electrolyte fed in contains 30 per cent. NaCl or KCl. This is reduced to 20 per cent. during its rapid passage through the cells, and is then re-saturated. Impurities, such as Na_2SO_4,[2] calcium and iron salts, etc., must be removed. The cathodic current density varies in different cells between 5 and 25 amps./dm.^{2}, being high for reasons already discussed. At the carbon or platinum anodes, particularly at the latter, it is still higher. The working temperature is about 50°, kept up by the heating effect of the current. A higher temperature saves voltage, but considerably lowers the current efficiency. The charged mercury must be moved away rapidly from the electrolyser to the decomposing vessel—otherwise it will become pasty and unworkable, and current losses will set in. The alkali metal content is usually kept below 0·02 per cent. The methods adopted for the removal and decomposition of the amalgam are many, and distinguish the various types of cells which we will now consider.

Castner Cell.—The reaction between the amalgam and water.

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[1] Compare pp. 30, 160, 361, 406.

[2] SO_4'' ions, if allowed to accumulate, destroy carbon anodes.

resulting in the formation of caustic alkali and hydrogen, takes place with liberation of free energy. If, therefore, this decomposition could be arranged to proceed electrolytically, the amalgam functioning as a soluble anode and hydrogen being evolved at the cathode, a *primary cell* of a certain definite E.M.F. would result, which, if coupled against the brine decomposition cell, should lower the resultant voltage required for the whole electrolyser. This was recognised by Castner, who designed for that purpose his well-known ingenious *rocking cell*,[1] which, though now nearly obsolete, merits a description here.

The combined cell (Fig. 80) consisted of a large slate box, four feet square and six inches high, divided by two vertical partitions into

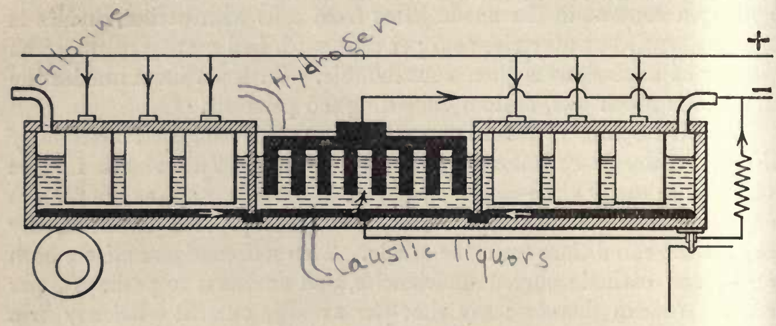

FIG. 80.—Castner Cell.

three equal compartments. These partitions stopped short $\frac{1}{16}''$ from the bottom of the cell, and there was, further, a shallow groove underneath each. The mercury, placed on the bottom of the cell, could thus pass from one compartment to another. In the two outer divisions the mercury was cathode, the anodes being of graphite securely cemented into the roof, and terminating about $\frac{1}{2}''$ from the mercury. The roof was also provided with chlorine outlets,[2] whilst the brine entered and left the cell through suitable openings in the sides. In the middle compartment, the mercury charged with alkali metal became anode in an alkali solution, the cathode being an iron grid. The mercury was circulated by pivoting one end of the cell and resting the other on a slowly revolving eccentric, by means of which it was every moment raised and lowered through a distance of $\frac{1}{2}''$. The mercury thus flowed backwards and forwards between the anode and cathode compartments, being alternately charged with and depleted of alkali metal. The alkaline liquors were continuously withdrawn at a concentration of 20 per cent.

As, however, the cathodic current efficiency in the brine compartment

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[1] *Electrochem. Ind.* 1, 12 (*1902*).

[2] In most alkali-chlorine cells the chlorine is, for obvious reasons, sucked off under slightly reduced pressure.

was only 90–95 per cent., it proved impossible to allow the whole current passing through the brine cell also to flow through the alkali cell. 90–95 per cent. only could enter the electrolyte from the anode as $Na^{\cdot}$ ions. The remaining 5–10 per cent. was necessarily associated with some other anode reaction. As oxygen overvoltage at mercury is very high, and as the $Hg_2^{\cdot\cdot}$ concentration in such an alkaline solution is very low,[1] thus favouring the ionisation of mercury, it was found that the mercury was indeed attacked, a black deposit of Hg_2O resulting. The loss of mercury made it necessary to avoid this, which was done by connecting a suitable resistance in shunt with the middle compartment, as is shown in the diagram. The fraction of current thus shunted corresponded to the current efficiency losses in the brine compartments, and was therefore about 8–10 per cent.

Such cells contained 45 kilos. of mercury and carried about 630 amperes $\left(14\ \frac{\text{amps.}}{\text{kilo.}}\right)$. They required about 4·1–4·3 volts. We should have expected this figure to have been lower, but the gain in voltage secured by the double cell is almost counterbalanced by the increased liquid resistance opposing the current. Their complicated structure and the small size of the units are further disadvantages, as they need (comparatively) much care and attention. Le Blanc and Cantoni[2] have made a laboratory study of their behaviour. With 30 per cent. KCl at 40°, using a current density of 10 amps./dm.^{2}, they got a 93 per cent. current efficiency. The total voltage varied from 5·1 to 3·7 volts, depending on the distance apart of the various electrodes.

Kellner's Arrangement.—Kellner's device for bringing about the decomposition of the amalgam is essentially different. Instead of, as in the original idea of Castner, causing the total current to pass through the electrolyte and gaining the total voltage of the 'sodium-amalgam primary cell,' or, as in Castner's technical cell, shunting a fraction only of the current through a metallic conductor, and gaining the greater part of this primary cell voltage, *no attempt* is made to utilise the energy of formation of hydroxide from amalgam, or, in other words, the *whole* of the current is shunted in the alkali compartment. The amalgam, on leaving the electrolysing vessel, is simply short-circuited with a conductor at which hydrogen overvoltage is low, usually iron, under which conditions its decomposition takes place almost instantaneously. The voltage and energy efficiency are determined then solely by the considerations discussed on pp. 347–349.

Several types of Kellner cell have been proposed, differing in the method of circulation of mercury, gravity and mechanical means being employed. We must first mention the combination of the Kellner

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[1] In consequence of the low solubility of Hg_2O.

[2] *Zeitsch. Elektrochem.* 11, 611 (*1905*).

caustic-compartment connections with the Castner rocking cell. The cell is as described above, only that instead of Castner's shunt circuit and an iron cathode dipping in an alkaline solution, the iron dips directly into the mercury.

Solvay Cell.[1]—But these cells still suffered from the defect that workable units were inconveniently small. Hence stationary cells of large size were developed, through which the mercury steadily flows, the amalgam being decomposed in separate vessels. Such cells are those of the Solvay Co. (Jemeppe, Belgium), and of the Castner-Kellner Co. at Weston Point. The former is illustrated diagrammatically in Fig. 81. The electrolyser consists of a large, slightly tilted, rectangular cement trough, through which continually flow streams of mercury and of brine, the latter being introduced closely above the surface of the former. The layer of mercury is a thin one,[2] and its rate of flow is chosen so that an amalgam of suitable concentration leaves the cell. The current enters through platinum anodes (of interlaced wire) securely cemented in the roof, and leaves by numerous connections passing through the bottom of the cell. The anodes are only 10–15 mm. above the mercury surface. The issuing amalgam flows by gravity into a separate trough, probably of iron, where it is decomposed by a counter-stream of water, strong alkaline liquors being continuously drawn off. The regenerated mercury is returned to the electrolysis tank by means of the well-wheel A. The units are large, carrying 10,000–15,000 amperes at the high current density (at the mercury) of 15–20 amps./dm.^{2}. Each takes about five volts. The advantages of the cell lie in its simple construction, the large size of the units, and the small amount of attention required.

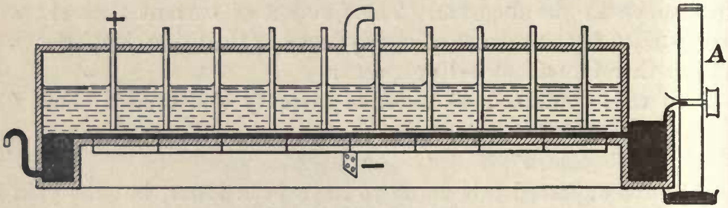

FIG. 81.—Solvay Cell.

The present cell used at Weston Point is very similar to the above. But carbon anodes are employed with lower current densities, and consequently lower voltages, and the mercury is circulated by an Archimedean screw. A unit takes 4,000 amperes.

Whiting Cell.—We may also mention the Whiting cell,[3] the feature

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[1] *Trans. Farad. Soc.* **5**, 258 (*1910*)

[2] 8–10 amperes pass per kilo. of mercury in the whole cell.

[3] *Trans. Amer. Electrochem. Soc.* **17**, 327 (*1910*).

of which is an automatic *intermittent* removal of the amalgam from the electrolyser. The cell consists of a shallow cement box, divided by a partition into electrolyser and amalgam denuding chamber. The electrolyser itself is subdivided by long glass partitions into five compartments, each containing its own graphite anode, and provided with a separate valve through which the charged mercury can flow out into the denuding chamber. These valves are alternately opened and closed by means of cams attached to a slowly revolving horizontal shaft. The amalgam rapidly passes out into the alkaline chamber (being replaced by fresh mercury from a constant level supply) and flows down by gravity through a series of channels in graphite slabs, where it is short-circuited and completely decomposed, pure mercury arriving at the bottom. This is pumped up again by a cup-wheel to the level of the electrolyser.

A cell six feet square takes 1,200–1,400 amperes, the current density at mercury and graphite being about 11 amps./dm.[2] The working temperature is about 40°. The current efficiency is 90–95 per cent. Four volts only are required. The chlorine is 98 per cent. pure, the residue being hydrogen. The anodes are only very slightly attacked. 20 per cent. NaOH is produced, but 40 per cent. can be readily made. A cell of the size described requires about 170 kilos. of mercury, 7–8 amperes passing per kilo.

Compressed-air Type.—Of cells with mechanical circulation of the mercury, the most important is perhaps that used at Jaice, Bosnia, where compressed air is employed.[1] The large shallow cement cell (Fig. 82) contains three compartments separated by partitions similar to those used in the Castner cell. In this case the middle one forms the anodic, the two outer ones the cathodic, compartments. The anode compartment is not completely covered over, but contains six large cement hoods, which carry the anodes. These consist of pieces of platinum gauze or netting, fused into glass tubes, and making contact with external leads by means of mercury and copper wires. Each electrode weighs one gram—there are 88 per hood—528 per 3,500–4,000

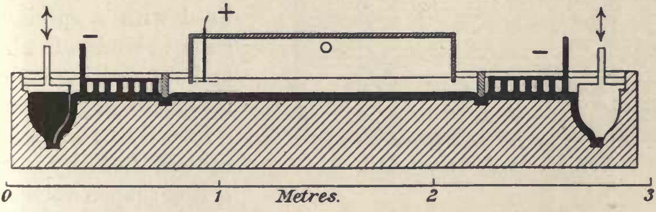

FIG. 82.—Jaice Cell.

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[1] See Taussig, *loc. cit.*

ampere unit. The current leaves the cell by the cast-iron grids in the cathode compartment, which make contact with the mercury and effect the decomposition of the amalgam.

For the circulation of the mercury the cathode compartments are provided with troughs at their outer edges. In these troughs, which, of course, are filled with mercury, there dip a number of iron vessels, inverted slightly truncated cones in shape, connecting below with the troughs, and above with an air-pump. When the pump works, air is alternately compressed into one series of vessels and exhausted from the other, and the mercury is thus made to travel backwards and forwards from anode to cathode compartment. This circulation is very efficient, and allows of the cell being worked with high current densities—viz. 15–20 amps./dm.^{2} at the mercury (as in the Solvay cell).

Rhodin Cell.—In this cell,[1] which was worked for a short time at Sault St. Marie, Canada, the hood containing the anode was rapidly revolved (30 times per minute) and the charged mercury thus driven centrifugally to the outer parts of the cathode vessel, where it was decomposed.

Wildermann Cell.—In conclusion, the Edser-Wildermann cell[2] (founded on English patents 18,958 [1898], 22,902 [1900], and 9,803 [1902]) must be considered. The transference of the amalgam from the brine to the alkali compartment is here effected by mechanical agitation. Fig. 83 shows the cell diagrammatically. It is constructed of iron, lined with a specially resistive kind of ebonite, and divided into a circular inner compartment and a special ring-shaped outer compartment by means of a ring-shaped vertical discontinuous partition, consisting, as the figure shows, of a number of shallow channels arranged one above the other, each having in section the shape of a ship's hull. By filling these channels with mercury to the necessary depth, the partition is made continuous, the two compartments being now separated from one another by mercury seals. The inner compartment is the electrolysis cell and is filled with brine. It contains graphite anodes[3] and a stirring arrangement[3] by which the mercury in the different channels is agitated.

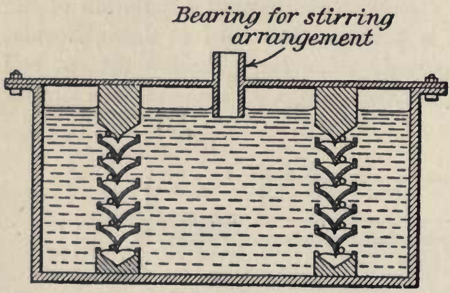

FIG. 83.—Wildermann Cell.

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[1] *Jour. Soc. Chem. Ind.* 21, 449 (*1902*).

[2] Taussig, *loc. cit.* Also in part private communication.

[3] Not shown in diagram.

This agitation causes the amalgam to pass over to the outer caustic compartment, where it is at once decomposed by the agency of rods of carbon or iron contained in the mercury troughs. 20–23 per cent. NaOH, containing at the most 0·2 per cent. NaCl, is continuously drawn off.

Very high current densities are used at the mercury. Even up to 60 amps./dm.^{2} can be employed without any trouble with the amalgam, so efficient is the circulation. At the anodes 10 amps./dm.^{2} is usual. The quantities of hypochlorite and chlorate formed in the anode liquors are very low. Further, as the amalgam is rapidly removed from the influence of any particles which have fallen from the electrodes, and as, further, the agitation renders it difficult for such particles to settle on the surface of the mercury, the current efficiency is high—97–98 per cent. The cell takes about five volts. 2,200-ampere units have been constructed. In spite of the apparent complication introduced by the stirrer, the cell is said to work very smoothly and to require practically no repairs or renewals. Thus anodes have lasted three years. A further advantage is that the vertical arrangement[1] of the mercury and the high current density lead to a far greater compactness than is usual with mercury cells.

The **advantages of mercury processes** lie in the concentrated caustic liquors that can be produced—24 per cent. NaOH can easily be made—and in the high current efficiencies. Further, the working current densities are high, though this advantage is usually neutralised by the horizontal arrangement of the mercury. Evaporation charges are saved, a purer product (99 per cent. $NaOH + Na_2CO_3 + NaCl$) is got, and the life of the carbon anodes is longer than in other processes. Against that must be put the higher voltages required and the first cost of the mercury. The latter item is the more important. The actual losses of mercury during working are usually very small, and should not exceed 2 per cent. in a year.

3. Diaphragm Cells with Stationary Electrolyte

In these cells the OH′ ions are actually liberated in the electrolyser. The disturbing effects of convection currents and gas evolution, which tend to bring together alkali and the anodic chlorine, are avoided. *Diffusion* of alkali from its region of high concentration (catholyte) to that of low concentration (anolyte) is also partly prevented. *But no attempt is made to prevent interaction caused by electrical migration of OH′ ions towards the anode.* The most important cell of this type is the Griesheim Elektron Cell, which, though relatively inefficient, came into use early, and is still very extensively worked on the Continent.

The means used to eliminate the effects of convection and of mass

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[1] Cf. p. 370.

movements of the electrolyte is the employment of a *porous diaphragm* separating anolyte and catholyte. We have already[1] discussed the essentials of a good diaphragm and considered some of the numerous proposed materials. For alkaline chloride electrolysis, the starting material is generally asbestos cloth, the necessary fine porous structure being attained by applying some suitable powder. In the Griesheim cell, instead of asbestos, cement is used.

Now a porous diaphragm offers no selective resistance to the transport of ions. We know that the current in an electrolyte is carried by the various ions present, positive and negative, and, moreover, in proportions depending on their relative concentrations and on their ionic conductivities. Hence some of the current will be carried in the present case by OH' ions, which, passing through the diaphragm into the anode compartment, will react with the chlorine and $H^{\cdot}$ ions there present. Thus the alkali yield will be lowered. As OH' ions have a high ionic conductivity,[2] they will carry a comparatively large fraction of the current, and the more so the greater their concentration in the catholyte—*i.e.* the stronger the alkali made. The following figures, got with 20 per cent. KCl, give an idea of the current efficiencies obtainable :—

TABLE LIII

Foerster and Jorre[3]		Winteler[4]	
Concentration of KOH produced	Current efficiency	Concentration of KOH produced	Current efficiency
Per cent.	Per cent.	Per cent.	Per cent.
4·3	78·4	5·26	85·1
8·3	72·6	8·03	70·7
11·2	68·4	11·37	68·9

The following calculation of current efficiency in a diaphragm process with non-percolating electrolyte we owe to Foerster and Jorre.[5] It is assumed that ordinary diffusion processes play no part.

At any moment let the respective molecular concentrations of the alkaline chloride and hydroxide at the diaphragm be $[C_1]$ and $[C_2]$, their degrees of dissociation a_1 and a_2, and their limiting molar conductivities $\Lambda_{\infty 1}$ and $\Lambda_{\infty 2}$. Let κ_1 and κ_2 be the specific conductivities which the electrolyte would have if chloride or hydroxide alone were respectively dissolved. With two such solutions of high and very similar degrees of dissociation we can assume that the conductivity of the mixed solution is equal to the sum of the single conductivities—*i.e.* equal to $\kappa_1 + \kappa_2$. Now let x be the *fraction of the current*

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[1] P. 154.
[2] See p. 67.
[3] *Zeitsch. Anorg. Chem.* **23**, 158 (*1899*).
[4] *Zeitsch. Elektrochem.* **5**, 10 (*1898*).
[5] *Loc. cit.*

at the diaphragm carried by the hydroxide. Then $1 - x$ is the fraction carried by the chloride. And we have—

$$\frac{x}{1-x} = \frac{\kappa_2}{\kappa_1} = \frac{[C_2]a_2\Lambda_{\infty 2}}{[C_1]a_1\Lambda_{\infty 1}}$$

whence

$$x = \frac{1}{1 + \dfrac{[C_1]a_1\Lambda_{\infty 1}}{[C_2]a_2\Lambda_{\infty 2}}} \qquad (a)$$

During the electrolysis $[C_2]$ continually increases and $[C_1]$ continually decreases owing to migration of Cl′ ions into the anolyte. Also $\Lambda_{\infty 2}$ is much greater than $\Lambda_{\infty 1}$. Therefore $\dfrac{[C_1]a_1\Lambda_{\infty 1}}{[C_2]a_2\Lambda_{\infty 2}}$ will decrease very rapidly during the electrolysis, and hence x continually increases, the yield of alkali at any moment falling off as the electrolysis proceeds.

Now let n be the transport number for OH′ in NaOH—*i.e.*, if only the NaOH were to conduct, a fraction n of the total current would be carried by the OH′ ions. But in reality the total current is divided between NaOH and NaCl, a fraction x being carried by the former. Hence the fraction of the total current carried by the OH′ ions is xn. Therefore, whilst one equivalent of alkali is being produced at the cathode, xn equivalents pass through the diaphragm and leave the catholyte. Then, if C.E. is the current efficiency at any moment,

$$\text{C.E.} = 100(1 - xn).$$

We can simplify the expression for x deduced above by putting $a_1 = a_2$, which is very nearly correct, and expressing the constant ratio $\dfrac{\Lambda_{\infty 1}}{\Lambda_{\infty 2}}$ by a. We finally get

$$\text{C.E.} = \left(1 - \frac{n}{1 + a\dfrac{[C_1]}{[C_2]}}\right) \times 100 \qquad (b)$$

n and a both being constants. We see that the current efficiency depends on the values of $[C_1]$ and $[C_2]$, and, in most practical cases, where the change in $[C_1]$ is small compared with the change in $[C_2]$, is essentially a function of $[C_2]$, the alkali concentration. It is an obvious advantage to work with a high chloride and a low alkali concentration. In practice, however, this means large evaporation charges, which consequently limit the increase of the ratio $\dfrac{[C_1]}{[C_2]}$. The following Table (LIV) contains the results of electrolysis of a 20 per cent. KCl solution, using a Pukall diaphragm :—

TABLE LIV

Period	Mean observed current efficiency	Gram-equivalents per litre		Current efficiency calculated for *end* of period
		$[C_1]$	$[C_2]$	
	Per cent.			Per cent.
First two hours .	88·06	2·382	0·418	81·3
Second two hours .	69·30	2·224	0·754	70·4
Third two hours .	66·50	2·096	1·071	62·6
Fourth two hours .	58·02	2·066	1·331	55·0

The mean yield calculated from the above instantaneous yield was 71 per cent., whilst the experiment gave 69 per cent. The agreement is very satisfactory.

Other formulæ have been deduced by Guye,[1] which allow us to follow the course of alkaline chloride electrolysis with a porous diaphragm and non-percolating electrolyte. With an electrolyte kept continually saturated with the alkaline chloride, and an initial alkali concentration of zero, the following formulæ hold :

$$\text{C.E. (instantaneous)} = 100 \times \frac{1}{(1 + a[\text{C}])^{\frac{1}{3}}} \qquad (c)$$

$$\text{C.E. (mean)} = 100 \times \frac{3}{2a[\text{C}]}\left[(1 + a[\text{C}])^{\frac{2}{3}} - 1\right] \qquad (d)$$

$$\text{F} = v \,.\, \tfrac{3}{4} \,.\, \frac{1}{a}\left[(1 + a[\text{C}])^{\frac{4}{3}} - 1\right] \qquad (e)$$

C.E. = current efficiency : a is a constant depending on the temperature and on the particular chloride used : [C] is the molecular concentration of alkali : v the volume of the catholyte : F the number of faradays passed through the cell. To test these formulæ, a brine solution kept saturated was electrolysed at 40° for nearly thirty hours with 1,150 amperes. a under these conditions was found to be 2·50. Rather more complex formulæ than the above were used, as the initial NaOH concentration was not zero, but 26·1 $\frac{\text{grams}}{\text{litre}}$. Substituting F by I . t (current × time) the following figures were got :—

TABLE LV

Time after beginning of electrolysis	[C] found	[C] calculated
0 hours	0·653	—
6·8	1·29	1·35
13·8	1·94	1·99
21·5	2·58	2·62
29·6	3·22	3·24

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[1] *Jour. Chim. Phys.* **1**, 121, 212 (*1903*).

For the whole experiment, C.E. (mean) was found to be 56 per cent. and calculated at 57 per cent.

For the case when the concentration of the chloride is not constant, but diminishes in proportion as the alkali content rises, Guye[1] and Briner[2] deduced:

$$\text{C.E. (instantaneous)} = \frac{1}{1 + a[\mathrm{C}]} \times 100 \qquad (f)$$

$$\text{C.E. (mean)} = \frac{2}{2 + a[\mathrm{C}]} \times 100 \qquad (g)$$

$$\mathrm{F} = \frac{v}{2}\left(2[\mathrm{C}] + a[\mathrm{C}]^2\right) \qquad (h)$$

whence

$$[\mathrm{C}] = \sqrt{\frac{1}{a^2} + \frac{2}{a} \cdot \frac{\mathrm{F}}{v}} - \frac{1}{a} \qquad (k)$$

In this case a is only constant during any particular experiment: it varies with the initial chloride concentration. Briner has confirmed these formulæ, using a brine solution under conditions for which a was 0·66. He obtained, for example—

TABLE LVI

F × 96540	C = 40 [C] observed	Weight of NaOH obtained = v C	Calculated weight of NaOH
Coul.	Grams/litre	Grams	Grams
25,000	14·7	9·0	9·3
50,000	28·3	17·0	17·0
75,000	39·1	23·7	23·5
100,000	50·0	29·8	29·5
125,000	59·1	35·6	35·1
150,000	68·0	40·7	40·1

Brochet[3] has carried out similar experiments with potassium and sodium chlorides. Some of his results, obtained at 40°, are contained in the following table (for NaCl), and in Fig. 84:—

TABLE LVII

[C]	C.E. (mean) found Per cent.	C.E. (mean) calculated Per cent.
0·120	96	—
0·45	90	88
0·835	83·5	82
1·17	78	76
1·47	73·5	72
1·76	70·4	68·8

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[1] *Loc. cit.*

[2] *Jour. Chim. Phys.* **5**, 398 (*1907*).

[3] *Bull. Soc. Chim.* (iv.) **3**, 532 (*1908*).

If now, returning to formula (*b*), we substitute the values for potassium and sodium salts, we obtain—

$$\text{C.E.}_{(\text{KOH})} = \left(1 - \frac{0{\cdot}74}{1 + 0{\cdot}545\frac{[C_1]}{[C_2]}}\right) \times 100$$

$$\text{C.E.}_{(\text{NaOH})} = \left(1 - \frac{0{\cdot}82}{1 + 0{\cdot}501\frac{[C_1]}{[C_2]}}\right) \times 100$$

Hence, under otherwise equal conditions, the yield of potash should exceed that of soda. Fig. 84 shows this to be actually so. The effect of temperature on the electrolysis can also be readily deduced from the same formula. In Chap. V we have seen that as the temperature rises the rates of migration of the different monovalent ions tend to become equal. Hence *n* and *a* in the formula approach more nearly the respective values of 0·5 and 1·0 as the temperature increases. Consequently the yield of alkali will rise, and the differences shown by the different chlorides tend to disappear. It must not, of course, be forgotten that the increased rate of *diffusion*[1] will simultaneously tend to lower the yield. Equation (*b*) tells us nothing about the effect of current density on the yield, but from formulæ (*g*), (*h*), and (*k*) we gather that the latter depends solely on the quantity of electricity passed through, and should be independent of the rate of electrolysis—*i.e.* the current density—if migration losses are the only ones to be considered.

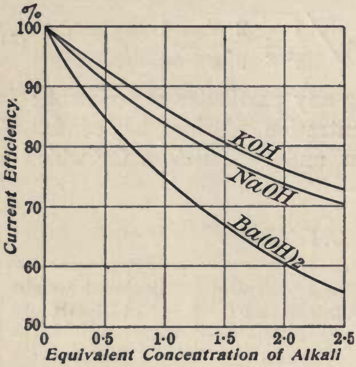

FIG. 84.

This is assumed in the deduction of the above formulæ, which only give correct results as far as the supposition is true, or nearly so. As a matter of fact, a certain amount of diffusion of alkali from catholyte to anolyte must necessarily occur, and results in the actually obtained alkali concentrations being less than the calculated ones.[2] The extent of diffusion depends on the porosity and thickness of the diaphragm,

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[1] See below.

[2] With high current densities at the diaphragm, this difference may be neutralised by another phenomenon—that of *endosmose*, which tends to cause the electrolyte to pass bodily through the diaphragm in the direction of the cathode. This phenomenon will not be further discussed here, as the part it plays in practice is a small one.

on the time, on the temperature, and on the cathodic concentration of alkali.

Diffusion losses will be less with a thick and dense diaphragm and at a low temperature. On the other hand, such conditions necessitate a higher voltage, and these various facts must be carefully weighed against one another when deciding on working conditions. A low catholytic alkali concentration is advantageous, as it also is from the point of view of migration losses. But it has been pointed out that working thus involves large evaporation charges. Finally, diffusion losses increase with time, and hence by using a high current density can be made proportionately less important.[1] Thus, in a certain experiment with KCl, the current efficiency was raised from 59 per cent. to 69 per cent. by increasing the current density five-fold. The voltage, of course, simultaneously rises. From the work of Guye and Tardy[2] we gain some idea of the magnitude of these diffusion losses. The following Table (LVIII) holds for different Pukall porous clay diaphragms at 50°, using a 25 per cent. brine solution in both chambers.

TABLE LVIII

Diaphragm	Surface of diaphragm in cm.^{2}	Per cent. volume occupied by pores	Grams $NaOH$ per litre		n	Grams $NaOH$ diffused
			In first chamber at beginning of experiment	In second chamber after n days		
1	57·76	31·4	162·11	17·36	1·75	13·02
2	64	29·2	65·89	6·02	2·8	6·32
3	64	28·3	65·89	3·86	2·64	4·05
				2·99	1·66	3·14
4	64	28·9	65·89	5·60	2·96	4·20
				3·51	1·68	2·63

The course of the electrolysis at the **anode** has already been discussed, and little needs to be added. In cells of this type carbon anodes were first used, but are now more or less completely replaced by anodes of magnetite. At carbon, as we have seen, OH' ions can be discharged under the prevailing conditions. Oxygen is evolved, and the electrolyte becomes acid. The $H^{\cdot}$ ions formed will migrate cathodewards, and will be neutralised by the OH' ions entering the anolyte. If a strong caustic solution is being made, this OH' influx will more than neutralise the $H^{\cdot}$ ions formed. In that case ClO' ions will be produced, and anodic chlorate formation will commence. But if a weak alkaline solution only is being made the anolyte may remain permanently acid. OH'

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[1] Cf. pp. 30, 160, 349, 406.

[2] *Jour. Chim. Phys.* **2**, 79 (*1904*). See also p. 156.

discharge will thus be hindered and the chlorate formation, assuming a high working temperature, will be chiefly chemical—

$$ClO' + 2HClO \longrightarrow ClO_3' + 2Cl' + 2H^{\cdot}.$$

An acid reaction in the anolyte is better with carbon electrodes, as, at the high temperatures employed (used for other reasons), the liberated oxygen largely forms CO_2, occasioning serious anode losses, and furnishing an impure chlorine. Even with best quality carbons, 5–8 per cent. CO_2 is not uncommon, the oxygen amounting to perhaps another 10 per cent. This fact of CO_2 formation furnishes an important additional reason for making dilute alkali. In some diaphragm cells it is stated that HCl is continually added to the anolyte to avoid this ClO′ and OH′ discharge as far as possible. The oxygen evolution will also depend, as has been pointed out, on the porosity of the carbons employed, a high current density being advantageous. The concentration of the dissolved chloride should also be kept high for the same reason. As oxygen formation always occurs to some extent even if the cathodic alkali is carefully kept away from the anode, the yield of chlorine will never quite reach that of the caustic. With magnetite anodes, the conditions are more favourable. No CO_2 is formed, the anode gas thus being of far better quality. Large quantities of chlorate are produced, but without appreciably deteriorating the electrodes.

From these considerations the following conclusions can be drawn as to the best working conditions for cells of this type:

(1) Anode. Magnetite is better than carbon. It is less porous and less oxygen will be evolved, no CO_2 will be formed, and a purer chlorine will result. Further, a stronger caustic can be made and a higher working temperature used without the electrode being destroyed.

(2) Brine concentration. Should be high, both current and energy efficiencies being thereby increased.

(3) Alkali concentration. A strong alkali is only obtained at the sacrifice of high current and energy efficiencies. Weak liquors involve high evaporation charges, a large plant, etc. These considerations must be weighed against one another, local power and fuel considerations being taken into account.

(4) Temperature. This should be high, as the voltage is thereby lowered. Alkali losses due to OH′ migration are also lessened, but those caused by diffusion are increased. With magnetite, the purity of the chlorine is unaffected.

(5) Current density. Should be high, particularly with carbon anodes. A rather higher voltage is thereby necessitated, but diffusion losses are rendered less important, and the plant gains in compactness.

Griesheim Cell.—This cell[1] is the most important of its type at

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[1] Häussermann, *Ding. Poly. Jour.* **315**, No. 30 (*1900*). Lepsius, *Chem. Zeit.* **33**, 299 (*1909*). Billiter [*Die Elektrochemischen Verfahren*, vol. ii. p. 166 (*1911*)]

present used, being worked to the total extent of about 33,000 H.P. (two-thirds of it in Germany). Both NaOH and KOH are made. It consists (Figs. 85 and 86) of a rectangular iron box, steam-jacketed, covered externally with some non-conducting material (heat), and carefully insulated electrically from the ground. In it are supported cement boxes (1 cm. thick), which act as diaphragms and contain the anodes. They are prepared by the method worked out by Breuer, Matthes, and Weber. The cement is made up with a brine solution containing HCl, and, after setting, the diaphragms are soaked in water. The salt, which has crystallised, is washed out, as are also the more soluble constituents of the cement which have been dissolved by the acid, and the result is a very porous diaphragm which offers but little resistance to the passage of the current, and is very durable against the chemical action of the alkali, chlorine, etc.

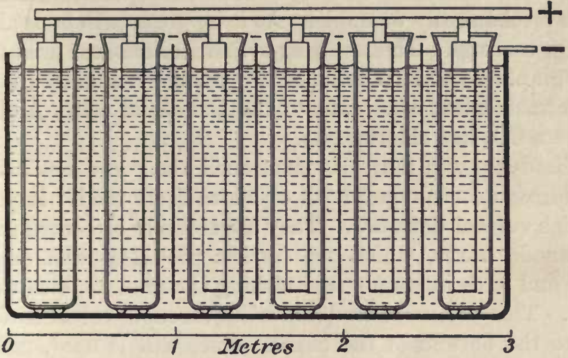

Fig. 85.—Griesheim Cell. Front Elevation.

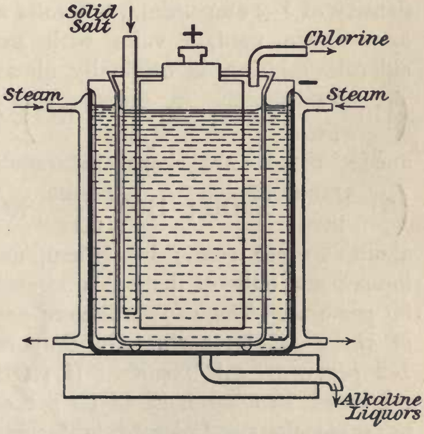

Fig. 86.—Griesheim Cell. End Elevation.

The anodes are of magnetite, and prepared according to Speketer's patent. Decopperised burnt pyrites, which is chiefly Fe_2O_3, is fused in the

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has described cells arranged somewhat differently, the anode chambers being *suspended* in the cathode compartment, the heating being effected by steam coils in the electrolyte, etc.

electric furnace, volatile constituents being thereby removed, and cast. To the molten mass before solidifying fresh powdered Fe_2O_3 is added. This converts the excess of FeO which has formed in the furnace into Fe_3O_4, and the result is a homogeneous mass of the latter. If this precaution is omitted, the FeO crystallises out separately, and the anode becomes mechanically unstable. As it is, great care is needed to produce large castings. The resulting cylindrical anodes[1] are one-fifth the price of graphite and have a life of two years, even under the unfavourable electrochemical conditions of the Griesheim cell. And of course they give a CO_2 free chlorine gas.

As disadvantages must be mentioned their low conductivity and high chlorine overvoltage,[2] both of which facts render impossible the use of high current densities. They are securely cemented into the lids of the anode boxes, which are further provided with exits for the chlorine and with inlets for replenishing the anolyte with the alkaline chloride. This is introduced as solid through tubes leading down almost to the bottom of the boxes. Pure salt is used, got from the alkali concentration pans. The walls of the outer trough act as cathode, and, in addition, a piece of sheet iron is hung between each pair of anode cells. The cathode chamber, into which crude brine is fed, is suitably covered in, and provided with hydrogen exits. All anodes and all cathodes in each cell are connected in parallel. The largest unit constructed takes 2200–2500 amperes.

The working temperature is 90°, and with a diaphragm current density of 1–2 amps./dm.^{2}, 3·6 volts are needed per cell when carbon anodes are used, 4 volts with magnetite anodes. The alkaline chloride solution is originally about 3N. in the cathode chamber $\left(170 \frac{\text{grams}}{\text{litre}} \text{NaCl}; 220 \frac{\text{grams}}{\text{litre}} \text{KCl}\right)$, the crude salt being used. The anode boxes are kept saturated. When making 2N. alkali $\left(80 \frac{\text{grams}}{\text{litre}} \text{NaOH}; 110 \frac{\text{grams}}{\text{litre}} \text{KOH}\right)$ the current efficiency is about 70 per cent.; but when, as more frequently happens, the liquors are only of half this strength, or little more, it rises to 80 per cent. The caustic liquors are drawn off intermittently when of the right strength. On evaporation, solid caustic alkali with 1–2 per cent. salt results. If KOH, it is sometimes merely concentrated to a strength of 50 per cent. (weight) and sold directly to soapmakers. Chlorate is formed in the anode compartment, and, if $KClO_3$, crystallises out, and is from time to time removed. Of recent years, owing to the competition of more efficient processes,

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[1] In the diagrams carbon anodes are represented, and are still used in some of the Griesheim process works.

[2] See p. 153.

this by-product has assumed considerable importance, and in some factories makes the difference between economic and uneconomic working.

Very imperfect electrochemically, the Griesheim cell owes its present large application to its simplicity and cheapness, and to the large amount of capital sunk in it. As at present worked, it can give a chlorine of good quality, has no diaphragm troubles, and is easy to run. For example, the re-saturation of the chlorinated anolyte with halide, usually a troublesome operation, is very simply done, and the cathodic brine needs no preliminary purification. Owing to its working temperature, the voltage is low. Against these advantages must be set its low current efficiency, the weak alkali made, and the small capacity of the units for their size, due to the low current density.

Outhenin-Chalandre Cell.—One other cell of this type should be briefly mentioned—viz. the Outhenin-Chalandre,[1] operated at works in France, Italy, and Spain. The box constituting the cell is divided by two vertical partitions into three divisions, the outer ones containing the catholyte, the inner one being the anode chamber. The diaphragms take the form of cylindrical tubes of unglazed porcelain, cemented into the dividing partitions of the cell, traversing the anode chamber, and, being open at both ends, connecting the two cathode compartments. Each tube contains an iron rod as cathode, these being all connected together. To facilitate the escape of hydrogen, the battery of tubes is sloped somewhat upwards. The anodes consist of Acheson graphite plates. A 1400-ampere unit contains 108 cathodes arranged in six rows one above the other, and 19 anodes.

With a freshly cleaned cell, the initial voltage is 3·5 volts; this rises slowly to 4 volts, when the cell is cleaned again. As a K.W. day is said to produce 6·7 kilos. NaOH when the apparatus is in good condition, it follows that the cathodic current efficiency is $\frac{6{\cdot}7 \times 96540 \times 3{\cdot}5 \times 100}{24 \times 3600 \times 40} = 66$ per cent. The anode compartment is charged with concentrated brine, whilst at the commencement dilute alkali, later water, is passed through the cathode chambers. The concentration of alkali made is unknown. To avoid the destructive effect on the anodes of OH' ions entering the electrolyte, dilute HCl is continually added to the latter. This lengthens the life of the anodes, but lowers the current efficiency. The cells are cleaned out fortnightly. These results are less favourable than those given by the Griesheim cell, whilst the apparatus is complicated and needs much attention and labour. A 1400-ampere cell requiring 108 porcelain tubes as diaphragms can hardly be regarded as satisfactory.

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[1] Brochet, *La Soude Electrolytique*, p. 103 (1909).

4. Cells with Moving Electrolyte

The characteristics of these cells are :—(*a*) alkali and hydrogen are formed in the electrolysis chamber ; (*b*) the effects of both convection *and* ionic migration in causing losses of alkali and chlorine are counteracted. In all cases there is a flow of liquid so arranged as to oppose the diffusion of alkali and migration of OH′ ions anodewards. In most cases diaphragms are also used.

Theory.—Consider the electrolysis of a strong brine solution taking place in a vessel of constant cross-section between anode and cathode, the electrolyte being stationary. At the cathode, hydrogen and alkali appear ; at the anode, chlorine, with small quantities of its hydrolysis products with water, and, if the electrode be of carbon, a certain amount of acid resulting from OH′ discharge. Suppose the hydrogen and chlorine to pass off without disturbing the neighbouring parts of the electrolyte. Then, owing to molecular diffusion and OH′ migration, alkali will gradually stream out from the cathode through the solution towards the anode, and acid and dissolved chlorine will similarly spread out from anode towards cathode.

Fig. 87 shows diagrammatically how the concentrations of these substances will vary at different distances along the electrolyser and at different stages of the electrolysis (represented by the different curves). At first the concentrations of both alkali and [acid + chlorine] fall practically to zero at points not far removed from their respective electrodes. As the electrolysis proceeds, these points approach one another until (curve 4) they coincide. Further electrolysis now results in interaction at the layer of contact between these alkaline and acid zones, giving water and ClO′ ions. There results an alkaline zone with a sharp boundary of a definite concentration, then a narrow neutral zone, then a zone containing acid and chlorine, whose total

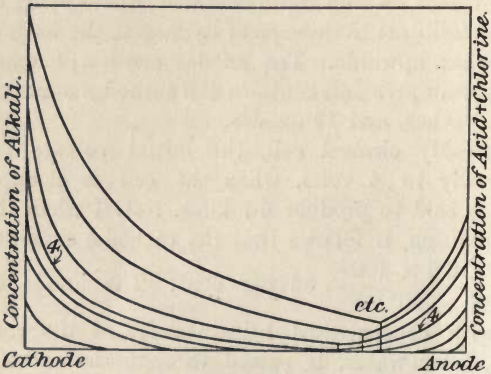

FIG. 87.

equivalent concentration at its boundary is equal to the alkali concentration at the other side of the neutral layer. The more quietly the electrolysis proceeds, the more sharply these boundaries will be defined and the narrower will be the neutral zone.

As now the amount of alkali proceeding anodewards far more than suffices to react with the chlorine + acid travelling in the opposite direction,[1] the alkaline boundary will have a resultant motion towards the anode, as is shown in the figure. We see, however (supposing the different curves to hold for equal intervals of time), that this velocity is *less* than the velocity of the alkaline layer before it encountered the acid layer; and it is, moreover, plain that if acid were produced in greater quantities at the anode than the diagram assumes, this velocity would be still further reduced. The nearer the alkali approaches the anode, the higher is its concentration in the limiting layer.

Finally, when the alkaline zone actually reaches the anode, where gaseous chlorine is being liberated, there will be strong interaction between the latter and the OH′ ions, and the cathodic current efficiency, which hitherto has only fallen below 100 per cent. by reason of the small quantities of acid and dissolved chlorine coming from the anode, will drop very considerably. To avoid this, the movement of the alkaline layer anodewards is checked in all cells of this type by a counter-movement of the electrolyte as a whole from the anode towards the cathode; and in order that this counter-movement shall keep down the alkali losses to the amounts neutralised by the chlorine, etc., contained in the liquors flowing from the anode, it is evident that the electrolyte must move with a velocity *not less than the OH′ ionic velocity under the voltage gradient prevailing at the boundary.* Under these conditions a steady state is soon reached, a brine solution containing a constant content of acid and chlorine passing into the alkaline zone at the boundary layer (which has a definite position in the apparatus and a definite concentration), and an alkaline solution of definite concentration streaming away regularly from the cathode.

Now, the current density being assumed constant throughout the apparatus, it is clear that the voltage gradient at any point will depend on the conductivity of the electrolyte at that point. In particular, the higher the concentration of the alkali in the boundary layer, the higher is the conductivity, the lower the voltage gradient, the lower the OH′ velocity, and the smaller the rate of counterflow of electrolyte needs to be.[2] We will first calculate for the above treated ideal case, in which

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[1] The solubility of chlorine in strong halide solutions is very low.

[2] When using carbon anodes, which produce appreciable quantities of acid in the anolyte, the alkali concentration at the boundary exceeds that present when platinum anodes, which produce but little acid, are used. Hence the necessary rate of counterflow of electrolyte is less with carbon than with platinum anodes, and, for the same current density, *stronger solutions at a lower current efficiency can be made.*

the alkali concentration gradient is undisturbed by gas evolution. Let the alkaline cathodic liquors be n normal. Let a be the cross-section of the apparatus in cm.², I the current, and hence $\frac{I}{a}$ the current density. In one second $\frac{I}{96540}$ equivalents of alkali are produced, and hence the number of c.c. drawn off per second is $\frac{1000\,I}{96540\,n}$. The velocity of flow of the electrolyte through the apparatus is therefore $\frac{1000\,I}{96540\,n\,a}$ cm./sec. Suppose now the current efficiency to be c. Then in one second $\frac{100-c}{100} \times \frac{I}{96540}$ equivalents of [acid + chlorine] enter the alkali boundary. These are dissolved in $\frac{I}{96540\,n}$ litres, their equivalent concentration being $\frac{100-c}{100} \times n$. This, therefore, is also the lowest alkali concentration possible at a stationary boundary under the experimental conditions, and the OH′ velocity under these same conditions gives an upper limit to the rate of flow of the electrolyte necessary to prevent alkali from reaching the anode.

A lower limit is given by the OH′ velocity when we assume that the alkali concentration gradient, owing to the mixing action of the hydrogen gas, is non-existent, and that the alkali concentration at the boundary is equal to that in the cathode liquors drawn off. All technical cases will lie between these two extremes.[1]

The following examples will illustrate the above deductions:—

In the Finlay cell,[2] $2n$.NaOH is made with a 98 per cent. current efficiency, the current density being 0·02 amps./cm.² The linear velocity of the brine towards the cathode must, therefore, be about $\frac{1000 \times 0{\cdot}02}{96540 \times 2} = 0{\cdot}000104$ cm./sec. Assuming an alkali concentration gradient in the catholyte to be possible, the brine at the boundary will be about $\frac{100-98}{100} \times 2 = 0{\cdot}04n$. The specific conductivity at 18° of the original brine used is about $0{\cdot}2\ \frac{\text{recip. ohms}}{\text{cm.}^3}$, and of the final catholyte ($2n$.NaOH + NaCl) about $0{\cdot}4\ \frac{\text{recip. ohms}}{\text{cm.}^3}$. We can suppose the conductivity of the solution at present in question to be $\kappa = 0{\cdot}21\ \frac{\text{recip. ohms}}{\text{cm.}^3}$. The current density being 0·02 amps./cm.², the voltage gradient is $\frac{0{\cdot}02}{0{\cdot}21} = 0{\cdot}095$ volt/cm., and the OH′ velocity under a potential gradient of 1 volt/cm. being 0·0018 cm./sec., the present

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[1] See also Brochet, *Bull. Soc. Chim.* (iv.) **3**, 1057 (*1908*).

[2] See p. 380.

velocity is $\frac{0{\cdot}02 \times 0{\cdot}0018}{0{\cdot}21} = 0{\cdot}00017$ cm./sec., considerably *greater* than the rate of flow of electrolyte. If, however, we assume that the concentration at the boundary is identical with that in the catholyte, we have a conductivity of 0·4 $\frac{\text{recip. ohms}}{\text{cm.}^3}$, a voltage gradient of $\frac{0{\cdot}02}{0{\cdot}4}$ volt/cm., and an OH′ velocity of $\frac{0{\cdot}02}{0{\cdot}4} \times 0{\cdot}0018 = 0{\cdot}00009$ cm./sec., appreciably lower than the rate of flow of liquid. As a matter of fact, this last condition corresponds very closely to the conditions in the actual cell, owing to the lively hydrogen evolution.

Similarly Foerster[1] states that the belljar process[2] can furnish 2·5 *n*. NaOH with a 90 per cent. current efficiency at a current density of 0·04 amp./cm.^{2} Calculating as before, we get 0·000166 cm./sec. as the rate of movement of the electrolyte. Assuming for the moment the alkaline gradient to be perfect, the alkali concentration at the boundary being therefore 0·25*n*., we get 0·00029 cm./sec. as the approximate velocity of the OH′ ions, considerably exceeding the rate of counterflow of the electrolyte. In order that this velocity may be brought down to 0·000166 cm./sec. we must have a solution at the boundary with $\kappa = \frac{0{\cdot}04 \times 0{\cdot}0018}{0{\cdot}000166} = 0{\cdot}43 \frac{\text{recip. ohms}}{\text{cm.}^3}$, which corresponds pretty closely to the conductivity of the final cathode liquors.

Advantages of Diaphragms.—We have mentioned that most cells of the counter-current type are provided with a diaphragm between anode and cathode, usually situated immediately in the neighbourhood of the latter. This diaphragm eliminates convection effects and mechanical disturbances, enables anode and cathode to be placed near to one another, and far higher current densities to be used than would otherwise be possible without great losses through interaction between the alkali and the chlorine. It is thus a great constructional advantage. Further, by allowing the hydrogen evolution to destroy the alkali concentration gradient in the catholyte without simultaneously destroying the alkali boundary itself, the use of a diaphragm renders it possible to work with a higher alkali concentration at that boundary, corresponding to a lower OH′ velocity, a slower current of electrolyte, and a more concentrated alkaline cathodic product.

Disadvantages of Diaphragms.—The accompanying disadvantages are the increased resistance offered to passage of current and passage of liquid. On the one hand, an additional voltage is necessitated, which may ultimately outweigh any gain resulting from the more compact structure of the apparatus. On the other hand, the frictional resistance in the diaphragm capillaries necessitates an increased hydrostatic pressure on the anode side, in order that the electrolyte shall be forced through at a rate sufficient to overcome the high OH′ velocity (high because of the steep voltage gradient in the diaphragm). If then a cell were working at constant current density and with the flow of brine regulated by a constant hydrostatic pressure difference, and supposing

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[1] *Zeitsch. Angew. Chem.* **23**, 1375 (*1910*).

[2] See p. 371.

this rate of flow to only just suffice to keep back the OH′ ions, then the substitution of a more finely porous diaphragm for the one normally used might easily, by allowing the OH′ ions to pass through, markedly lower the current efficiency.

It is also important that the diaphragm should be of perfectly uniform structure, as the frictional resistance to passage of liquid is inversely proportional to the *fourth* power of the radius of the capillary pores. Hence, whilst in those parts of the diaphragm with pores of comparatively large cross-section the velocity of the electrolyte might suffice to counteract the motion of the OH′ ions, this would not be so in the more finely porous parts, and either losses would ensue or the brine velocity would have to be increased, thus giving a weaker alkali than would be the case with a diaphragm of uniform structure.

Horizontal and Vertical Diaphragms.—The diaphragm can be arranged either horizontally (the cathode being beneath it, the brine percolating through from above, and the heavier alkaline liquors passing away underneath) or vertically; the respective advantages and disadvantages of the two arrangements have been discussed by Billiter.[1] Vertical diaphragms allow of a more accessible cell construction, can be readily changed, etc., and, for the same power consumption, give a far more compact cell. Further, impurities settle on the bottom of the cell instead of on the diaphragm. Horizontal diaphragms have, however, two advantages. If for any reason (*e.g.* irregular structure) alkali does actually pass through, being heavier than the brine solution, it will remain as a layer covering the upper side of the diaphragm, provided that there are no mechanical disturbances due to evolved chlorine (and always presupposing, of course, a sufficiently rapid flow of electrolyte). With vertical diaphragms this is not so. Any alkali passing through will fall away from the diaphragm and mix and react with the anolyte, the more so because the flow of brine will be less regular and uniform than with horizontal diaphragms.

As in all these counter-current processes the unavoidable losses are due to the dissolved chlorine and acid coming from the anode, all further losses being due to such mechanical mixing, it follows that, other things being equal, cells with horizontal diaphragms must give better yields than those with vertical diaphragms, and particularly when making stronger alkali. The second point is that, whereas one side of a vertical diaphragm is practically always in contact with an acid chlorine solution, with horizontal diaphragms, as we have seen, this solution can often be alkaline. As it is still far more easy to prepare diaphragms chemically resistant against alkali than against acid, the horizontal arrangement has here a manifest advantage.

Of other conditions which affect the working of these counter-

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[1] *Die Elektrochemischen Verfahren*, vol. ii. p. 203 (1911).

current cells, we have already discussed the differences shown by carbon and platinum anodes. The brine used should be concentrated. Apart from reasons previously considered, a concentrated brine means a higher conductivity, and a lower voltage gradient and OH′ velocity at constant current density, and hence the possibility of making stronger alkaline liquors. A high **current density,** apart from the increased voltage, means a more rapid flow of brine or else a more concentrated alkali at a lower current efficiency. The increased mechanical disturbances must also be reckoned with. Working with a definite alkali concentration, the best current efficiencies will be given with a high current density and correspondingly rapid brine velocities, as convection and mechanical disturbances are then rendered less important.

A high **temperature** does *not* appreciably affect the actual OH′ velocity. It increases, of course, the velocity under a constant potential gradient, but as it decreases the potential gradient in the electrolyte in nearly the same ratio, the resultant ionic velocity is hardly changed. There is in fact a slight decrease, and hence, *convection and diffusion effects apart,* a counter-current cell working without a diaphragm should do rather better at high temperatures than at low. There is, further, the fact that the solubility of chlorine decreases with rise of temperature, and hence also the 'unavoidable' losses. With diaphragms the advantage is greater, as not only are the increased convection and diffusion effects largely avoided, but also the capillary resistance of the diaphragm to the passage of liquid is much decreased.

Belljar Cell.—There is only one cell of the counter-current type working technically without any kind of diaphragm[1]—the well-known belljar or gravity cell (worked to a total extent of about 6,000 H.P., of which half is at the original works at Aussig, Bohemia). It is shown diagrammatically in Fig. 88. A belljar A of non-conducting and non-porous material is inverted in a vessel B, containing an alkaline chloride solution. Outside and around the base of A is a ring-shaped cathode.

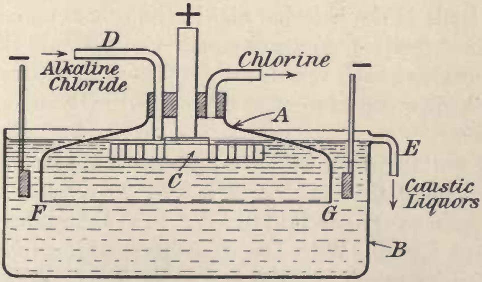

FIG. 88.—Belljar Cell.

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[1] *Cf.* p. 373.

A contains the anode C, and is further provided with a chlorine exit and an inlet D for fresh brine. The outer vessel has an overflow for the caustic liquors.

From what has already been said, the working of the cell will readily be understood. At the cathode alkali is formed, and, in consequence of its specific gravity and the mixing due to the hydrogen evolution, distributes itself fairly regularly throughout the whole of the cathode vessel B. By virtue of OH′ migration it tends to ascend the belljar, but is prevented by means of the downward directed counter-current of brine coming from the anode, a sharp alkali boundary and a neutral layer forming at some level above FG and below C. The position of this boundary and the alkali concentration prevailing at it are determined by the various factors already discussed. At E, alkali of a constant strength is continually drawn off. It contains a certain amount of hypochlorite and chlorate, some of which is decomposed during the subsequent concentration and fusion, but part of which is found in the final product.

In practice the belljars are of small size, rectangular, and of considerably greater length than breadth. They are constructed of sheet iron (serving as cathode), lined inside with cement. The anodes are of graphite and are bored with a large number of small vertical holes through which the chlorine can stream away. They are placed horizontally a few cm. above the lower edge of the belljar, the section of which they almost completely fill. Their life is very long. The brine enters through a hollow duct in the anode support, and is evenly distributed by two horizontal glass tubes pierced with fine holes over the whole surface of the anolyte. The belljar has three exit pipes above. One leads to the chlorine main; the others communicate with the two adjacent belljars to ensure equality of pressure throughout the system. Twenty-five such vessels are supported in a large cement tank serving as cathode compartment, and provided with an overflow for the causticised brine.

Of actual working data we have few. We know, indeed, that the belljars are of small size, taking each only 20–30 amperes, and that the process requires very careful attention to avoid mixing of the liquors and consequent losses. With larger belljars, owing to flow of liquid and current density varying in different parts, it is practically impossible to obtain a satisfactory alkali boundary. From the laboratory results of Adolph[1] and Steiner[2] we conclude that in all probability 2*n*. alkali is made with a current efficiency of 85 per cent. and employing four volts, the temperature being 30°, and the current density in the belljar not exceeding 2 amps./dm.^{2} According to Foerster[3] indeed, 4 amps./dm.^{2}

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[1] *Zeitsch. Elektrochem.* **7**, 581 (*1901*); **10**, 449 (*1904*).

[2] *Zeitsch. Elektrochem.* **10**, 317 (*1904*).

[3] *Zeitsch. Angew. Chem.* **23**, 1375 (*1910*).

can be used continuously on a laboratory scale, giving 2·5*n*. NaOH at 4·4–4·5 volts and 90 per cent. current efficiency, the chlorine being 99 per cent. pure. 3*n*.NaOH and 97·5 per cent. pure chlorine can be obtained with 80 per cent. current efficiency. Temperatures of 45° can be worked at without trouble. These results would indicate that not convection currents, but mechanical disturbances due to evolving chlorine, limit in practice the current density and size of the belljar. These limitations are decidedly the weakest point of the process.

Billiter Belljar Cell[1] (Billiter-Leykam Cell).—The gravity process has been modified by Billiter, who has constructed a cell which, though carrying large currents, contains one belljar only, and in which, by decreasing the distance between anode and cathode, and by working at a high temperature, the voltage has been considerably reduced. Figs. 89 and 90 show diagrammatically two cross-sections of this cell

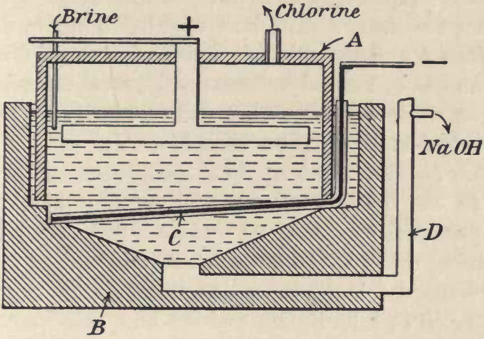

Fig. 89.—Billiter Belljar Cell.

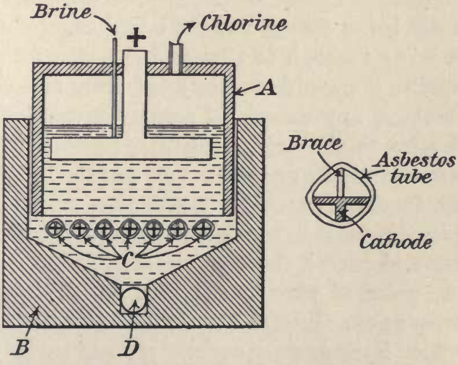

Fig. 90.—Billiter Belljar Cell.

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[1] English Patent 11693 (*1910*). Also private communication from Dr. Billiter.

at right angles to one another. A large rectangular cement box A is inverted in an outer trough B. As in the belljar process, A is provided with a chlorine exit and entrances for brine, and the large horizontally placed graphite anodes, pierced through with numerous holes, are carefully cemented into it. The cathodes consist of a number of pieces of T-iron CC, enclosed in suitably braced porous asbestos tubes to catch the hydrogen and to prevent it from disturbing the main electrolyte, and arranged almost horizontally and parallel to one another immediately under the lower edge of A. Some 90 per cent. of the section of the belljar is occupied by these asbestos tubes. The heating can be effected by steam pipes arranged in a manner at present kept secret, but this is not necessary. The best working temperature is 80°–90°. Brine is fed into A and the alkaline liquors drawn off from B through the pipe D. As the cell is fed automatically, it requires little attention, and is found to work very smoothly and regularly in practice.

The current density can be varied within wide limits—2·5 to 16 amps./dm.^{2} at the anodes. The most convenient value is 5–7 amps./dm.^{2} In the belljar it is some 15 per cent. smaller. During a two months' practically continuous test on a 250 ampere unit, making liquors containing up to 12–15 per cent. NaOH and 16 per cent. NaCl, the voltage averaged 3·1–3·2 volts, and the cathodic current efficiency 92–93 per cent. 0·45 kilo. NaOH and 0·4 kilo. chlorine were produced per K.W.H. On a technical scale much larger units will ultimately be constructed, taking up to 4,000 amperes. The first installation consists of 1,250-ampere cells.

These figures are more favourable in all respects (concentration of alkali, current efficiency, voltage) than those given by the belljar process. The immediate cause of the improved results is that, owing to its direction not being changed at the lower edge of the belljar, the velocity of the brine through the latter is practically constant at all points. This makes it possible to use large units and to work at high temperatures without any danger of serious current efficiency losses, such as would arise in the ordinary belljar process, with its unequal brine velocities in the middle and at the edges of the belljar and its much greater liability to disturbance by convection effects. This regular and directed flow of brine is in turn made possible by the position of the hooded cathodes underneath the belljar. The asbestos hoods must, of course, from one point of view be regarded as diaphragms, as all the *current* necessarily passes through them ; but as they in no way affect the alkali boundary layer or separate anolyte and catholyte, it is somewhat straining matters to do so. They are, of course, of as open a structure as is consistent with completely retaining the hydrogen. Continued electrolysis hardly affects them in any way. Impurities in the brine do not settle on them, but pass away with the cathode liquors.

Billiter Diaphragm Cell[1] (Billiter-Siemens Cell).—Of cells with horizontal diaphragms the only one needing a description here was also designed by Billiter (previous to the modified belljar cell just considered). Fig. 91 shows the cell diagrammatically in section. In a large cement-lined iron trough—the cathode chamber—are inverted one or more cement or slate boxes closed underneath by diaphragms which are almost in contact with the bottom of the outer vessel. These 'belljars' carry large horizontal graphite anodes, exits for chlorine, inlets for feeding in brine (not shown), and earthenware pipes, the horizontal limbs of which are immersed in the brine above the anodes as shown. Through these circulates a suitable heating liquid which serves to keep the cell at its high working temperature.

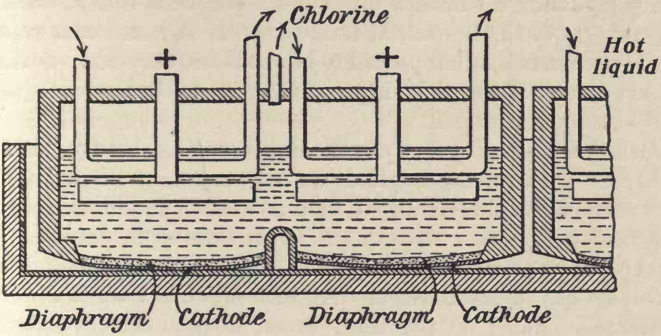

FIG. 91.—Billiter Diaphragm Cell.

The diaphragm closing each anode compartment consists of woven asbestos cloth, resting on an iron-wire network (the cathode) and carefully cemented all round its edges to the belljar. It is slightly sloped as shown, to allow of escape of hydrogen. Its upper (anode) surface is uniformly covered with a mixture of asbestos wool and $BaSO_4$ which forms the active part of the diaphragm, the asbestos cloth merely serving as a support and to eliminate all disturbing effects caused by the hydrogen evolution. Such a diaphragm, provided that the $BaSO_4$ mixture is uniformly made up and applied, is of excellent quality. The fine insoluble powder, while offering an adequate resistance to convection and diffusion, has no great electrical resistance, and gives a diaphragm of very uniform properties at all points.

The current density employed is 4–6 amps./dm.², and at the working temperature of 85°–90° the bath voltage is 3·4–4·0 volts. Starting with concentrated brine[2] $\left(300 \frac{\text{grams}}{\text{litre}}\right)$, 3 *n.* (12 per cent.) and

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[1] *Zeitsch. Angew. Chem.* **23**, 1072, 1375 (*1910*).

[2] As in other diaphragm percolation cells (*e.g.* Townsend, Finlay), the brine must first be purified by removing iron and magnesium salts. Otherwise these will subsequently be precipitated by the cathodic alkali in the pores of the diaphragm,

4 *n*. (16 per cent.) NaOH can be made at 95 per cent. and 90 per cent. current efficiency respectively. Quite similarly 18–23 per cent. KOH can be produced. The chlorine is very pure, containing $<1{\cdot}5$ per cent. CO_2 even with the strongest alkaline liquors, and for 2–3 *n*. alkali merely traces. Oxygen is absent. The life of the anodes is consequently very long. Provided that the brine does not contain iron or magnesia salts to any extent, the same is true for the diaphragms. Otherwise their porosity gradually diminishes with time. This is, of course, one of the disadvantages of the horizontal arrangement. A convenient capacity for each cement belljar has proved to be about 500 amperes. Several of these are combined together in practice in one cathode trough to give a 2,000–3,000-ampere cell.

A detailed laboratory study of the Billiter cell has been published by Mühlhaus.[1] He first investigated the diaphragm, and found that, to obtain constant results, the $BaSO_4$ used must be in equilibrium with the strong caustic liquors with which it is surrounded in practice. It is best prepared by precipitation in the hot. At current densities exceeding 6–7 amps./dm.^{2} it deteriorates. At first Mühlhaus worked at room temperature. Using 30 per cent. brine, he got current efficiencies varying from 98–99 per cent. for 3 *n*. NaOH to 75 per cent. for 6 *n*. NaOH. The chlorine varied correspondingly in purity between 99·5 per cent. and 93 per cent. 3 *n*. NaOH was practically free from chlorate. 4 *n*. NaOH gave about 1 per cent. $NaClO_3$ in the *solid* product, 6 *n*. NaOH gave 7·2 per cent. $NaClO_3$. Using more dilute brine, lower current efficiencies were obtained. From the point of view of current efficiency and purity of liquors, a high current density and a rapid brine velocity are better than a small current and a small velocity. The best working conditions at room temperature are 4 amps./dm.^{2} and 30 per cent. brine, making 4 *n*. NaOH.

Working at higher temperatures (70°–80°) the cathodic product was purer, the current efficiency somewhat increased, and the voltage reduced by 0·5 volt. Here again it is most advantageous to make 4 *n*. NaOH, which is possible with a 99 per cent. current efficiency. The product is practically free from chlorate. These favourable results arise partly from the increased conductivity of the electrolyte, partly from the decrease of frictional resistance in the diaphragm.

Hargreaves-Bird Cell.—Cells with vertical diaphragms will now be considered. The oldest is the Hargreaves-Bird cell, worked by the Electrolytic Alkali Co., Middlewich. In one form (Fig. 92) it consists of an iron box lined with cement (length 10′, width 2′, height 5′), divided vertically along its length into three compartments. The middle one

and thus lower the efficiency of the latter. These substances are best removed by treatment with the necessary quantity of alkali, being then allowed to settle. Excess of alkali must be carefully avoided.

[1] *Dissertation* (Dresden, 1911).

contains the anodes, the outer ones the cathodes. The separating partitions are of asbestos or an asbestos-cement composition of some kind, and serve as diaphragms. The cathodes consist of copper gauze spread over the whole outer surface of each diaphragm and thus supporting the same. In presence of the brine, iron would be too strongly attacked by the CO_2 which, together with steam, is led into the cathode compartments. The copper gauze in turn is suitably braced against the outer cell walls. The anodes[1] are of carbon, probably graphite, and are cemented in through the roof of the anode chamber, which also contains an exit for the chlorine.

The brine enters at the bottom of the anode compartment and leaves by an overflow at the top. Part of it percolates through the diaphragms and is subjected to electrolysis at the copper gauze. Owing to the CO_2 which dissolves in the percolating liquid, $H^{\cdot}$ discharge is much facilitated, and for the same reason very few OH' ions result. The solution drawn off from the cathode chamber contains essentially, therefore, a mixture of NaCl and Na_2CO_3, which are separated by crystallisation. In practice saturated brine is fed into the anode chamber and the greater portion of it transformed at one operation into carbonate. We can suppose about 3 *n*. (16 per cent.) carbonate solutions to result. Very little is known definitely of other working details. A cell of the size described takes about 2,000 amperes at a diaphragm current density of about 2 amps./dm.², and a somewhat greater one at both anode and cathode. The current efficiency is probably 85–90 per cent., and the voltage should not exceed 3·5–4 volts at the working temperature of 85°. These figures are for cells with satisfactorily working diaphragms. Under contrary conditions both current efficiency and voltage will be much less favourable.

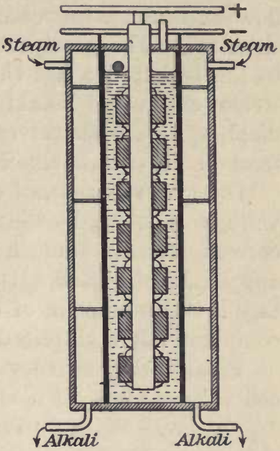

FIG. 92.—Hargreaves-Bird Cell.

Indeed, the Hargreaves-Bird cell seems open to some practical objections arising from the diaphragms. These diaphragms must be fairly thick or dense, or else the hydrostatic flow through them at 85° would be too rapid, and would not allow of making concentrated carbonate liquors. This is at once a disadvantage from the point of view of voltage. Further, the *rate* of percolation of brine cannot be satisfactorily regulated—in fact, to materially change it without seriously diminishing the efficiency of the cell would probably

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[1] See p. 153 and Fig. 40.

necessitate the substitution of a new diaphragm more or less porous than the old one. Thirdly, the hydrostatic pressure forcing the brine through varies enormously at different levels of the diaphragm, increasing continuously, of course, towards the bottom. This means that, even with a diaphragm of perfectly uniform structure, a uniform flow of brine is impossible; and the effect of all irregularities in structure will be greatly magnified. Again, the diaphragms are subjected to the action of a hot chlorine solution on one side and to that of steam and a hot weakly-alkaline solution on the other. Asbestos diaphragms are almost certain to frequently break down when thus treated. If caustic alkali were made, matters would be still worse.

Other advantages, of course, are gained by passing in CO_2. The voltage is lowered owing to the facilitated $H^{\cdot}$ discharge, and the current losses are much diminished, as only a few OH' ions can appear, and $l_{CO_3''}$ and $l_{HCO_3'}$ are far less than $l_{OH'}$. The great disadvantage is the production of cheap soda crystals and soda ash instead of comparatively high-priced caustic alkali.[1]

Finally, the efficiency of the diaphragm determines essentially the cell voltage also. If it is working well the voltage will be low, owing to the low OH' concentration at the cathode, to the high conductance of the electrolyte and the absence of overvoltage effects at the high temperature, and to the low current density. But if the diaphragm is inordinately thick or dense, or becomes pulped or choked during working, it will entirely alter the voltage relations.

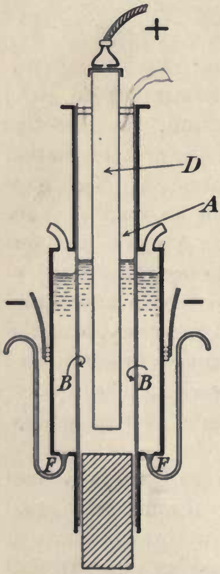

FIG. 93.—Townsend Cell.

Townsend Cell.—A cell somewhat similar in construction to the above, but working under very different conditions, is the Townsend cell[2] (Figs. 93 and 94), which has been successfully operated for some years by the Hooker Electrochemical Co. at Niagara. The centre compartment, A, again forms the anode chamber. Its two ends and bottom are constructed of cement and form a shallow U (Fig. 94 *a*). In the thickness of the cement are several channels as shown, which serve to introduce and draw off the brine, to lead away the chlorine, and for cleaning purposes. The sides of the anode compartment are formed by asbestos diaphragms, B, on the outside of which press the iron grids, C, which serve as cathodes. These grids

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[1] The Electrolytic Alkali Co. has also attempted the manufacture of $NaHCO_3$.

[2] *Electrochem. Ind.* 5, 209 (*1907*); 7, 313 (*1909*).

simply form one face of the iron side-pieces (Fig. 94 *b*) which constitute the two cathode compartments, and which are securely bolted into position. The graphite anodes, D, are cemented in through the roof of the anode compartment, of which they occupy the greater part of the space. The whole construction of the cell is very simple, and it can be rapidly dismantled or set up.

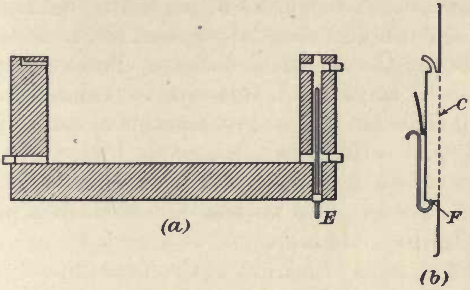

FIG. 94.—Townsend Cell.

The cathode compartments have hydrogen exits and adjustable swan-necks at the bottom for drawing off the causticised brine. In order to rapidly remove this product from the region of the cathode, they are partly filled with a liquid indifferent to and immiscible with caustic alkali. This device constitutes the novel feature of the cell. Kerosene oil is the liquid used in practice. In running the cell, the relative levels of the anodic brine and the cathodic oil are regulated by means of the adjustable overflow E in the concrete wall. For rapid percolation E is raised, and *vice versa*. The brine thus passing through the diaphragm is charged with alkali at the cathodes. But it does not remain in the neighbourhood of cathode or diaphragm. Owing to contact with the paraffin, the drops of electrolyte at once become spherical, and are whirled away by the hydrogen gas into the main bulk of the oil, subsequently falling to the bottom of the cathode compartment, collecting in the pocket F, and siphoning off. In this way losses due to OH' migration are to a great extent avoided, and very high current efficiencies, together with high strength caustic liquors, result. The same is true of the anodic chlorine. As ClO' production is almost excluded, very little oxygen or CO_2 is evolved, and a pure anode gas at a high current efficiency is obtained.

Another essential improvement on the Hargreaves-Bird cell effected by this oil filling must be mentioned. The hydrostatic pressure on the two sides of the diaphragm is thereby largely equalised. A thinner diaphragm can consequently be used, which means a gain in voltage; and a percolation of brine is attained which is practically uniform at all parts of the diaphragm. This is of great importance.

The removal of the alkali is so effective that very high current densities giving concentrated alkali can be united with excellent current efficiencies. A 2,500-ampere-unit measures 8′ × 3′ × 1′, and takes 15 amps./dm.^{2} at the diaphragm. Such a current density far exceeds anything possible with other diaphragm cells, and in fact approaches the values reached with modern types of mercury cells with the most efficient mercury circulation. Under these conditions the Townsend cell gives a current efficiency of 90–95 per cent., producing 15 per cent. NaOH, which still contains some 20 per cent. NaCl. 4·5–5 volts per cell are necessary at the above current density. But, working with figures still as high as 10 amps./dm.^{2}, this can be reduced to 4–4·2 volts. Saturated brine is used in the anode compartment, and the total distance between anode and cathode hardly exceeds 1 cm. The great uprush of chlorine gas effectually circulates the brine and prevents any local depletion at the anode. The working temperature is probably about 50°–60°, kept up by joule heat.

The diaphragm is, as usual, one of the most important parts of the cell. It is made according to Baekeland's patent, and consists of woven asbestos cloth painted with a mixture of asbestos fibre, Fe_2O_3, and colloidal ferric hydroxide. It appears to act very well, and only needs a monthly scraping and repainting, the operation being very simple. The crude brine must, however, be purified. In practice, after removal of the iron by adding alkali and then settling, it is made slightly acid before being fed into the cell. The anodes are only very slowly attacked during the electrolysis. This is due to the very high current densities used and to the practical absence of hypochlorites in the anolyte. The value of ($HClO + HClO_3$) can fall as low as $0{\cdot}1 \frac{\text{gram}}{\text{litre}}$. The loss of kerosene is negligible.

Other diaphragm cells of simple construction are at work, particularly in the U.S.A., their output being consumed by the maker. Paper and pulp mills more particularly use them, the chlorine being the product required. The **Macdonald** cell,[1] though obviously not very efficient electrochemically, seems to answer such purposes well.

Finlay Cell.[2]—Finally must be considered this ingenious cell, which, though so far technically operated on a small scale only, gives results which in some respects exceed those furnished by any other cell. Instead of the flow of electrolyte taking place from the anode through a diaphragm to the cathode, *two* diaphragms are placed between anode and cathode, and the electrolyte, introduced between these, percolates through them both towards the respective electrodes. Thus not only is OH' migration from cathode to anode more or less counteracted, but

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[1] *Electrochem. Ind.* 5, 43, 259 (*1907*).

[2] E.P. 1716 (*1906*), 16853, 17492 (*1907*). Also private communication from Mr. Finlay.

also $H^{\cdot}$ migration and chlorine diffusion from anode towards cathode. In practice, interaction between chlorine and OH' ions is probably almost completely eliminated; but the rate of flow will be insufficient to overcome the velocity of $H^{\cdot}$ migration, and neutralisation of OH' ions will take place in or near the cathode diaphragm.

Fig. 95 shows diagrammatically the principle of the cell. A is the anode; B the cathode; C the cathode diaphragm; D the anode diaphragm; E the cathode chamber; F the anode chamber; G the intermediate chamber. The supply of brine enters G under a constant adjustable head, of which the level is indicated by a gauge attached to the cell. The liberated hydrogen leaves at K, the chlorine at L. The cathode and anode effluents are drawn off by the adjustable swan-necks M and N. By varying the level difference HM, the rate of percolation of the brine through C, and hence, at constant current, the alkalinity of the catholyte, can be regulated. A similar statement holds for the anolyte.

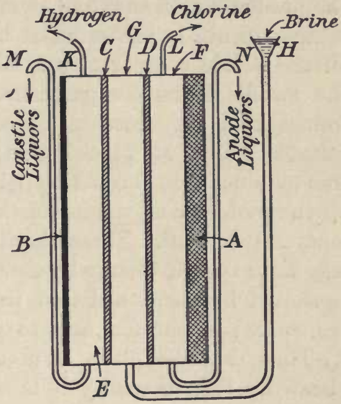

FIG. 95.—Finlay Cell.

In order, for technical purposes, to reduce the distance between anode and cathode as far as possible, and at the same time to produce a unit capable of giving a large output for its size, the cell is constructed somewhat similarly to a filter-press. The cathodes are of sheet iron mounted in shallow wooden frames, and both sides are active. Over these frames are stretched the cathode diaphragms. Under the working conditions of the cell (comparatively weak alkali, low temperature, and almost complete absence of ClO' ions) cloth acts very satisfactorily. The narrow vertical spaces bounded by cathodes, wooden frames, and diaphragms form the cathode compartments. On the other side of each cathode diaphragm is put a 'separator,' a rectangular frame of waxed cardboard $\frac{1}{10}''$ thick. On this in turn is laid an anode diaphragm of about the same thickness, consisting of well-woven asbestos cloth, treated with some indifferent powder in order to decrease its porosity and make its structure more regular.[1] Into the compartment thus formed brine is fed. The anodes consist of vertical Acheson graphite

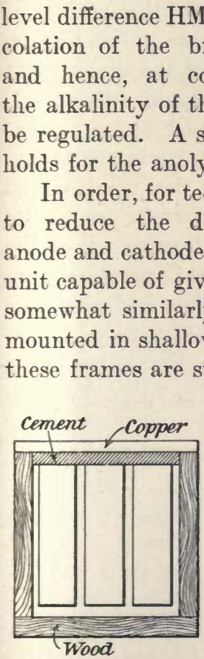

FIG. 96.—Finlay Cell. Anode Compartment.

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[1] Compare pp. 375, 380.

plates sealed into a copper trough by means of lead (Fig. 96). This trough forms the top of an anode frame ($1\frac{1}{4}''$ thick), the other three sides being of teak. The copper is protected inside from the action of the chlorine by a cement coating. The anode frame is placed between two anode diaphragms, thus constituting an anode compartment, and there follow successively (*a*) separator, (*b*) cathode diaphragm, (*c*) cathode, and so on until a convenient size of unit is reached, when the whole is bolted together between two stout teak end-frames.

All like electrodes are connected in parallel. In order to collect the products with ease and to ensure that the level of liquid in similar compartments is the same, it becomes necessary to connect together all the anode compartments, all the cathode compartments, and all the middle brine compartments. This is done by perforating the frames and the borders of the diaphragms and separators with suitable holes, so placed that, when the cell is put together, continuous ducts are formed by which the brine can be distributed into all the middle compartments, and the cathode and anode products separately led off. These channels are put into connection with their respective compartments by slots cut through the separators or frames. It should be mentioned that the edges or borders of the diaphragms are soaked in paraffin wax to prevent leakage of liquid outwards.

Thus described, the structure of the Finlay cell appears complicated. But in reality it is not so. Its different parts are cheap, it is quickly put together and dismantled, and the whole is so bolted together that leakage from the numerous joints is practically eliminated. The feeding in of the brine and the drawing off of the catholyte are effected automatically, and the cell needs practically no attention when working. The life of both diaphragms and anodes is very long. A standard 1,000-ampere unit measures $3' \times 2\frac{1}{2}' \times 2'$, including the heavy wooden end-frames, but not including space taken by supports, leads, etc. A 2,000-ampere unit is $5' \times 2\frac{1}{2}' \times 2'$. The cell is therefore very compact.

The best working current density at diaphragms and cathodes is 2 amps./dm.^{2} Each cathode then takes 100 amperes. Under these conditions, making 8 per cent. NaOH from purified brine containing originally 30 per cent. NaCl, a cathodic current efficiency of 98–99 per cent. results, the cell voltage being only 2·9 volts, or, including the drop in leads and connections, 3·0 volts. This result depends, of course, on the very low current density and the close proximity of the electrodes. If the rate of flow be decreased, a stronger liquor (12–15 per cent. NaOH) can be made, but the current efficiencies fall to 85–90 per cent. The voltage remains almost unaltered. If current density and rate of flow be doubled, the current efficiency increases slightly, and the voltage rises to 3·4–3·5 volts. The working temperature is about 30°–35°, kept up by joule heat. The chlorine obtained is very pure (99·4 per cent.), corresponding to the high cathodic current efficiency. It contains traces only (0·05 per cent.) of CO_2 and small quantities of oxygen. Under normal working conditions, the anode liquors are nearly free from bound active chlorine.[1]

A laboratory investigation of the Finlay cell has been carried out by Donnan, Barker, and Hill.[2] The results obtained did not quite equal those given by a technical unit. The current efficiencies were from 1–5 per cent. lower, and the voltage averaged 3·4 volts. The discrepancies are due to the somewhat unsatisfactory behaviour of the Bernfeld diaphragms used, and to certain slight constructional differences inherent in the small size (20 amperes) of the cell employed.

5. Comparative

In order to compare the energy efficiencies of the various processes considered, it is necessary to know the theoretical decomposition voltage of a NaCl solution, or rather the E.M.F. of the cell $\mathrm{H_2} \mid \substack{\mathrm{NaOH} \\ \mathrm{NaCl}} \mid \mathrm{NaCl} \mid \mathrm{Cl_2}$. And this E.M.F., of course, varies somewhat with the NaOH and NaCl concentrations. Polarisation measurements made by different experimenters vary between 2·23–2·45 volts. The Helmholtz-Thomson rule gives 2·3 volts, and it is perhaps best to use this conventional value for purposes of calculation. Then we can make up a comparative table of electrochemical data, *which holds for those conditions under which the cell in question is normally worked.*

TABLE LIX

Cell	Normality of alkali	Cathodic current efficiency	Voltage	Energy efficiency	K.W.H. per kilo. NaOH.
		Per cent.	Volts	Per cent.	
Castner (rocking cell)	5 *n.*	92	4·2	50	3·1
Kellner (platinum anodes)	5–6 *n.*	97	5·0	45	3·4
Kellner (carbon anodes)	5–6 *n.*	95	4·5	49	3·1
Whiting	5 *n.*	92	4·0	53	2·9
Wildermann	5–6 *n.*	97	5·0	45	3·4
Griesheim (carbon anodes)	1–2 *n.*	70–80	3·6	45–51	3·0–3·4
Griesheim (magnetite anodes)	1–2 *n.*	70–80	4·0	40–46	3·3–3·8
Outhenin-Chalandre	(2 *n.* ?)	66	3·7	41	3·7
Belljar	2 *n.*	85	4·0	49	3·1
Billiter ' membrane '	3 *n.*	92	3·1	68	2·3
Billiter ' diaphragm '	3–4 *n.*	95	3·7	59	2·6
Hargreaves-Bird	3*n* Na_2CO_3	85	3·7	—	—
Townsend	4 *n.*	94	4·8	45	3·4
Finlay	2 *n.*	98	3·0	75	2·0

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[1] The dissolved *gaseous* chlorine must of course be removed if the spent anode liquors are re-saturated, and again fed into the middle cell compartments.

[2] *Trans. Farad. Soc.* **5**, 49 (*1909*).

It has been repeatedly made clear that electrochemical data are not the only points to be considered in a comparison of different kinds of cells. Nevertheless the preceding table seems to show that in localities where power is dear the Finlay cell will have a certain advantage over all others, in spite of the fact that it is only designed to make dilute alkali solutions. This is, of course, its weak point. But even when making stronger alkali (3–4 *n.*) it is still a very good cell, giving almost the same results electrochemically as the Billiter 'membrane' cell. Under those conditions it would have the advantage of being far more compact than the latter, but the disadvantage of the possibility of diaphragm troubles. In particular the simple cloth cathode diaphragms could probably not be used.

Where, on the other hand, power is very cheap, recent types of mercury cells are undoubtedly the most suitable. They furnish very strong caustic liquors almost free from chloride, and give a pure anode gas. But their first cost is high. The Townsend cell is free from this defect, and, moreover, works at high current densities and gives strong alkaline liquors. These, of course, contain much salt. In districts with moderately cheap power the two Billiter cells should find large application. The diaphragm cell furnishes results similar to those of the Townsend cell as far as current efficiency and concentration of alkali are concerned, whilst the voltage is much lower. The 'membrane' cell gives a somewhat weaker alkali, but at a still better energy efficiency. Its low voltage closely approximates to that of the Finlay cell. Both these cells unfortunately demand a large floor space, but need very little attention when working. The other cells described compare rather unfavourably with the above. Their energy efficiency is low or they make weak alkali,[1] and require constant attention during working.

The Chlorine Question.—The future of the electrolytic alkali industry depends essentially on fresh outlets being found for the chlorine.[2] The demand for bleaching powder is, as matters stand, actually decreasing. This is partly due to the growing number of small electrolytic bleaching liquor installations now in operation. Further, the methods of using bleaching powder solutions now generally employed are more rational and efficient than the old methods, and the consumption of bleach is consequently less. Many large pulp and paper works, moreover, now make their own bleach, often using cells such as the Macdonald cell.[3] Finally, the introduction of electrolytic alkali processes means the production of free chlorine where the Leblanc process gives HCl.

The discovery of fresh uses for chlorine is therefore imperative, and the following methods of utilisation, other than bleach production, may be mentioned[4]:

1. Combination with cathodic hydrogen to form HCl, which is

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[1] Or Na_2CO_3.

[2] See *e.g.* Askenasy, *Zeitsch. Elektrochem.* **17**, 675 (*1911*).

[3] See p. 380.

[4] See also *Chem. Ind.* **31**, 404 (*1908*).

readily carried out. This is chemically a step backward, but there are conditions under which it is a gain economically. And if a gas cell which would work at technical current densities could be designed, using the chlorine as soluble cathode, the hydrogen as soluble anode, the problem would be finally solved.[1]

2. Liquefaction of the chlorine. This is increasingly carried out in Germany and U.S.A., the chlorine being used by small customers. Its application in metallurgy has also been suggested.

3. Detinning. The Goldschmidt method of detinning tin-scrap by the action of dry chlorine will probably completely replace the electrolytic method[2] in the future, and should form a valuable outlet.

4. Production of substances used in the artificial dye and indigo industries. Such are $CH_2Cl \cdot COOH$ (*e.g.* the Badische Anilin und Soda Fabrik uses a large part of the chlorine from its Griesheim cells for this purpose), C_6H_5Cl, $C_6H_3(NO_2)_2Cl$, $C_6H_5CH_2Cl$, $C_6H_5CHCl_2$, etc.

5. Production of solvents such as CCl_4, S_2Cl_2, chlorides of ethylene and acetylene, etc. The Weston Chemical Co. utilises some of the Castner-Kellner Co.'s chlorine for this purpose, using the process of Askenasy and Mugdan.[3]

6. Other organic compounds, such as chloroform, chloral, etc.

Methods of utilising the hydrogen are also important. At present most of it is lost. But, besides the formation of HCl mentioned, there are other possibilities. Its use has been suggested (in the Griesheim cells which work at 80°) to reduce nitrobenzene to aniline, the nitrobenzene being simply fed into the cathode compartment, copper cathodes being employed. Some can be compressed and used for filling balloons and air-ships, or in the oxyhydrogen blowpipe. And it can be mixed with the producer gas and burnt in the gas-engines if the latter are used for power raising. Finally, two catalytic reactions must be mentioned, viz. the reduction of nitrogen by hydrogen to ammonia,[4] using osmium as a catalyst, and the reduction of unsaturated fatty acids and glycerides to the saturated products, the catalyst being reduced nickel. Both processes have lately attracted much interest. To avoid 'poisoning' of the catalyst a very pure gas is probably needed, and this pure gas electrolytic alkali-chlorine cells are particularly adapted to furnish.

Literature

Billiter. *Die elektrochemischen Verfahren der chemischen Gross-Industrie*, vol. ii.

Brochet. *La Soude Electrolytique.*

Lucion. *Elektrolytische Alkalichloridzerlegung mit flüssigen Metallkathoden.*

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[1] See p. 219.

[2] See p. 288.

[3] See *Zeitsch. Elektrochem.* **15**, 773 (*1909*).

[4] See p. 479.

CHAPTER XXII

OTHER ELECTROLYTIC PROCESSES

In this chapter will be discussed the technical electrolytic preparation of several less important substances not, so far, considered. We shall deal with

Hydrogen and oxygen.	Potassium ferricyanide.
White lead; chrome yellow etc.	Permanganates.
Bromine and bromates.	Perchlorates.
Bromoform and iodoform.	Persulphates.
Chromic acid.	Hydrogen peroxide.
Anthraquinone.	Hyposulphites.

Hydrogen and Oxygen.—Where one only of these gases is needed, its preparation by electrolysis is usually uneconomical. Hydrogen is produced in large quantities in electrolytic alkali works, and can be manufactured very cheaply from water-gas, whilst oxygen is best obtained by fractional distillation of liquid air. But where both gases are required, and particularly for the oxyhydrogen flame, used extensively in platinum working and in some kinds of lead burning, electrolysis is the most convenient method of preparation. Technical electrolysers employ solutions of either H_2SO_4 or of KOH or NaOH. In the first case they are constructed of lead, and of iron when using alkali. The voltage of each cell is composed of the reversible decomposition voltage (in this case 1·23 volts at room temperature), the oxygen and hydrogen overvoltages, and the voltage necessary to overcome the electrolytic resistance. The alkaline solutions used (10–25 per cent.) have a lower conductivity than the 20–30 per cent. H_2SO_4 employed. On the other hand, hydrogen and oxygen overvoltages at lead are considerably greater than at iron. So on the whole electrolysers using alkaline solutions have a lower working voltage than those using acid. The current efficiency invariably approaches 100 per cent. The purity of the gases is usually 97–99 per cent. *Distilled* water must be added to replace that electrolysed, otherwise the vessels will be ultimately attacked.

The only well-known electrolyser using H_2SO_4 is that of **Schoop.**[1] It consists of a cylindrical lead-lined vat, some feet high, containing a number of electrodes vertically placed. These electrodes (Fig. 97) take the form of long tubes, filled with fine lead wire to increase the active surface, and perforated round the bottom to allow entrance to electrolyte and current. Each electrode is surrounded by a cylindrical hood of non-conducting material, open underneath and perforated round the bottom for the passage of the current, but closed round the top of the electrode. This joint is further protected by a water-seal. The gas generated inside the hood streams out through the top of the tube. By regulating the taps and the level of the electrolyte in the outer vessel, the gases can be delivered at varying pressures. One such electrolyser may contain perhaps four oxygen and eight hydrogen electrodes connected in parallel, and will take 150–200 amperes at 3·3–3·6 volts. PbO_2 is continually formed at the anodes, and the oxygen usually contains ozone. A cubic metre of mixed gases requires about 5·9 K.W.H.

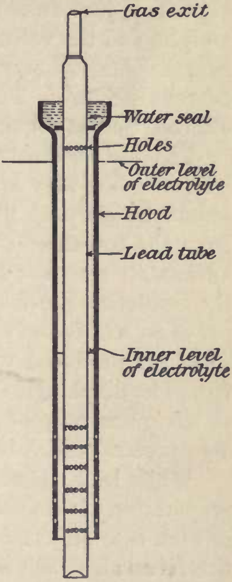

Fig. 97.—Schoop Electrolyser.

The **Schmidt**[2] (Oerlikon) electrolyser uses an alkaline electrolyte, and in construction resembles a filter-press and the Finlay alkali-chlorine cell, to which the reader is referred.[3] The electrodes are of iron, lightly corrugated; the diaphragms of asbestos, with rubber packing round the edges. Instead, however, as in the Finlay cell, connecting all like electrodes in parallel and passing through large currents at small voltage, the electrodes are *bipolar*, as in the series system of copper-refining and the Kellner bleaching-liquor electrolysers. A high voltage is impressed on the two end electrodes, and the same current passes through all the chambers. In the present case, shunt current losses[4] are very small. The current efficiency is practically 100 per cent., and the voltage per compartment in the latest form only about 2·3 volts. A cubic metre of mixed gases requires 3·7 K.W.H.

The **Garuti** apparatus is largely used in Europe. An inverted iron box is divided into a number of narrow compartments by vertical iron diaphragms,[5] and suspended in an outer wooden tank, lined with iron.

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[1] *Electrochem. Ind.* 1, 297 (*1903*).

[2] *Zeitsch. Elektrochem.* 7, 296 (*1900*).

[3] P. 380.

[4] Pp. 259, 327, 392.

[5] The lower half of the diaphragms can be perforated to allow of passage of electrolyte without fear of any mixing of gases.

The compartments are provided alternately with iron anodes and cathodes, connected in parallel and suitably insulated, and all anode and all cathode chambers are connected with their respective common gas reservoirs. The pressure at which the gases are evolved is readily regulated, just as in the Schoop apparatus. Strong KOH is the electrolyte, and the voltage is kept below 3·4 volts. If it exceeds this, the iron diaphragms may act as bipolar electrodes and give an explosive gaseous mixture. The normal figure is 2·5 volts, and a cubic metre of electrolytic gas requires 4·1 K.W.H.

The last electrolyser we will describe is that of **Schuckert.**[1] An iron trough of fifty litres capacity is divided into a number of compartments by vertical partitions of good insulating material, extending from the top three-quarters of the way down the cell. These contain alternately iron anodes and cathodes. Iron hoods suspended between the insulating partitions carry off the gases. The electrolyte is 15–20 per cent. KOH, and a unit of this size takes 600 amperes at 2·5–3 volts. The heat produced warms up the cell, which is well lagged, to about 70°. The diaphragms are stable, but the iron anodes, as in other alkaline electrolysers, must occasionally be renewed, owing to traces of chlorides, etc., present, which render them non-passive.

White lead : chrome yellow : lead peroxide : cuprous oxide.—The preparation of these four substances is considered together, as it depends in each case on the same principle, due to Luckow. Lorenz[2] showed that, if an alkali salt is electrolysed between cathode and a soluble anode, the cathodic alkali reacts with the salt dissolved at the anode to form hydroxide of the anode metal, of excellent quality, which can be readily washed free from adsorbed salts. The reason is that no excess of alkali is employed, the alkali and the anodic salt being produced in equivalent quantities. Thus, if Na_2SO_4 be the electrolyte, copper the anode, and the electrolysis be carried out at 90°, CuO is produced.

Suppose now the electrolyte is a salt whose anion forms an insoluble salt with the anodic metal—*e.g.* Na_2SO_4 and lead. Then, on electrolysis, $Pb^{\cdot\cdot}$ ions will dissolve, and $PbSO_4$ will be precipitated—but in the form of a dense adherent layer on the anode. If now the electrolyte contains only a small proportion of Na_2SO_4, the great mass of dissolved salt (*e.g.* $NaClO_3$) giving no precipitate with solutions containing lead, then on passing a current $PbSO_4$ will still be formed as before, but no longer as adherent anodic crusts. The surface of the metal will remain perfectly clean and metallic, the $PbSO_4$ streaming away from it as a fine precipitate. The reason is that, when the small number of SO_4'' ions in the neighbourhood of the anode are removed as $PbSO_4$, others can only be

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[1] *Electrochem. Ind.* **1**, 579 (*1903*). *Elektrochem. Zeitsch.* **14**, 230, 248 (*1908*).

[2] *Zeitsch. Anorg. Chem.* **12**, 436 (*1896*).

furnished by diffusion or by ionic migration. As the greater part of the current is carried by the anion (ClO_3') which is present in excess, the SO_4'' ions are removed before they reach the anode by the excess of $Pb^{\cdot\cdot}$ ions streaming away, and the $PbSO_4$ is precipitated at a short distance from the electrode, a distance increasing if the concentration of the 'precipitating' ion is reduced.

Luckow worked out similar methods for the preparation of many insoluble salts, including those mentioned at the beginning of the section. For white lead[1] he recommended a 1·5 per cent. solution of a mixture of 9 parts $NaClO_3$: 1 part Na_2CO_3, electrolysed between a pure lead anode and a hard lead cathode, CO_2 being passed in as required. The anodic current density was about 0·24 amp./dm.², the bath voltage being 1·4 volts. He obtained 3·5–4 kilos. white lead per K.W.H. For chrome yellow ($PbCrO_4$) the same conditions and the same electrolyte were employed, with the exception of the substitution of Na_2CO_3 by Na_2CrO_4, chromic acid being constantly added to replace that removed in the precipitate. The electrolyte for PbO_2 was a 1·5 per cent. solution of a mixture of 99·5 parts Na_2SO_4 + 0·5 part $NaClO_3$, slightly acidified with H_2SO_4. 2·8 volts were required. Cu_2O requires copper electrodes and an electrolyte of NaCl,[2] with a small quantity of alkali.

Of these substances the author believes that small quantities of Cu_2O and white lead only are now technically prepared. For the latter substance the temperature is kept below 50°, and the bath requires about two volts. Instead of leading in pure CO_2, a gas diluted with air is employed, as it gives a precipitate of the required basicity. Unfortunately, a pigment with the great 'covering power' of Dutch process white lead has not yet been prepared.

The Luckow processes have been studied by Le Blanc and Binschnedler,[3] Isenburg,[4] Burgess and Hambuechen,[5] Miller,[6] and Gillett.[7] The necessity has been shown of employing very low concentrations of the precipitating salt and low current densities if precipitates, and not crusts, are to result. At the same time, as would be expected, and as work on Cu_2O actually showed, the precipitated particles are finer the higher the concentration and the greater the current density—*i.e.* the more quickly the precipitate is formed. These two opposing sets of conditions render it impossible to produce particles beyond a certain degree of fineness, which explains why electrolytic white lead has not been an unqualified success, as 'covering power' and fineness of division are intimately connected.

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[1] *Zeitsch. Elektrochem.* **9**, 797 (*1903*).

[2] In which copper dissolves anodically as $Cu^{\cdot}$ ions.

[3] *Zeitsch. Elektrochem.* **8**, 255 (*1902*).

[4] *Zeitsch. Elektrochem.* **9**, 275 (*1903*).

[5] *Trans. Amer. Electrochem. Soc.* **3**, 299 (*1903*).

[6] *Jour. Phys. Chem.* **13**, 256 (*1909*).

[7] *Jour. Phys. Chem.* **13**, 332 (*1909*).

Bromine and Bromates.—The chief sources of the world's bromine are the Stassfurt salt deposits in Europe and certain brine deposits in America. The residual liquors obtained from these contain small quantities of bromine as $MgBr_2$. This bromine is usually recovered by means of chlorine, but electrolysis is sometimes employed. Bromates are readily prepared by electrolysing alkaline bromide solutions, and find some small application as oxidising agents, etc.

The electrolysis of alkaline bromides has been thoroughly studied by Pauli,[1] Kretzschmar,[2] Boericke,[3] and Foerster and Yamasaki.[4] The value of $E.P._{\frac{1}{2}Br_2 \longrightarrow Br'}$ is $+ 1{\cdot}098$ volts at 25°. If a neutral alkaline bromide solution be electrolysed with a platinised platinum anode free from oxygen, Br′ discharge takes place reversibly as soon as this potential value is exceeded. Traces of oxygen are simultaneously produced (the *reversible* OH′ discharge potential in a neutral solution is $+ 0{\cdot}82$ volt). This oxygen dissolves in the anode, perhaps forming some platinum oxide, and renders the Br′ discharge irreversible, a small and increasing overvoltage being now necessary. In alkaline solution, in spite of the depolarisation of the bromine discharge effected by the OH′ ions, the formation of anodic oxygen is so facilitated that the condition of the electrode is quickly altered, a considerable overvoltage being associated with Br′ discharge. With smooth platinum, oxygen is immediately evolved, and in turn brings the bromine overvoltage into play, an excess polarisation of about 0·33 volt in neutral solution being finally required.

The anodically produced bromine is, like chlorine, partly hydrolysed as follows: $Br_2 + H_2O \rightleftarrows HBrO + H^{\cdot} + Br'$, but much less than was the case with chlorine.[5] If now the cathodic OH′ ions are kept separated from the bromine by a diaphragm or other means, the bromine can be continuously produced and finally distilled off. If, however, the OH′ ions gain access to the anode, the above hydrolysis, now better written

$$Br_2 + OH' \rightleftarrows Br' + HBrO,$$

continues, and excess of OH′ ions will lead to the neutralisation of the HBrO thus :—

$$HBrO + OH' \rightleftarrows H_2O + BrO'.$$

Still the hydrolysis of the bromine and the neutralisation of the acid are both very incomplete, HBrO and bromine existing side by side in the same solution with OH′ ions. ClO_3' formation was shown[6] to take

[1] *Zeitsch. Elektrochem.* **3**, 474 (*1897*).
[2] *Zeitsch. Elektrochem.* **10**, 802 (*1904*).
[3] *Zeitsch. Elektrochem.* **11**, 57 (*1905*).
[4] *Zeitsch. Elektrochem.* **16**, 321 (*1910*).
[5] Cf. page 319.
[6] Pp. 320, 323.

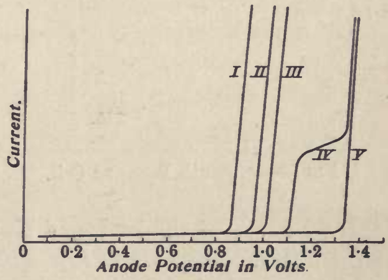
place in two ways—in alkaline solution by ClO′ discharge (primary formation), and in acid solution by the chemical interaction of HClO and ClO′ ions (secondary formation).

In the present case the production of bromates under both conditions results from a secondary reaction. In acid or neutral solution the equation is similar to that with chlorates—

$$2HBrO + BrO' \longrightarrow BrO_3' + 2H^{\cdot} + 2Br'.$$

This reaction[1] proceeds 100 times more quickly than the corresponding chlorate reaction, and anodic bromate formation consequently takes place in slightly acid solution with great ease, giving a very high yield, particularly at higher temperatures. In alkaline solution the formation of bromates is the result of direct oxidation of BrO′ ions by anodic oxygen—$BrO' + 2O \longrightarrow BrO_3'$. But, as this reaction proceeds more slowly than the first, there are consequently oxygen losses, and, the voltage being also higher, the method is not used.

The crude bromide liquors contain large quantities of $MgCl_2$ and, in America, NaCl. The ratio $\frac{[Br]}{[Cl]}$ varies between $\frac{0{\cdot}05}{1}$ and $\frac{0{\cdot}006}{1}$. Fig. 98 contains current anode-potential curves taken by Bose[2] in 0·965 *n.* HCl containing varying amounts of KBr. The first three curves rise sharply, corresponding to Br′ discharge. Curve IV shows an initial rise (Br′ discharge), then a horizontal part, followed by a second rise, which corresponds to Cl′ discharge. Curve V is practically that of HCl, the influence of the bromide being imperceptible. Using these results, we conclude that solutions with a ratio $\frac{[Br]}{[Cl]} > 0{\cdot}01$ will give only bromine on anodic polarisation, whilst solutions with a ratio $\frac{[Br]}{[Cl]}$ of 0·001 will furnish pure bromine at low current densities. There is consequently no fear of chlorine being liberated under technical conditions if the anodic current density be kept fairly low.



KBr successively 1·0,0·1,0·01,0·001,0·0001 normal.

FIG. 98.

Of technical bromine cells, we may first briefly describe that of **Wünsche,** formerly worked at Westeregeln. A unit consisted of a rectangular cement bath, through the cover of which entered the electrodes. The cathodes were enclosed in cylindrical clay diaphragm cells. They

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[1] See p. 320.

[2] *Zeitsch. Elektrochem.* 5, 159 (*1899*).

were originally carbon tubes, connected with a system of channels embedded in the cover of the bath. The electrolyte flowed from cell to cell through these channels, entering each cell through the cathode. Later, copper cathodes were used, two for each cell, the electrolyte being forced to flow past both of them by means of a vertical wooden partition dividing the cell into two parts. The anodes were of carbon, cemented into the roof of the bath. The electrodes were connected in parallel. The liquors, heated to 80°, flowed through the anode compartment, were charged with bromine, and passed out. After being suitably freed from bromine, they entered the cathode system. There they became charged with $Mg(HO)_2$. This mostly remained dissolved, owing to the high content of $MgCl_2$. The current density, however, had to be kept low, and the liquors were very rapidly circulated. Using a current density (at both electrodes) of 1·15 amps./dm.^{2} and 3·4 volts, the yield of pure redistilled bromine corresponded to a current efficiency of 68–70 per cent. The material losses were small.

The process was eventually abandoned on account of its complications (clay cells, etc.) and because the separation of magnesia inside the cathode compartments could not be entirely avoided. The only process now working in Europe is that of **Kossuth.** His apparatus is essentially simpler, which accounts for its success. Fig. 99 shows the electrolyser in plan. A long open cement trough contains a number of parallel vertical carbon plates resting on the bottom of the bath and rising some distance above the level of the liquid. They are so arranged that the electrolyte, which flows rapidly through, is forced to take a zigzag path, passing between the whole series of plates. These plates are bipolar electrodes, the two end ones being connected to the source of current. During its passage through the electrolyser the liquor is charged with bromine and magnesia. The latter is largely precipitated, and under those conditions does not readily react with the bromine. The temperature is about 60°.

FIG 99—Kossuth Bromine Cell.

Using 100 amperes and 3–3·5 volts between each pair of plates, corresponding to about 100 volts for a cell containing thirty electrodes, a mean current efficiency of 40 per cent. is obtained. The losses as hypobromite and bromate do not exceed 2–4 per cent., but much bromine is reduced back again to Br′ ions at the cathodes, and the shunt current losses are considerable. Some 2·7–3·0 K.W.H. are necessary per kilo. of bromine. In spite of the low current efficiency, the simplicity of the Kossuth cell and the ease with which it can be cleaned have led to its being preferred over forms employing diaphragms.

Of the important **Dow** cell, used in U.S.A., nothing is generally known beyond the fact that diaphragms are used. This is necessary because of the high NaCl content of the electrolyte, which would otherwise lead to a considerable bromate formation.

Bromates.—Of the actual technical preparation of bromates nothing is known. The best conditions are undoubtedly the electrolysis at 40°–50° of a fairly strong bromide solution containing perhaps 2 $\frac{\text{grams}}{\text{litre}}$ $K_2Cr_2O_7$. This imparts the acidity necessary for a rapid production of bromate according to the equation $2HBrO + BrO' \longrightarrow BrO_3' + 2H^{\cdot} + 2Br'$, and provides the cathode membrane which prevents the reduction of hypobromite and bromate.[1] As anode, smooth platinum must be used. Carbon or platinised platinum would tend to disintegrate owing to the crystallisation of the sparingly soluble bromates. As cathode, graphite can be employed. Working with an anodic current density of 10–15 amps./dm.^{2}, the current efficiency should be nearly 100 per cent.

Bromoform and Iodoform.—These substances, bromoform slightly, iodoform largely used in medicine, can be chemically prepared by the interaction of alkali and either alcohol or acetone, with bromine or iodine respectively. Thus iodoform is readily made by adding iodine at 60°–70° to an aqueous alcohol solution containing some Na_2CO_3. The equation is

$$CH_3.CH_2.OH + 8Na_2CO_3 + 5I_2 + 2H_2O \longrightarrow CHI_3 + 9NaHCO_3 + 7NaI.$$

Only 30 per cent. of the iodine, however, appears as iodoform, the greater part being converted into NaI. If now the iodine be anodically produced in the system itself as needed, the losses of this expensive substance are avoided, whilst the method of preparation is simpler and the product purer. Electrochemical methods are now almost exclusively used for producing these substances.

If a solution of an alkaline iodide or bromide containing a little alkali and some alcohol or acetone be electrolysed, the first step is the liberation of hydrogen and alkali at the cathode and of halogen at the anode. The halogen is immediately partially hydrolysed, giving hypohalogenous acid and some alkaline hypohalogenite.

$$R_2 + Na_2CO_3 + H_2O \longrightarrow HRO + NaR + NaHCO_3$$
$$HRO + Na_2CO_3 \longrightarrow NaRO + NaHCO_3.$$

But in both cases a considerable proportion (greater with iodine) of the free halogen remains unattacked. The next step is the substitution of the hydrogen of the organic substance by the free halogen.

$$CH_3.CH_2.OH + 3R_2 \longrightarrow CR_3.CH_2.OH + 3HR$$
$$CH_3.CO.CH_3 + 3R_2 \longrightarrow CR_3.CO.CH_3 + 3HR.$$

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[1] Cf. p. 322. ClO_3' ions are *not* cathodically reduced, except at iron.

These derivatives then react further. With alcohol[1] the hypohalogenous acid present causes further oxidation, with acetone there is simply a hydrolysis.

$$CR_3.CH_2.OH. + 2HRO \longrightarrow CHR_3 + 2HR + CO_2 + H_2O$$
$$CR_3.CO.CH_3 + H_2O \longrightarrow CHR_3 + CH_3.CO.OH.$$

The various acids formed are neutralised by the excess of alkali present. Summing up all these reactions, including the first electrolysis, we obtain—

$$CH_3.CH_2.OH + 3NaR \longrightarrow Na_2CO_3 + CHR_3 + NaOH + 5H_2 + 3H_2O$$
$$CH_3.CO.CH_3 + 3NaR \longrightarrow CH_3.CO.ONa + 2NaOH + CHR_3 + 3H_2. + 3H_2O$$

Using alcohol, five molecules, using acetone, three molecules of hydrogen are liberated, corresponding to the passage of ten and six faradays respectively. The greater consumption with alcohol is due to the necessity of liberating halogen to effect (indirectly) the oxidation of part of the molecule to CO_2. In both cases alkali is eventually produced, more being formed using acetone. Certain by-reactions diminish the current efficiency in practice. There is cathodic reduction of hypohalogenous acid and of free halogen; also the reaction $2HRO + RO' \longrightarrow RO_3' + 2H^{\cdot} + 2R'$ is liable to occur. The former loss can be reduced by employing a suitable diaphragm, the latter by suitably regulating the alkalinity of the solution. Excess of either alkali or acid favours the formation of bromate or iodate.

Bromoform is best prepared according to Müller and Loebe.[2] They employ a solution containing 55 grs. KBr, 20 c.c. acetone, and 0·3 gr. K_2CrO_4 (to prevent cathodic reduction) in 140 c.c. of water. No alkali needs to be added; indeed a strong CO_2 stream must be continually passed in. Working at 25° with an anodic current density of about 0·07 amps./cm.^{2} at a smooth platinum anode and without a diaphragm, a 90 per cent. current efficiency is obtained. The losses are due to cathodic reduction, oxidation of acetone, bromate formation, and, to a slight extent, oxygen liberation.

For **iodoform,** either alcohol or acetone can be employed. The former is better in spite of the smaller yield per coulomb, as the method is simpler. Working with acetone (B.P. 56°) at the favourable temperature of 60°–70° is difficult, and the large quantity of alkali liberated is also a complication. Further, the reaction does not proceed as smoothly as with alcohol. To avoid cathodic reduction, Elbs and Herz[3] used a diaphragm, but the best and simplest way of preparing iodoform from

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[1] If R is bromine, the reaction with alcohol does not proceed smoothly.

[2] *Zeitsch. Elektrochem.* **10,** 409 (*1904*).

[3] *Zeitsch. Elektrochem.* **4,** 113 (*1897*).

alcohol was worked out by Foerster and Meves.[1] They employ an electrolyte containing per litre 50 grams Na_2CO_3, 170 grams KI, and 100 grams 96 per cent. alcohol. The anode is smooth platinum, the cathode lead, surrounded by a simple diaphragm of parchment paper. Working at 60°–70° with an anodic current density of 1–2 amps./dm.^{2} and a voltage of 2–2·5 volts, about 1·32 $\frac{\text{grams}}{\text{amp. hr.}}$ CHI_3 can be produced, corresponding to a current efficiency of 90 per cent. The losses are due to iodate formation and cathodic reduction. The beautifully crystalline product, when washed, is very pure. Fresh alcohol and KI must be continually added, and the alkalinity regulated by a slow stream of CO_2. The $(Na_2CO_3 + K_2CO_3)$ content of the bath must also be kept at the right value.

The electrolytic production of iodoform from acetone has been studied by Abbott,[2] Teeple,[3] and Roush.[4] Abbott, working at 75°, added the acetone in small quantities at a time, and obtained a current efficiency of 60 per cent. Teeple worked at room temperature and obtained good current efficiencies. But he neutralised the liberated alkali with iodine instead of acid. His method was therefore partly chemical, partly electrochemical. Roush obtained satisfactory results by using two cathodes, one enclosed in a diaphragm cell, and thus regulating the amount of alkali which mixed with the main electrolyte. But all these methods introduce complications, and the use of alcohol is preferable.

Anthraquinone and the Regeneration of Chromic Acid.—The oxidation of anthracene to anthraquinone, the basis of alizarin, is often carried out electrochemically. If anthracene be suspended in H_2SO_4 and the mixture used as anolyte, employing a platinum anode, a certain amount of oxidation occurs, but accompanied by much liberation of oxygen and by a high anode potential. The depolarisation of the oxygen discharge by the anthracene is slow. To render it rapid, a catalyst must be added. Two are employed, ceric sulphate $[Ce(SO_4)_2]$ and chromic acid, their mode of action being perfectly simple. They oxidise the anthracene directly and smoothly to anthraquinone—

$$C_{14}H_{10} + 3O \longrightarrow C_{14}H_8O_2 + H_2O,$$

being reduced in the process to $Ce_2(SO_4)_3$ or $Cr_2(SO_4)_3$ respectively. By the anodic action of the current, the original oxidising salts are regenerated, and the reaction proceeds.

Both furnish an equally good product, but there is one difference. $Ce(SO_4)_2$ oxidises far more quickly than $H_2Cr_2O_7$. The anthracene can

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[1] *Zeitsch. Elektrochem.* **4**, 268 (*1897*).
[2] *Jour. Phys. Chem.* **7**, 84 (*1903*).
[3] *Jour. Amer. Chem. Soc.* **26**, 170 (*1904*).
[4] *Trans. Amer. Electrochem. Soc.* **8**, 281 (*1905*).

be directly added to the electrolyser in which the $Ce(SO_4)_2$ is regenerated. The oxidation is so rapid that, as long as anthracene is present, there is no possibility of $Ce(SO_4)_2$ being *cathodically* reduced to $Ce_2(SO_4)_3$, thus causing current losses. (No diaphragm is used.) $H_2Cr_2O_7$, on the other hand, reacts much less quickly. The oxidation must be carried out in a suitable vat, the spent liquors drawn off, electrolytically regenerated elsewhere, and returned to the oxidising vessel.

The $Ce(SO_4)_2$ process is carried out by the Farbwerke vorm. Meister, Lucius und Brüning, according to a patent of Moest. The electrolyser is a lead-lined vessel which acts as anode, the electrolyte 20 per cent. H_2SO_4 with 2 per cent. $Ce(SO_4)_2$. The temperature is raised from 70° to 100° during the operation, and the liquors are well agitated. Using an anodic current density of 5 amps./dm.^{2} and 2·8–3·5 volts, the current efficiency is practically 100 per cent., the product being very pure. $Ce(SO_4)_2$ is yellow, $Ce_2(SO_4)_3$ colourless. The rapidity of depolarisation may be gauged from the fact that the liquors remain colourless till the finish of the oxidation, which is indeed announced by this change. Fontana and Perkin[1] have studied this reaction (experimenting also with chromium and manganese salts as catalytes). They showed that the use of a diaphragm makes little difference. Using an anodic current density 1 amp./dm.^{2} at 70°–80° and 2·5–3·5 volts, they obtained an 80 per cent. current efficiency.

The electrolytic regeneration of $H_2Cr_2O_7$ has received much attention. Darmstädter wished to add the anthracene directly to the electrolyser, as is the case with $Ce(SO_4)_2$, but, as Le Blanc pointed out, cathodic reduction would cause considerable current losses. According to the Farbwerke Höchst patent, the best solution for the oxidation contains 100 $\frac{\text{grams}}{\text{litre}}$ Cr_2O_3 and 350 $\frac{\text{grams}}{\text{litre}}$ H_2SO_4, and a current density at the lead anode of 3 amps./dm.^{2} is recommended. Regelsberger[2] showed that this anode really functions as a PbO_2 anode. An oxidation current efficiency of about 100 per cent. can be obtained with it, whereas no oxidation takes place at platinum.

Le Blanc[3] studied the subject thoroughly, employing the diaphragm described on p. 155 and working according to the conditions used by the Höchst dye-works. At 50° and using 3·5 volts, the current efficiency was 70–90 per cent. The equation involved in the oxidation of anthracene by $H_2Cr_2O_7$ and in the anodic electrolytic regeneration of the latter is

$$H_2Cr_2O_7 + 3H_2SO_4 = Cr_2(SO_4)_3 + 4H_2O + 3O.$$

the oxygen being in the one case given up to the anthracene, in the

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[1] *Electrochem. Ind.* 2, 249 (*1904*).

[2] *Zeitsch. Elektrochem.* 6, 308 (*1900*).

[3] *Zeitsch. Elektrochem.* 7, 290 (*1900*).

other produced electrolytically. A complete cycle therefore leaves the H_2SO_4 content of the solution unaffected. But during the electrolysis SO_4'' ions wander continuously from the catholyte to the anolyte, increasing the acidity. If therefore, using H_2SO_4 as catholyte, as Le Blanc first did, the same solution is continually used and regenerated anodically, its H_2SO_4 content will gradually rise until it is useless. To avoid this, Le Blanc employed the spent liquor itself as catholyte, causing it to circulate through the cell from cathode through diaphragm to anode. By suitably adjusting the rate of flow, a continuous regeneration takes place, undisturbed by H_2SO_4 concentration changes.

Le Blanc later introduced a technical apparatus similar to the bell-jar alkali-chlorine cell,[1] thus dispensing with the diaphragm. The spent liquors flow downwards through the cathode compartment (the inside of the belljar) and into the outer vessel, containing the anodes. A suitable rate of flow leads to the formation of an unalterable middle layer in the belljar. The current efficiency is 85 per cent., 87·5 per cent. of the total dissolved chromium leaving the anode chamber as $H_2Cr_2O_7$. The anodic current density is high, and the process cheap and effective.

Müller and Soller[2] have investigated the behaviour of the PbO_2 electrode, and shown it to act catalytically, as in the oxidation of HIO_3 to HIO_4.[3] There is no question of an overvoltage effect, as the potential of a platinum anode under the same conditions (when no oxidation takes place) is more positive than that of the PbO_2 electrode. But whilst the potentials of the Pt and PbO_2 electrodes in H_2SO_4 alone are very similar, that of the PbO_2 electrode is lowered on the addition of $Cr^{\cdot\cdot\cdot}$ ions owing to their depolarising action, and that of the Pt electrode is raised. The following table contains some of their figures ($\theta = 20°$). This behaviour is closely connected with the powerful chemical oxidising action of PbO_2 in the same case. The influences of current density, temperature, and concentration were also investigated.

TABLE LX

Current density	Platinum anode		PbO_2 anode	
	N. H_2SO_4	N . H_2SO_4 + 36·1 $\frac{\text{grams}}{\text{litre}}$ Cr_2O_3	N . H_2SO_4	N . H_2SO_4 + 36·1 $\frac{\text{grams}}{\text{litre}}$ Cr_2O_3
Amp./cm.^{2}	Volts	Volts	Volts	Volts
0·0046	+ 1·997	+ 2·003	+ 1·985	+ 1·758
0·023	2·027	2·104	2·064	1·974
0·046	2·065	2·208	2·129	2·052

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[1] P. 371.

[2] *Zeitsch. Elektrochem.* 11, 863 (*1905*).

[3] P. 146.

Schmiedt[1] has also studied the subject, particularly investigating the effect of various addition agents on the oxidation, several of which are used technically. He found, for example:

TABLE LXI

Addition	Current efficiency At start Per cent.	 At finish Per cent.
—	82·2	71·3
1 per cent. KF	93·4	86·2
0·1 per cent. KF	92·8	73·9
1 per cent. Na_2HPO_4	98·2	82·8

Small quantities of boric acid, KCN, and sodium vanadate and molybdate also had marked effects. The mechanism of their action is not understood.[2]

Potassium Ferricyanide.—This salt, previously chemically prepared by passing chlorine into K_4FeCy_6, the reaction being $2K_4FeCy_6 + Cl_2 \longrightarrow 2\,K_3FeCy_6 + 2KCl$, is now almost exclusively made by electrolytic oxidation. The net result of the anodic reaction is simply

$$FeCy_6'''' \longrightarrow FeCy_6''' + \ominus.$$

Whether it actually proceeds thus or by the intermediate action of discharged oxygen is uncertain. At the cathode alkali and hydrogen are produced. The total reaction is therefore

$$2K_4FeCy_6 + 2H_2O \longrightarrow 2K_3FeCy_6 + 2KOH + H_2.$$

The electrolysis has been studied by v. Hayek.[3] Working at room temperature with a well-agitated, saturated, slightly alkaline K_4FeCy_6 solution, and a current density 0·3 amp./dm.², he could reduce the K_4FeCy_6 concentration from 20 per cent. to 1·7 per cent. with a 100 per cent. current efficiency. The last fractions were also readily oxidised, and the K_3FeCy_6 separated by crystallisation.

Potassium Permanganate.—This important salt is prepared from potassium manganate, K_2MnO_4, made in its turn by fusing together MnO_2 and potash in presence of air, the reaction being

$$MnO_2 + 2KOH + \tfrac{1}{2}O_2 \longrightarrow K_2MnO_4 + H_2O.$$

The chemical method formerly used for the further transformation into permanganate consisted in leading in CO_2 into the dissolved melt. K_2CO_3 and $KMnO_4$ resulted, and MnO_2 was precipitated

$$3K_2MnO_4 + 2CO_2 \longrightarrow 2K_2CO_3 + 2KMnO_4 + MnO_2$$

We see that one-third of the MnO_2 originally used had to be worked up again, and, more important still, that two-thirds of the alkali originally used were converted into carbonate.

These losses are now avoided by electrolytically oxidising between

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[1] *Dissertation* (Charlottenburg, *1909*).

[2] Cf. p. 146.

[3] *Zeitsch. Anorg. Chem.* **39**, 240 (*1904*).

iron or nickel electrodes. As catholyte, alkali is used, which becomes stronger during the electrolysis. The anolyte consists of the alkaline solution obtained by lixiviating the original melt. Its alkali content also increases, owing to OH′ migration from the catholyte, and if the original manganate concentration was sufficiently high, the permanganate finally crystallises from the strongly alkaline liquors. The equation for the electrolysis is

$$2K_2MnO_4 + 2H_2O \longrightarrow 2KMnO_4 + 2KOH + H_2.$$

There is no trouble with MnO_2, and *caustic* alkali is formed, which is evaporated down, and used for the next fusion.

Two types of processes are used. In one there is no diaphragm, and the light catholyte rests on top of the heavy anolyte. As $K^{\cdot}$ ions are the only ones which migrate from anolyte to catholyte, there is no danger of mixing from that reason, whilst the diffusion of the manganese salts upwards is more than neutralised by MnO_4'' and MnO_4' migration downwards. There is, however, some loss owing to oxygen liberated at the anode carrying permanganate with it up to the cathode, where reduction ensues. Also the catholyte must continually be diluted to maintain the density difference.

This process has been studied by Askenasy and Klonowski.[1] Their electrolyser was a cylinder, the electrodes iron. Using an electrolyte containing about 88 $\frac{\text{grams}}{\text{litre}}$ K_2MnO_4, and working at 60° with 2·8–2·9 volts, they obtained with anodic current densities of 8·5–13 amps./dm.^{2} the following relations between current efficiency and percentage of manganate oxidised.

Percentage oxidised Per cent.	Current efficiency Per cent.
70–75 (maximum)	24
50	50
48	64
27	67

For technical work they recommend a current density of 8·5 amps./dm.^{2} at the anode (a containing vessel of iron), that at the cathode being ten times as great. Using 2·8 volts, about 0·7 K.W.H. would be required per kilo. $KMnO_4$. This corresponds to a 67 per cent. current efficiency, which in turn denotes an oxidation of only about one-third of the manganate.

The second type of process employs a diaphragm of cement or some other suitable alkali-resistive material. It has been studied by Askenasy and Klonowski,[2] also by Brand and Ramsbottom.[3] The former investigators used, as before, sheet-iron electrodes, the latter

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[1] *Zeitsch. Elektrochem.* **16**, 170 (*1910*).

[2] *Loc. cit.*

[3] *Jour. Prakt. Chem.* **82**, 336 (*1910*).

electrodes of iron and nickel gauze. The following Table (LXII) contains some of the results given by iron electrodes.

TABLE LXII

Composition of anolyte $\frac{\text{grams}}{\text{litre}}$	θ	Voltage	Anodic current density	Per cent. oxidised	Current efficiency	Observers	Remarks
76·45 K_2MnO_4 50KOH	60°	7 volts	0·152 amp./cm.^{2}	61·5	57	A.K.	Anolyte not stirred
Do.	do.	6·5	0·083	68·4	60	do.	do.
Do.	do.	do.	do.	81·5	36	do.	do.
Do.	do.	5	0·11–0·0275	70–75	55	do.	Anolyte stirred
58K_2MnO_4 55KOH,	18°–20°	4·02–4·62	0·02	100	36·8	B.R.	do.
Do.	do.	3·23–3·48	0·0125	100	57·7	do.	do.
Do.	do.	2·47–2·52	0·005	100	76·3	do.	do.

Askenasy and Klonowski also worked with lower manganate concentrations, which gave worse results, and at 25°, which made little difference.

It will be noticed that the current efficiencies obtained by Brand and Ramsbottom were much better, and their voltages lower, in spite of the lower temperature. The reasons were undoubtedly the lower current densities employed, and the fact that the gauze anode permits far better circulation, and consequently lessens polarising effects. Table LXIII contains their figures for nickel anodes, which are seen to be even better.

TABLE LXIII

Anolyte grams per litre	θ	Anodic current density	Voltage	Per cent. oxidised	Current efficiency	Remarks
					Per cent.	
40K_2MnO_4 140KOH	18°–20°	0·0083–0·0208 amp./cm.^{2}	—	100	48–53	Electrolyte not stirred
Do.	do.	do.	—	80	100	Electrolyte stirred
Do.	do.	do.	—	100	86·6	do.
58K_2MnO_4 55KOH	do.	0·005	2·06–2·11	100	83·4	do.
Do.	do.	0·0125	2·77–2·87	100	72·6	do.
Do.	do.	0·02	3·60–4·56	100	55·2	do.

Better current efficiencies are obtained and lower voltages required than with iron. Stirring obviously has a great influence. Without it oxygen evolution commences at the beginning of the electrolysis. Brand and Ramsbottom believe that the oxidation does not simply proceed as follows:

$$MnO_4'' \longrightarrow MnO_4' + \ominus,$$

but that oxygen plays a part. The special influence of nickel is ascribed to the formation of a nickel superoxide on the electrode, which acts as an oxygen carrier, as PbO_2 perhaps does in the $H_2Cr_2O_7$ regeneration.[1]

They also followed the changes in the anode potential during the electrolysis. At nickel anodes the initial potential difference was about + 0·65 volt.[2] It rose slowly to + 0·7 volt, then rapidly, then slowly again, finally reaching + 1·1 volts. With iron, an initial figure of + 0·88, rising to + 0·93 volt, was observed. The first slow rise with the nickel is ascribed to concentration polarisation; the rapid rise accompanies the initial oxygen evolution, and the final slow rise corresponds to the usual overvoltage increase. With iron the first two stages do not appear. Oxygen is evolved from the start, as no oxide is formed which catalyses the oxidation of the manganate. The figures, in fact, correspond well with parallel experiments made with KOH solutions (no manganate), and with similar experiments of Foerster and Piguet.[3]

Brand and Ramsbottom finally showed that Na_2MnO_4 oxidises just as easily as K_2MnO_4. With a strongly-agitated solution, and a current density of 0·0125 amp./cm.² at a nickel anode, the current efficiency was 90 per cent.

Perchlorates.[4]—Of these salts, potassium and ammonium perchlorates are important, being used in the firework and explosives industries. The sodium and calcium salts are also prepared, but only as intermediate stages in the production of the first named.

The oxidation of the ClO_3' ion to the ClO_4' ion occurs readily and with high current efficiency if the anode potential is sufficiently high. It has been shown to take place in all probability as follows

$$\begin{aligned}
&(a) \quad 2ClO_3' \longrightarrow 2ClO_3 + 2\ominus;\\
&(b) \quad 2ClO_3 + H_2O \longrightarrow ClO_4' + ClO_2' + 2H^{\cdot} + \tfrac{1}{2}O_2;\\
&(c) \quad ClO_2' + \tfrac{1}{2}O_2 \longrightarrow ClO_3'.
\end{aligned}$$

ClO_3' ions are first discharged and decompose water, giving a mixture of $HClO_4$ and $HClO_2$ and liberating oxygen. (Concentrated $HClO_3$

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[1] Cf. pp. 133–134, 146, 152 (footnote), 397.

[2] Foerster has found the potential of the NiO_2 electrode in 2·8 *n*. KOH to be + 0·60 volt.

[3] *Zeitsch. Elektrochem.* **10**, 714 (*1904*).

[4] Winteler, *Zeitsch. Elektrochem.* **5**, 50, 217 (*1898*); **7**, 635 (*1901*); Oechsli, *Zeitsch. Elektrochem.* **9**, 807 (*1903*); Couleru, *Chem. Zeit.* **30**, 213 (*1906*).

breaks up similarly into $HClO_4$ and $HClO_2$.) The $HClO_2$ is then oxidised by the liberated oxygen to $HClO_3$, the total result being

$$ClO_3' + H_2O \longrightarrow ClO_4' + 2H^{\cdot} + 2\ominus.$$

Any direct OH′ discharge means a loss of current, the ClO_3' ions being unaffected by oxygen. The oxidation is therefore carried out in acid solution, in which OH′ discharge is difficult, and an electrode is used with a high oxygen overvoltage, such as smooth platinum. If this be platinised, or if the electrolyte contain a little free alkali, the current efficiency at once falls. Other circumstances favouring high overvoltage, and therefore good results, are high current density and low temperature. With these conditions fulfilled, the ClO_3' concentration in the electrolyte is of minor importance.

In practice a concentrated (perhaps 60–70 per cent.) slightly acid solution of the soluble $NaClO_3$ is electrolysed between smooth platinum anodes and iron cathodes. The temperature is kept below 10° by cooling coils. The electrodes may also be cooled. An anodic current density of about 8 amps./dm.^{2} is employed. Under these circumstances, with 6·5–7 volts on the bath, the total chlorate present can be oxidised at a mean current efficiency of 85 per cent. At the commencement it is 100 per cent., but falls throughout. Good circulation is necessary. The high voltage is due partly to the great resistance of the electrolyte at such a low temperature, and partly to the high anode potential. The oxygen evolved in the later stages contains much ozone. The production of one kilo. of $NaClO_4$ (from chlorate) needs

$$\frac{1000}{122} \cdot \frac{100}{85} \cdot \frac{96540 \times 2}{3600} \cdot \frac{6{\cdot}8}{1000} = 3{\cdot}5 \text{ K.W.H.}$$

As the sodium salt is deliquescent it is not worked up as such, but $KClO_4$ is precipitated by adding KCl. In this connection it is important for all the chlorate to have been oxidised; otherwise the precipitated $KClO_4$ will contain some $KClO_3$ dissolved in it as a solid solution, which cannot be removed by washing. NH_4ClO_4 is prepared similarly by adding NH_4Cl. According to Angeli it is also conveniently made by oxidising a strong $CaCl_2$ solution anodically until all is converted into perchlorate, adding NH_4Cl and subsequently evaporating.

Persulphates and Hydrogen Peroxide.—Persulphuric acid was discovered by Berthelot, and the solid salts first prepared by Marshall.[1] The formulæ given below show the close relationship between $H_2S_2O_8$, H_2O_2, and the interesting acid H_2SO_5 discovered by Caro.[2]

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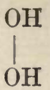
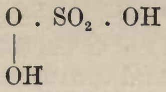
[1] *Trans. Chem. Soc.* **59,** 771 (*1891*).

[2] *Zeitsch. Angew. Chem.* **11,** 845 (*1898*).



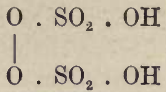
$$\begin{array}{c}\mathrm{OH}\\ |\\ \mathrm{OH}\end{array}$$

Hydrogen peroxide



$$\begin{array}{l}\mathrm{O\,.\,SO_2\,.\,OH}\\ |\\ \mathrm{OH}\end{array}$$

Caro's acid

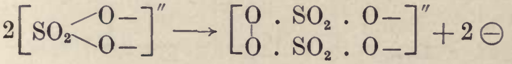


$$\begin{array}{l}\mathrm{O\,.\,SO_2\,.\,OH}\\ |\\ \mathrm{O\,.\,SO_2\,.\,OH}\end{array}$$

Persulphuric acid

Caro's acid and $H_2S_2O_8$ are respectively monosulphonated and disulphonated hydrogen peroxide, while if $H_2S_2O_8$ be hydrolysed the first product is H_2SO_5 and the second H_2O_2. The salts of $H_2S_2O_8$ are exclusively prepared by electrolysis, and extensively used as oxidising agents and in photography. H_2O_2, now prepared to an ever-increasing extent from $H_2S_2O_8$ or its salts, finds great application on account of its disinfectant, germicidal, oxidising, and bleaching qualities.

As in the oxidation of chlorates, the anodic process consists in the discharge of the anions—here SO_4'' ions.



$$2\left[\mathrm{SO_2}\begin{array}{l}\diagup \mathrm{O}-\\ \diagdown \mathrm{O}-\end{array}\right]'' \longrightarrow \left[\begin{array}{l}\mathrm{O\,.\,SO_2\,.\,O}-\\ \mathrm{O\,.\,SO_2\,.\,O}-\end{array}\right]'' + 2\ominus$$

To bring about this reaction, the same conditions are necessary as in preparing perchlorates—viz. low temperature, high current density at a smooth platinum anode, and an acid solution, or at least one free from alkali. All these circumstances render OH′ discharge difficult. The necessary anode potential is, however, higher than is the case with perchlorates. Oxygen is evolved from the start, and, of course, contains ozone. A low temperature is also necessary, on account of the tendency of persulphate solutions to decompose as follows:

$$R_2S_2O_8 + H_2O \longrightarrow R_2SO_4 + H_2SO_4 + \tfrac{1}{2}O_2.$$

The production of persulphates has been much studied.[1] Two methods can be employed, both designed to avoid cathodic reduction. A diaphragm can be used. In the anode compartment is, perhaps, a concentrated $(NH_4)_2SO_4$ solution, in the cathode compartment H_2SO_4 of medium strength. The electrolyte is well cooled by means of coils, as the temperature is best kept at about 15°. The anode is smooth platinum and the anodic current density high; the cathode can be lead and of a much larger surface. Crystalline $(NH_4)_2S_2O_8$, containing a few per cents. of $(NH_4)_2SO_4$ continually precipitates, whilst fresh $(NH_4)_2SO_4$ is continually added. The current efficiency exceeds 70 per cent. In the catholyte, hydrogen is evolved, and the total reaction is

$$(NH_4)_2SO_4 + H_2SO_4 \longrightarrow (NH_4)_2S_2O_8 + H_2.$$

It is simpler to use no diaphragm (Müller and Friedberger) and to add instead 0·2 per cent. K_2CrO_4 as in the chlorate process. Cathodic reduction is thereby sufficiently avoided. With smooth platinum electrodes and an anodic current density of 50 amps./dm.^{2}, the electrolyte being concentrated $(NH_4)_2SO_4$, the current efficiency is 70–80 per

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[1] Particularly see Elbs and Schönherr, *Zeitsch. Elektrochem.* 2, 245 (*1896*); Müller and Friedberger, *Zeitsch. Elektrochem.* 8, 230 (*1902*).

cent. and the voltage about 7 volts. Working thus, the solution becomes alkaline at the cathode, and if the OH′ ions reach the anode oxygen evolution, meaning increased current losses, will be facilitated. Hence acid must be continually added. This can be avoided by using, instead of $(NH_4)_2SO_4$, the soluble $KHSO_4$. $K_2S_2O_8$ is precipitated, and at the cathode hydrogen evolved without OH′ production. The total equation is

$$2KHSO_4 \longrightarrow K_2S_2O_8 + H_2.$$

The yield is not as good as when making $(NH_4)_2S_2O_8$. One kilo. of the $(NH_4)_2S_2O_8$ ~~latter salt~~ requires about 2·4 K.W.H.

It should be finally mentioned that, exactly as in the electrolytic regeneration of $H_2Cr_2O_7$, certain ions exert a markedly favourable catalytic influence on the oxidation. Particularly active are the Cl′ and F′ ions.[1]

Hydrogen Peroxide is technically prepared either from $H_2S_2O_8$ solutions or from solid $K_2S_2O_8$. The former method is used by the Consortium für elektrochemische Industrie,[2] the latter method is due to Pietzsch and Adolph.[3] In the former process, H_2SO_4 solutions (S.G. about 1·5), cooled by suitable coils and with the addition of some HCl or HF, are electrolysed without a diaphragm, using platinum electrodes at high current densities. An $H_2S_2O_8$ solution results at about 50 per cent. current efficiency,[4] containing up to 40 per cent. of the acid together with unoxidised H_2SO_4. This is distilled under reduced pressure. The $H_2S_2O_8$ is hydrolysed to H_2O_2, which distils off, and the residue, after cooling and diluting, is re-electrolysed. The losses as oxygen during the distillation are small, provided that no traces of platinum resulting from anodic attack during the electrolysis are present. Lately hollow cooled *anodes* have been used, instead of having the cooling coils in the electrolyte. The current efficiency is thereby considerably raised.

Pietzsch and Adolph gently heat or distil $K_2S_2O_8$ with 1·4 S.G. H_2SO_4, $KHSO_4$ and H_2O_2 resulting. The latter, after cooling, can be sucked off from the precipitated $KHSO_4$ (which is reoxidised electrolytically) or else distilled off at 80°; 20–30 per cent. solutions result directly, and the distillation apparatus is small for its output. The loss as oxygen is very low, whilst $K_2S_2O_8$ can be prepared with a better current efficiency than $H_2S_2O_8$.

Hyposulphites.—Up to now these very valuable reducing agents, of which $Na_2S_2O_4$ is the most used, have been prepared by the chemical reduction of $NaHSO_3$ solutions by metallic zinc ($4NaHSO_3 + Zn \longrightarrow Na_2S_2O_4 + Na_2SO_3 + ZnSO_3 + 2H_2O$). Electrolytic methods have achieved little success,[5] owing to incomplete understanding of the

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[1] See p. 146.

[2] D.R.P. 217538, 217539 (*1905*); E.P. 23548 (*1910*).

[3] E.P. 23158, 23660 (*1910*).

[4] See also *Zeitsch. Elektrochem.* **1**, 417 (*1895*).

[5] *Zeitsch. Elektrochem.* **10**, 361, 450 (*1904*).

processes and factors involved. The subject has been lately thoroughly studied by Jellinek.[1] His work has put the matter on a different footing, and it is highly probable that a technical electrolytic method will be shortly introduced.

Consider a solution containing bisulphite and hyposulphite ions. The ions HSO_3' are in equilibrium with small quantities of the ion S_2O_5'',

$$2HSO_3' \rightleftarrows S_2O_5'' + H_2O$$

and S_2O_4'' formation perhaps actually takes place through the intermediation of these ions.

$$S_2O_5'' + 2H^{\cdot} \longrightarrow S_2O_4'' + H_2O + 2\oplus.$$

But the relations are rendered clearer if we use the equation

$$2HSO_3' + 2H^{\cdot} \longrightarrow S_2O_4'' + 2H_2O + 2\oplus.$$

The potential of an indifferent electrode in a solution containing these ions is given by the equation

$$\mathcal{E} = \text{E.P.} + 0{\cdot}029 \log \frac{[H^{\cdot}]^2[HSO_3']^2}{[S_2O_4'']}$$

and Jellinek has shown E.P. to be $-0{\cdot}009$ volt. A solution in which $[HSO_3'] = [S_2O_4''] = 1$ will have $[H^{\cdot}] = \text{circ.}\ \sqrt{5}\,.\,10^{-3}$, and we calculate the electrode potential under these circumstances to be $-0{\cdot}163$ volt. As the reversible potential of a hydrogen electrode under these conditions is about $-0{\cdot}157$ volt, such a solution would decompose spontaneously according to the equation

$$Na_2S_2O_4 + 2H_2O \longrightarrow 2NaHSO_3 + H_2$$

if the hydrogen were given an opportunity of being evolved. Further, the reverse process—*i.e.* cathodic HSO_3' reduction at a platinised platinum cathode—would be impossible, as the reaction $H^{\cdot} \longrightarrow \frac{1}{2}H_2 + \oplus$ would preferably set in. If, however, an electrode be used with a considerable hydrogen overvoltage the reduction can take place.

In the chemical reduction process, the zinc used is such a metal, and the reaction can be regarded as essentially electrochemical. The anodic process is $Zn \longrightarrow Zn^{\cdot\cdot} + 2\ominus$. Owing to the high hydrogen overvoltage at zinc, reduction sets in, instead of $H^{\cdot}$ discharge. The total reaction becomes

$$Zn + 2H^{\cdot} + 2HSO_3' \longrightarrow Zn^{\cdot\cdot} + S_2O_4'' + 2H_2O,$$

or

$$Zn + 4HSO_3' \longrightarrow S_2O_4'' + 2SO_3'' + Zn^{\cdot\cdot} + 2H_2O,$$

which is the equation on p. 404, written ionically. As E.P. for the $HSO_3' - S_2O_4'' - H^{\cdot}$ electrode is $-0{\cdot}009$ volt, and $\text{E.P.}_{Zn^{\cdot\cdot}\longrightarrow Zn} -0{\cdot}76$ volt, it is obvious that much chemical energy is wasted in the reduction by

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[1] *Zeitsch. Elektrochem.* **17**, 157, 245 (*1911*).

zinc. Iron, for which E.P. $_{Fe^{\cdot\cdot} \longrightarrow Fe}$ is $-0{\cdot}44$ volt, would be more suitable, but it unfortunately is made passive by the HSO_3' ion, and does not reduce. The electrochemical method, which allows of the use of the necessary cathodic polarisation and no more, is the most economical.

Previous workers had noticed that, after a certain S_2O_4'' concentration, varying under different conditions, had been reached, no more was apparently formed, but S_2O_3'' ions instead. This was attributed to further reduction as follows,

$$S_2O_4'' + 2H^{\cdot} \longrightarrow S_2O_3'' + H_2O + 2 \oplus.$$

Jellinek showed the formation of thiosulphate to be due rather to a chemical decomposition of the hyposulphite

$$2Na_2S_2O_4 + H_2O \longrightarrow Na_2S_2O_3 + 2NaHSO_3.$$

Practically none is produced by reduction. The discovery of this fact led him to recognise that the essential condition for the production of a high hyposulphite concentration is a high *current concentration*[1]—*i.e.* a current which is very large compared with the volume of the catholyte. The rate of electrochemical formation of the hyposulphite is thus made great in comparison with its rate of chemical decomposition, and its concentration rises. To keep a hyposulphite solution at a given strength a definite current concentration is needed. If exceeded, the solution becomes stronger; if not reached, weaker.

For example, working on this principle, Jellinek, starting with 5 *n*. $NaHSO_3$, could prepare a 10 per cent. $Na_2S_2O_4$ solution with an 80 per cent. current efficiency, using 5 amperes for every 100 c.c. of catholyte. Of this, 1·06 amperes was the critical current necessary to neutralise the chemical decomposition. Besides low current concentrations,[2] a high temperature and $H^{\cdot}$ migration from the anode (where the reaction is $HSO_3' + OH' \longrightarrow HSO_4' + H^{\cdot} + 2 \ominus$) must also be avoided. Current density is of minor importance. The electrode processes are almost reversible. To neutralise the heat resulting from the high current concentration, efficient artificial cooling must be employed. To prevent entrance of $H^{\cdot}$ ions, Jellinek employed an apparatus divided by two diaphragms into three compartments, an Na_2SO_4 solution flowing through the middle neutral chamber.

Literature

Engelhardt. *Die Elektrolyse des Wassers.*
Schlötter. *Ueber die elektrolytische Gewinnung von Brom und Iod.*
Haber-Moser. *Die elektrolytischen Prozesse der organischen Chemie.*

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[1] See p. 30.

[2] It should be noticed that the successful results of the chemical reduction by zinc are largely due to the fact that the conditions are those of an electrolysis at a very high current concentration.

CHAPTER XXIII

METALS FROM FUSED ELECTROLYTES—CAUSTIC SODA AND CHLORINE FROM FUSED SALT

General.—Strongly electropositive metals (*i.e.* those having a great affinity for oxygen) are not easily prepared by chemical methods. For the liberation of the metal from its very stable compounds—generally oxides or halides—demands a still more electropositive metal or other powerful reducing agent, and often very high temperatures. Such operations are therefore costly, destructive to apparatus, difficult to carry out, and furnish poor yields. The chemical processes for sodium and aluminium manufacture are examples.

Turning to electrochemical methods, we are often debarred from depositing from aqueous solutions, as strongly electropositive metals decompose water. On the other hand, the electrolysis of anhydrous fused salts can be employed. Chemically it is simple and direct. It generally requires lower temperatures than the corresponding chemical methods. And there are other advantages. Thus we know that the satisfactory electrodeposition of zinc from aqueous solution is not easy.[1] From fused $ZnCl_2$ the metal is obtained molten. Again, current densities can be employed much higher than with aqueous solutions. For with a fused product there is no trouble owing to spongy or powdery deposits, and no concentration polarisation to be feared. On the other hand, more care and attention are necessary for successful working. The heat required to warm up the starting materials and to neutralise radiation losses must be considered. Also wear and tear of plant due to the high temperatures and the fused electrolytes are often increased. Further, there are electrochemical defects peculiar to the electrolysis of fused salts.[2]

Processes of this kind are the only ones which have ever been used for the production of magnesium and calcium, have displaced older chemical methods in the manufacture of sodium and aluminium, and have been applied on a large experimental scale to the production of zinc.

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[1] Pp. 282–283.

[2] Chap. XII.

1. Sodium

It is unfortunate that the melting-point of NaCl is so high as 800°, for the direct production of sodium from it is thereby made very difficult. The conditions otherwise are ideal—a cheap and pure raw material containing 40 per cent. metal and nothing else but chlorine. Other salts have been suggested (notably $NaNO_3$ by Darling), but the only one used technically to any extent is NaOH. It is cheap (only dear compared with NaCl), and its low melting-point allows easy working and handling of the inflammable sodium. The most important processes using NaOH are the *Castner* process and the *Rathenau-Suter* ' contact electrode ' process.

Castner Process.—The molten NaOH is contained in a cast-iron pot A (Fig. 100). This is provided underneath with an extension, B, through which passes the cathode C, sealed into B by NaOH which has solidified. C may be of iron, nickel or copper; preferably of iron. Resting on the flange of the pot and insulated from it is hung the ring-shaped nickel[1] anode D, sometimes perforated with holes to allow free circulation of the electrolyte. Between the electrodes is hung a short cylindrical screen, E, which dips beneath the liquid surface, forming a cathode chamber, and is continued below by an extension of fine wire gauze. The whole is of nickel or iron, and is carefully insulated. The gauze prevents globules of sodium reaching the anode, they being unable to pass through the meshes. The top of the vessel is suitably covered to minimise heat losses. The covers can be readily detached, and are provided with holes permitting the escape of evolved gases. The metal liberated at the cathode is ladled out by means of perforated spoons, which retain the sodium, allowing the NaOH to flow through. The whole apparatus is bricked in, and in order to protect the cell walls the bath is designed to work at the right temperature with a layer of solidified electrolyte coating the sides.

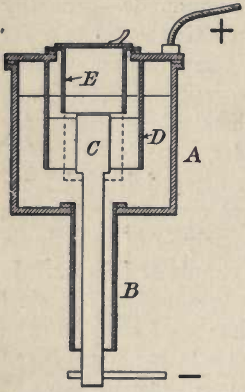

FIG. 100.—Castner Sodium Cell.

The temperature must be kept as low as possible. This was fully recognised by Castner, who specified that it should not rise more than 20° above the melting-point. This is 327°[2] for pure NaOH, but the impure material can melt as low as 300°, and electrolysis is most conveniently carried out at 315°–320°. Above 325° the yield practically falls to zero. The temperature must also be kept constant, as

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[1] Preferable to iron, as it is more passive in NaOH containing any NaCl.

[2] *Zeitsch, Elektrochem,* **15**, 539 (*1909*).

convection currents disturb the electrolysis. Whilst working, a number of slight explosions occur. They are generally harmless, but account for the use of small units.

According to J. W. Richards[1] the cells at Niagara are about 18″ in diameter and 2′ deep. The cathode[2] is provided with an enlargement at the top, 4″ in diameter, which constitutes the active cathodic surface. A unit holds about 250 lbs. of molten NaOH, takes 1,200 amperes at about 5 volts, and works with 45 per cent. current efficiency.[3] Assuming the cathode enlargement to be 6″ long, its active surface will be about 4·8 dm.^{2} and the cathodic current density 250 amps./dm.^{2}. The units used in England are of smaller size (500 amperes), work at slightly lower current densities, and take about 4·5 volts.

Theory.—The mechanism of this electrolysis was first recognised by Janeczek,[4] who showed that when anhydrous NaOH is electrolysed hydrogen is at first not produced at the cathode, but results on continuing the electrolysis. He considered the successive reactions to be

$$(a) \qquad 2NaOH \longrightarrow \underset{\substack{\downarrow \\ \text{Metal at cathode.}}}{2Na^{\cdot}} + \underset{\substack{\downarrow \\ \text{Water + oxygen at anode.}}}{2OH'}$$

$$(b) \qquad 2Na + 2H_2O \longrightarrow 2NaOH + H_2.$$

Thus the hydrogen is the product of a second *chemical* reaction, and we see at once one of the causes of the poor yield of sodium. The question was later treated more fully by Le Blanc and Brode.[5] They found that if fresh commercial NaOH be taken and electrolysed hydrogen and oxygen are evolved. As the electrolysis is continued, hydrogen is produced with more and more difficulty, until, at a certain decomposition voltage, sodium is liberated. If the melt has been dehydrated previous to the electrolysis by heating or by treatment with metallic sodium, no hydrogen is evolved. They therefore regard the cathodic production of hydrogen as rising from the water contained in the molten NaOH, which they showed to be very hygroscopic, and to part with its water with difficulty. Investigating the anodic process, they conclusively proved the *formation* of water.

Their final formulation of the processes occurring is

$$(1) \qquad NaOH \longrightarrow \underset{\substack{\downarrow \\ \text{Sodium} \\ \text{at cathode.}}}{Na^{\cdot}} + \underset{\substack{\downarrow \\ \text{Water + oxygen at anode.}}}{OH'}$$

$$(2) \qquad H_2O \longrightarrow \underset{\substack{\downarrow \\ \text{Hydrogen} \\ \text{at cathode.}}}{H^{\cdot}} + \underset{\substack{\downarrow \\ \text{Water + oxygen at anode.}}}{OH'}$$

This is the chief source of loss if the temperature be kept low.

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[1] *Electrochem Ind.* 1, 14 (*1902*). [2] Said (obviously erroneously) to be of carbon.

[3] Richards' calculation of the daily yield is incorrect. He assumes 90 per cent. current efficiency, whereas about half is obtained in practice.

[4] *Ber.* 8, 1018 (*1875*). [5] *Zeitsch. Elektrochem.* 8, 717 (*1902*).

$$(3)\qquad \underset{\text{(dissolved from cathode)}}{Na} + \underset{\text{(formed at anode)}}{H_2O} \longrightarrow NaOH + \tfrac{1}{2}H_2$$

This can occur in both anode and cathode compartments. It takes place to a greater extent at the anode at higher temperatures, when the rate of diffusion of the dissolved sodium is greater. When this happens, both hydrogen and oxygen are liberated at the anode, and explosions may result.

$$(4)\qquad \underset{\text{(from cathode)}}{2Na} + O_2 \longrightarrow Na_2O_2$$

This occurs at the anode.

$$(5)\qquad \begin{array}{l} Na_2O_2 + 2Na \longrightarrow 2Na_2O \\ \qquad\qquad\qquad\qquad\quad \downarrow 2H_2O \\ \qquad\qquad\qquad\qquad\quad 4NaOH \end{array}$$

$$(6)\qquad 2Na + 2\oplus \longrightarrow 2Na^{\cdot}$$

This ionic process can occur at the anode if the melt is saturated with sodium at a high temperature. No gas is liberated, and the current efficiency is zero.[1]

Equations (2)–(6) all represent sources of loss in the Castner process. When it is well worked, (2) is the most important, but at higher temperatures the others come into play. As Le Blanc and Brode point out, the Castner process *as worked* can never give higher than 50 per cent. current efficiencies, but better figures would result if the water could be kept away from the cathode and the sodium from the anode. A cathode diaphragm is needed, uncorroded by molten NaOH; and a current of dry air passed through the anode compartment to remove the water would be advantageous. Ewan[2] has patented both devices. He suggests a diaphragm of Al_2O_3 or sodium aluminate, but its efficiency is very doubtful.

The reasons for the frequent explosions are therefore as follows:—

(1) In the cathode compartment. Hydrogen and air which enters from above.

(2) In the anode compartment. Sodium diffusing through and liberating hydrogen from the anodic water.

(3) The screen and gauze acting as a bipolar electrode. This would cause explosions in both compartments, but is unlikely to occur except in a badly designed cell or with a gauze of too fine a mesh.

The immediate cause of explosions would be the action of anodic oxygen or air on tiny globules of molten sodium, small enough in case (2) to pass through the gauze screen.

It can now be clearly seen why the temperature must be kept low and constant. Convection and diffusion are minimised (the elec-

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[1] See p. 415.

[2] E.P. 14,739 (1902).

trolyte becomes far more viscous near its melting-point), and losses are consequently lessened. One might imagine that the rapid fall of the current efficiency above 330° is due to increased solubility of the metal in the melt. The work of v. Hevesy[1] shows this to be incorrect. He determined the solubilities of sodium and potassium in their anhydrous molten hydroxides, conclusively showing them to be cases of *real solubility*, not of colloidal suspension or formation of sub-oxide. For sodium he obtained—

θ	Grams Na per 100 grams NaOH
480°	25·3
600°	10·1
800°	6·9

The solubility thus decreases rapidly with rising temperature.

With potassium the solubilities are much smaller. Le Blanc and Brode had attributed the impossibility of preparing this metal by the Castner process to its enormous affinity for oxygen. v. Hevesy showed the correctness of this view by parallel experiments on the production of the two metals, using cathodes capped in magnesite crucibles and thus protected from the air. Much higher yields of potassium than sodium resulted (at the same temperatures), corresponding to the greater solubility of sodium in its fused hydroxide. Thus, between 320°–340°, a 27 per cent. yield of Na and a 55 per cent. yield of K resulted. Finally, to confirm the idea that the rapid decrease in the yield of sodium with rising temperature is due essentially to its increased rate of diffusion, diffusion experiments in their fused hydroxides were carried out with both sodium and potassium. The rate of diffusion of K was found to be very low and practically constant between 300° and 550°, whereas that of sodium rose perceptibly at 330° and very rapidly at 340°.

The Helmholtz-Thomson rule, applied to the decomposition voltage of molten NaOH, gives the very uncertain figure of 3·1 volts. Fortunately we have experimental determinations by Sacher[2] and by Le Blanc and Brode.[3] The decomposition voltage of the *water* present in moist NaOH was found to be 1·3 volts at about 330°, the voltage for sodium formation 2·2 volts. Assuming a current efficiency of 45 per cent. and an average voltage of 4·5 volts, we have for the energy efficiency of the Castner process—

$$\frac{2{\cdot}2}{4{\cdot}5} \times 45 = 22 \text{ per cent.}$$

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[1] *Zeitsch. Elektrochem.* **15,** 539 (*1909*).

[2] *Zeitsch. Anorg. Chem.* **28,** 385 (*1901*).

[3] *Zeitsch. Elektrochem.* **8,** 697 (*1902*).

Also that one ton of sodium requires

$$\frac{4{\cdot}5 \times 100 \times 96540 \times 1000 \times 1000}{45 \times 23 \times 3600 \times 1000} = 11700 \text{ K.W.H.}$$

Or 1 H.P. year gives 0·56 ton sodium.

Becker Process.[1]—In this process, said to be worked in France, a mixture of NaOH and Na_2CO_3 is electrolysed in a cell similar to the Castner, but with one or two essential differences. Firstly, no wire-gauze curtain is used. Secondly, above the cathode (in shape a truncated cone sloping in upwards) is put a 'collector' dipping into the melt, under which the sodium aggregates together. This collector, provided with a deep vertical flange to prevent electrolyte getting on its upper surface, has a discharge pipe through which the sodium is drawn off. It can, if necessary, be cooled from above. This collector is connected electrically with the cathode, Becker stating that the re-solution of the sodium—thus made 'negative'—is thereby prevented. The working temperature near the electrodes is 550°, and solidified electrolyte coats the walls. 5000-ampere units can be constructed. It is claimed that explosions are avoided, and that Na_2CO_3 and not NaOH is decomposed. The inventor states that fourteen 5000-ampere units running for 24 hours would produce 500 kilos. of metal. The current efficiency would then be—

$$\frac{100 \times 50 \times 1000 \times 26{\cdot}8}{5000 \times 14 \times 24 \times 23} = 35 \text{ per cent.}$$

He further says that not less than one kilo. of sodium is produced per 18 K.W.H. We have seen that the production of one kilo. by the Castner process requires 11·7 K.W.H.

The only essential advantage which this process would appear to have, *i.e.* the cheapness of the raw material, a $Na_2CO_3 - NaOH$ mixture, with Na_2CO_3 subsequently fed in, has been shown by Le Blanc and Carrier[2] to be quite illusory. They worked with varying proportions of Na_2CO_3 and NaOH, and, as one would expect, never obtained any CO_2 in the anode gas, which was, on the contrary, nearly pure oxygen. With a 55 per cent. Na_2CO_3 melt, sodium was obtained above 480°, and with a 60 per cent. melt at 550°, but in very small amounts. On raising the temperature, the yields diminished. Variations of electrolyte composition and current density gave no better results. They conclude that the Becker process is merely the Castner process, slightly modified and by no means improved.

'Contact Electrode' Process.—The other important method for sodium production from NaOH is the 'contact electrode' process, used by the Griesheim Elektron Co. Its principle is Bunsen's idea

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[1] E.P. 11,678 (1899). Also Becker, *Elektrometallurgie der Alkalimetalle.*

[2] *Zeitsch. Elektrochem.* **10**, 568 (*1904*).

of using a cathode which does not dip into the electrolyte, but is as far as possible merely in contact with it.[1] The liberated metal is thus much less exposed to the electrolyte, and larger yields should be possible. The apparatus employed is very simple. A large iron anode in the middle of a shallow NaOH bath is surrounded at a suitable distance by a ring of metal cathodes, which make contact with the electrolyte by the surface film only. The distance apart of the electrodes is so regulated that no anodic gases come into contact with the sodium. Screens, such as in the Castner process, or as were used in a former 'contact electrode' process, are unnecessary. Cathodic current densities up to the high figure of 1000 amps./dm.^{2} can be used. Above that value, overheating at the contact film occurs. The current efficiency is stated to be 35 per cent. The voltage is not known, but will doubtless be very high with such enormous current densities.[2] To this disadvantage we must add the further probable one that the Na has to be collected in much smaller quantities at a time than in the Castner process.

Sodium from Fused Salt.—The production of sodium by electrolysing fused NaCl has been the subject of much investigation. The difficulties are enormous, and no satisfactory solution has been yet reached. Pure NaCl melts at 803°—impure material down to 775°. The metal boils at 877°, and at 800° its vapour pressure is already very high. It is difficult to thoroughly separate the anodic and cathodic products. And, lastly, the wear and tear of the apparatus is very great. Grabau and Hulin came nearest to solving the problem, but their cells proved unsuitable when tried on the large scale. At present it is believed that small quantities of metal are being prepared directly from fused salt at Holcomb Rock, Virginia, by a method due to Seward and v. Kügelgen, and at Basel, using a process devised

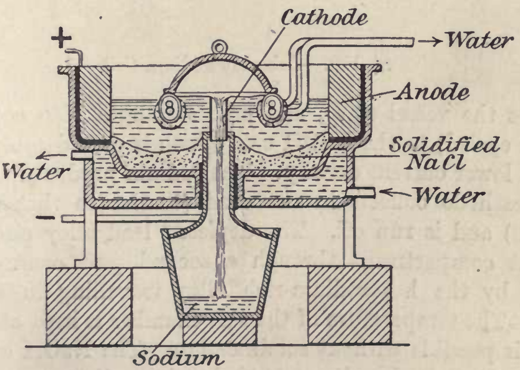

FIG. 101.—Seward-v. Kügelgen Sodium Cell.

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[1] Cf. p. 419.

[2] Compare pp. 419, 420.

by Stockem. The former inventors surround their cathode with a metal water-cooled hood. Under this the sodium collects, eventually running off through the hollow electrode into a vessel below. The graphite anode forms the side lining of the cell, the bottom of which is also water-cooled (Fig. 101).

Ashcroft Process.—A few years back a method for the production of sodium from molten salt was patented by Ashcroft.[1] Though it, too, has been thoroughly tested, and is at present abandoned, a brief description of it may find a place here, as the problem itself is an attractive one and the proposed solution ingenious. The electrolysis was carried out in a double cell. In the first compartment fused salt was electrolysed between a carbon anode and a molten lead cathode. The molten lead-sodium alloy formed was transported to the second chamber, where it became anode in a bath of molten NaOH, metallic sodium being deposited at the cathode.

The essential parts of the cell are shown in Fig. 102. Salt is charged in at A, at B chlorine is led off, and C is the anode. The lead-sodium alloy leaves the vessel at D, and passes along a pipe connection (in which it is cooled) to the NaOH cell, which is considerably larger and works at a lower current density. The sodium produced at the cooled spherical cathode collects in the cone (similar to that used in the Becker cell) and is run off. The depleted lead alloy circulates back to the salt compartment through a second pipe connection, being heated up by the hot sodium-rich alloy travelling in the opposite direction. The temperature of the salt chamber is kept at about 770°, as low as is possible without solidification. The NaOH compartment is at 330°. Pure lead melts at 326°, but its sodium content makes it quite easily fluid at that temperature.

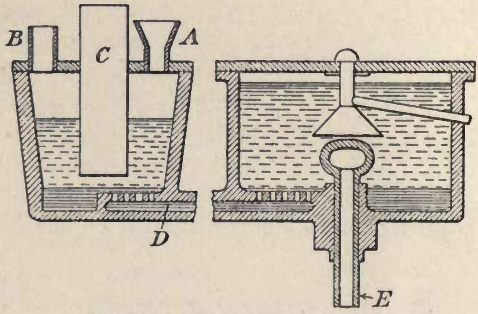

FIG. 102.—Ashcroft Sodium Cell.

The current density at the cathode in the salt chamber is about 200 amps./dm.[2] At the anode it is probably more, though Carrier[2]

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[1] *Trans. Amer. Electrochem. Soc.* **9**, 123 (*1906*).

[2] *Electrochem. Ind.* **4**, 477 (*1906*).

states that at 300 amps/dm.[2] a graphite anode becomes rapidly corroded. At the lead-sodium alloy in the caustic chamber it is far lower. The salt compartment takes about 7, the NaOH compartment 2 volts. Ashcroft claimed a current efficiency of 90 per cent. when working smoothly. One ton of sodium would thus require

$$\frac{1000 \times 100 \times 96540 \times 9 \times 1000}{23 \times 90 \times 3600 \times 1000} = 11700 \text{ K.W.H.}$$

or 1 H.P. year gives 0·56 ton of sodium, exactly as in the Castner process. The surprisingly high current efficiency is due to the very small solubility of both sodium and chlorine in the molten salt, to the small sodium vapour pressure of the lead-sodium alloy, and to the absence in the NaOH cell of any complications due to water and oxygen.

This NaOH compartment must, however, be kept at a low temperature. For example, Carrier[1] worked on a similar process in which the NaOH and NaCl cells were not spatially separated, but in very close contact. The NaOH cell was at 700°–800°, and yielded no trace of sodium or any other product even with large currents (800 amperes) passing. Of course at this high temperature the sodium would at first rapidly dissolve, but after saturation of the melt one would expect it to deposit. This interesting phenomenon may result from one of two causes. The metal dissolved in the *electrolyte* may ionise ($Na + \oplus \longrightarrow Na^{\cdot}$) at the anode more easily than the metal dissolved in the *lead*. Then anode and cathode reactions would be the converse of one another, and the electrolyte would remain unchanged, $Na^{\cdot}$ ions being discharged at the cathode, the metal diffusing to the anode, and there becoming re-ionised. Or the melt, in virtue of its large content of dissolved metal, may perhaps simply behave as an electronic or metallic conductor, as do solutions of sodium in liquid ammonia. Which view is correct we cannot yet decide.

There are no experimental data on the decomposition voltage of molten NaCl. But we know that at 800° calcium can displace sodium to a great extent from NaI, and that at lower temperatures the reaction is reversed.[2] The same statement probably holds for the chlorides. We also know that the decomposition voltage of $CaCl_2$ at 800° is 3·24 volts.[3] That of NaCl is consequently a little lower. We will suppose it to be 3·0 volts. The energy efficiency of the complete Ashcroft process, of which the final result is the splitting up of NaCl into sodium and chlorine, is thus

$$90 \times \frac{3}{9} = 30 \text{ per cent. (Castner process 22 per cent.).}$$

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[1] *Metall. Chem. Engin.* **9**, 253 (*1911*). Cf. also *Trans. Amer. Electrochem. Soc.* **9**, 362 (*1906*).

[2] Danneel and Stockem, *Zeitsch. Elektrochem.* **11**, 209 (*1905*).

[3] See p. 419.

The decomposition voltage in the Ashcroft NaCl compartment is of course less than 3 volts, as not sodium, but an unsaturated lead-sodium alloy, is the product. The high voltage is due to the large current density. The conductivity of molten NaCl is very high. According to Poincaré,[1] κ is 4·09 at 780°; according to Arndt,[2] whose figures are probably more correct, it is rather lower, 3·34 at 800.°

The practical difficulties preventing the smooth running of the process are enormous. Crude salt is apt to deposit its impurities as a crust on the cathode, sending the voltage up. And the widely differing temperatures needed in the separate parts of the apparatus cause considerable strains and wear and tear. Reasons such as those have led to an abandonment which may be permanent. By using, not crude rock salt, but a suitable low melting mixture of chlorides, and continuously feeding in a purer salt, different results might perhaps be obtained.

2. Magnesium

Magnesium was first electrochemically prepared by Bunsen by the electrolysis of fused anhydrous $MgCl_2$. It is now made technically by the electrolysis of fused anhydrous carnallite, preferred to $MgCl_2$ because it occurs naturally, is less volatile, and can be dehydrated far more easily. When a $MgCl_2$ solution is evaporated to dryness and fused, the salt is hydrolysed, much HCl is lost, and the resulting residue contains MgO. The magnesium in a carnallite solution is largely present as the complex $MgCl_3'$ anions, not as $Mg^{\cdot\cdot}$ ions, and the above reaction is much less to be feared.

The electrolysis is said to take place in an iron pot which serves as cathode, and using a carbon anode. No descriptions of exact technical apparatus are available, and it seems more probable that the electrolyte is allowed to solidify round the walls of the pot, and that the iron cathode, like the anode, is dipped into the melt. Some kind of anode screen or diaphragm will be necessary, as fused magnesium is lighter than fused carnallite, and will swim about on the surface of the electrolyte. Magnesium melts at 633°. $MgCl_2$ melts at 708°, and anhydrous carnallite therefore lower. The best working temperature would appear to be about 650°, and A. Oettel[3] has shown that under these conditions in fact the current efficiency is highest. It is, however, difficult to keep the temperature of the melt sufficiently constant to avoid solidification of the magnesium, and the process can easily be disturbed on that account. Oettel recommends 700°–750°. Borchers[4] also worked at 700°.

No data exist on the decomposition voltage of carnallite melts.

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[1] *Ann. Chim. Phys.* [6], **21**, 289 (*1890*).

[2] *Zeitsch. Elektrochem.* **12**, 337 (*1906*).

[3] *Dissertation* (Dresden, *1908*).

[4] *Zeitsch. Elektrochem.* **1**, 361 (*1895*).

The value will *probably* be higher than that for pure $MgCl_2$, particularly as the magnesium may, even in the fused state, be largely present as complex anions. The decomposition voltage of fused $MgCl_2$ is also unknown. But we know that sodium displaces magnesium from its fused salts. Hence the decomposition voltage of fused $MgCl_2$ must be less than that of fused NaCl at the same temperature. The latter is approximately 3·0 volts at 800°.[1] At 700° it will be greater, perhaps 3·2 volts (for super-cooled fused NaCl). We can therefore say that at 700° the decomposition voltage of $MgCl_2$ is less than 3·2 volts, and will assume the value for carnallite to be equal to this figure. Borchers used 5–8 volts in the electrolysis, A. Oettel 4–8 volts, depending on current density and temperature. We will assume for calculation 6 volts, and a current efficiency of 75 per cent.[2] The energy efficiency is therefore

$$75 \times \frac{3{\cdot}2}{6} = 40 \text{ per cent.}$$

One kilo. of metal requires

$$\frac{1000 \times 2 \times 96540 \times 100 \times 6}{24{\cdot}3 \times 75 \times 3600 \times 1000} = 17{\cdot}7 \text{ K.W.H.}$$

F. Oettel[3] has elucidated certain points in connection with this process. Under ordinary conditions, when magnesium globules are formed at the cathode, they do not easily coalesce; the yield is consequently collected with difficulty, and the small particles readily catch fire. Oettel found that this disinclination to aggregate together could be removed by the addition of a little CaF_2 (first recommended by Deville and Caron). This acts very powerfully, undoubtedly through a surface tension effect, though, according to Oettel, it also dissolves traces of oxide from the surface of the globules. A source of loss in the use of impure carnallite is, for a reason already discussed,[4] the presence of a small quantity of $FeCl_3$. If too high a voltage is used, or if the $MgCl_2$ content of the bath becomes too low, the magnesium may contain potassium. In that case it is liable to catch fire during the electrolysis.

The Aluminium und Magnesium Gesellschaft, Hemelingen, uses a rather different electrolyte,[5] consisting of a molten mixture of equimolecular proportions of $MgCl_2$, KCl, and NaCl. It is prepared from carnallite by the addition of the necessary amount of NaCl, none of the materials needing a special purification. During the electrolysis (a continuous one), anhydrous $MgCl_2$ is added to keep

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[1] See p. 415.

[2] 90–95 per cent. in practice, according to F. Oettel. A. Oettel obtained up to 75 per cent.

[3] *Zeitsch. Elektrochem.* 2, 394 (*1895*).

[4] P. 162.

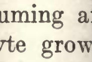
[5] *Zeitsch. Elektrochem.* 7, 408 (*1901*).

the bath composition constant. The electrolyte is further always kept basic by a suitable quantity of alkali, and CaF_2 is added as usual. This process has been studied on a small scale by Hohler.[1] The best working temperature was found to be 750°–800°, when a 70 per cent. current efficiency was obtained. A cathodic current density of 27–30 amps./dm.^{2} was used. (Borchers employed 10 amps./dm.^{2}, A. Oettel 30–40 amps./dm.^{2})

Finally, according to Lorenz,[2] one must believe, judging from the appearance of some of the magnesium sticks now on the market, that the 'contact electrode' method[3] has been applied to the production of this metal also. A. Oettel[4] has shown this, by laboratory experiments, to be quite possible. At the same time, it is inconvenient, as the metal rod formed is somewhat brittle. Further, in consequence of the high current densities, the potassium content is likely to rise high.

3. Calcium.

Calcium is now technically prepared by the electrolysis of the fused chloride. The scale of production must be small, as the only application of the metal is to make calcium hydride, sometimes employed to generate hydrogen.

The electrolysis of fused $CaCl_2$ is subject to a disturbance also encountered with $MgCl_2$ and $ZnCl_2$.[5] It is difficult to prepare the pure anhydrous salt from the hydrated chloride, owing to hydrolysis and the gradual formation of some hydroxy-chloride such as  $Ca\genfrac{<}{}{0pt}{}{OH}{Cl}$. In consequence the liberated metal is slowly attacked by the melt, displaces the hydrogen, and forms an insoluble oxy-chloride. The bath thickens, the conductivity decreases, and the yield of calcium falls. As much as 17 per cent. of metallic calcium can be taken up by the melt, together with several per cents. of iron (assuming an iron containing vessel), and the condition of the electrolyte grows worse with each cooling and re-heating. Fresh $CaCl_2$ should be used each time for small-scale work, and when operating continuously the electrolyte must be occasionally completely changed. Regeneration by HCl is hopelessly slow.

Bunsen and Matthiessen[6] were the first to investigate the electrolysis of the molten alkaline earth chlorides, including $CaCl_2$. They could not get satisfactory yields of metal, which, liberated at a high temperature and in a finely divided condition, readily caught fire, making the melt basic. Pure $CaCl_2$ melts at 780°, and pure calcium

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[1] *Dissertation* (Zürich, 1904)

[2] *Elektrochemie geschmolzener Salze*, p. 72. *Zeitsch. Elektrochem.* **7**, 252 (*1901*).

[3] See pp. 412, 419. [4] *Loc. cit.* [5] Pp. 416, 421.

[6] *Lieb. Ann.* **93**, 277 (*1855*).

higher—800°. Hence, allowing for impurities, 750° will give a lower limit to the working temperature, and, as the finely divided metal burns in air not far above 800°, and as the molten metal very easily forms 'metal-fog,' there is only a small range of safe working temperature. They made several attempts to overcome this difficulty, using low-melting mixtures of alkaline earth chlorides and a very high cathodic current density, but only succeeded in preparing small quantities of very finely divided calcium-rich alloy.

Many years later, Borchers & Stockem[1] and Ruff & Plato[2] worked on the same subject, but on a larger scale, and eventually produced small quantities of fairly pure compact metal. The latter authors, after many preliminary experiments, used a mixture of 100 parts $CaCl_2$ and 16·5 parts CaF_2, melting at 660°. Keeping the mass of the electrolyte at about 760°, the temperature in the immediate neighbourhood of the cathode was raised above 800° by the use of a very high cathodic current density (3–5 amps./mm.^{2}). The calcium was consequently produced molten, and, on moving away, quickly chilled and solidified. About 30 volts were required, the high value being essentially due to the enormous current density. (The decomposition voltage of molten $CaCl_2$ at 800° has been found by Arndt and Willner[3] to be 3·24 volts.) Ruff and Plato's work forms a comprehensive study of *one* method of electrolytically winning metallic calcium, but it is unlikely that a similar process will ever be technically used.

The process now employed[4] is based on the contact electrode principle used for the production of sodium.[5] But the relative positions of the melting-points of metal and electrolyte permit an important modification. Not only does the iron cathode barely dip under the surface of the melt, but it can be steadily raised by means of a gearing. A solid rod of the precipitated metal is thus continually removed from the electrolyte and itself forms the cathode, the iron merely acting as a lead. The advantages are obvious. The metal is at once obtained in massive coherent form, free from any impurity except an adhering skin of $CaCl_2$; and a much better current efficiency results than with the older method, any tendency of metal to dissolve or to form 'metal-fog' being minimised. The published technical details are extremely meagre. The electrolyte contains $CaCl_2$ only, no CaF_2 being added. The temperature must consequently lie between 780°–800°. The current density is very high, 100 amps./cm.^{2}

Several laboratory investigations of the process have been published. Wöhler[6] used a cast-iron vessel externally heated, a carbon anode,

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[1] *Zeitsch. Elektrochem.* **8**, 757 (*1902*).

[2] *Ber.* **35**, 3612 (*1902*).

[3] *Zeitsch. Elektrochem.* **14**, 216 (*1908*).

[4] Rathenau, *Zeitsch. Elektrochem.* **10**, 508 (*1904*).

[5] P. 412.

[6] *Zeitsch. Elektrochem.* **11**, 612 (*1905*).

and an 8 mm. iron rod as cathode. A water-cooled cathode presented no particular advantage. His electrolyte consisted of 100 parts $CaCl_2 : 17$ parts CaF_2 (M.P. 660°).[1] The bath was kept at 665°–680°, the latter temperature being reached near the cathode where the current density was high. The electrolyte deteriorated with time, as has already been described. With a fresh bath 38 volts were used. The cathodic current density was varied between 50–250 amps./dm.^{2}, but had little effect on the current efficiency. On the other hand, it is of prime importance that the cathode be regularly and rapidly raised from the electrolyte, as the chief source of loss is the metal-fog formation. The current efficiency obtained was 82 per cent. With too high an anodic current density the anode effect was observed (at 5·6 amps./cm.^{2} with carbon or 8 amps./cm.^{2} with graphite), and the bath voltage rose to about 80 volts.

Goodwin[2] worked under rather different conditions. He employed a $CaCl_2$ bath and kept it at just above 800°. Fused calcium was consequently produced. It, however, solidified immediately above the surface of the melt, and by continually raising the cathode massive metal resulted in the form of a rod of very irregular cross-section. An absolutely regular rate of raising the cathode is essential. An average run gave a 26·6 per cent. current efficiency,[3] using 17·7 volts and 163 amperes. The best run was with 160 amperes at 19 volts and gave a 41·2 per cent. yield. The cathodic current density varied between 3·2–20 amps./dm.^{2}, much lower than was the case with Wöhler. This is one cause of the far lower voltage used. Another reason would be the higher working temperature. The lower current density was doubtless also partly responsible for the low current efficiency. Other causes would be the greater tendency to 'metal-fog' formation at the higher temperature, and the loss of liquid globules of metal.

Frary, Bicknell and Tronson[4] used a containing vessel of Acheson graphite (water-cooled at the bottom) which acted as anode, and a water-cooled iron cathode 1″ in diameter. They found $CaCl_2$ without any addition of CaF_2 to be the most suitable electrolyte. Two important conditions were the regular and continuous raising of the cathode rod and the careful regulation of the cathode temperature. If the latter were allowed to rise too high, liquid globules of metal floated away; when it fell too low, spongy masses of calcium resulted. The best current density was about 9·3 amps./dm.^{2} The voltage varied between 18 and 31 volts, usually near the latter figure; and the current efficiency between 45 per cent.–100 per cent., usually exceeding 80 per cent.

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[1] See Ruff and Plato, p. 419.

[2] *Jour. Amer. Chem. Soc.* **27**, 1403 (*1905*).

[3] Using a similar apparatus, Tucker and Whitney obtained 60 per cent. *Jour. Amer. Chem. Soc.* **28**, 85 (*1906*).

[4] *Trans. Amer. Electrochem. Soc.* **18**, 117 (*1910*).

In consequence of the high voltage, the methods proposed are very imperfect as far as energy efficiency goes. In the actual technical process the voltage will be less than that observed by Wöhler, owing to the higher temperature, and greater than that observed by Goodwin, owing to the heavier current density. We will assume 25 volts, and with an 80 per cent. current efficiency we have

$$\text{Energy efficiency} = 80 \times \frac{3{\cdot}24}{25} = 10 \text{ per cent.}$$

The production of one kilo. of metallic calcium requires

$$\frac{1000 \times 2 \times 96540 \times 100 \times 25}{40 \times 80 \times 3600 \times 1000} = 42 \text{ K.W.H.}$$

All investigators agree as to the enormous voltage losses, and they can only be ascribed to the use of the contact electrode and very high current densities. The specific conductivity (κ) of fused $CaCl_2$, according to Arndt and Gessler,[1] is 1·9 at 800°. According to Poincaré [2] it is 1·22 at 760°, but this lower figure probably holds for impure basic material.

4. Zinc

The electrolytic production of zinc from fused $ZnCl_2$ has been fully investigated, both in the laboratory and technically. It has been proposed to prepare $ZnCl_2$ from crude ZnO and HCl, to evaporate, fuse, and electrolyse, the metal being thus obtained in a compact molten state. Again, fused $ZnCl_2$ is a principal product of the Swinburne-Ashcroft and Baker processes of chlorine smelting of complex sulphide ores.

The electrolysis of fused $ZnCl_2$, or rather its preparation previous to electrolysis, presents peculiar difficulties which have been investigated by Lorenz and his pupils.[3] If $ZnCl_2$ be melted in an open crucible in air and electrolysed between carbon electrodes, large quantities of gas are evolved at both electrodes, carrying away $ZnCl_2$ vapours, the melt becomes badly conducting and turbid, and no zinc is produced. After stopping the current, the electrolyte is found to be strongly basic. If, before melting, some NaCl be added, the electrolysis proceeds a little better, and some zinc, though not much, results. The reasons for this behaviour are that $ZnCl_2$ can never be procured in the pure state, but always contains water, whilst water vapour is further produced by the flame used for heating. If the $ZnCl_2$ be fused in a vessel to which the flame gases have no access, and, before electrolysing,

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[1] *Zeitsch. Elektrochem.* **14**, 662 (*1908*). Also p. 159.

[2] *Ann. Chim. Phys.* [6] **21**, 289 (*1890*).

[3] *Zeitsch. Anorg. Chem.* **10**, 78 (*1895*), **20**, 323 (*1899*), **23**, 284 (*1900*), **39**, 389 (*1904*).

heated until fuming has ceased, on passing the current, hydrogen and oxygen are still at first evolved. But gradually the conductivity increases, the stream of hydrogen becomes less, chlorine appears instead of oxygen, and zinc is produced. The fused salt is now a perfectly clear highly refracting liquid which solidifies to a porcelain-like hygroscopic white mass. The water can therefore to a large extent be removed by heat and the last portions electrolysed out. Lorenz recommends for the same purpose the addition of strong HCl or the bubbling through of HCl gas during the last stages of evaporation, thus neutralising the hydroxy-compounds and producing water which is blown off.

Pure $ZnCl_2$ melts at 365°,[1] a considerably higher temperature than that previously given for impure material. But traces of water lower its M.P. very considerably. The most reliable figures for the conductivity of the pure fused material are those of Lorenz and H. Schultze,[2] viz. :—

$$\begin{aligned}\kappa = {} & 0{\cdot}026 \text{ at } 400^\circ \\ & 0{\cdot}057 \text{ at } 450^\circ \\ & 0{\cdot}104 \text{ at } 500^\circ.\end{aligned}$$

These figures are exceptionally low for a fused salt. When electrolysed it furnishes zinc and chlorine readily and with good current efficiency. Thus Lorenz obtained 98 per cent. at 500° in a V-tube apparatus. Within certain limits the results are better the higher the current density. The deficiency is due to vaporisation and metal-fog formation. Grünauer[3] found that this second source of loss is much diminished if a mixture of $ZnCl_2$ and an alkaline chloride is used.[4] Thus, working at 600°, and with lower current densities than in the case quoted above, he obtained the following figures:

TABLE LXIV

Electrolyte	Current efficiency Per cent.
$ZnCl_2$	73·9–75·9
$[ZnCl_2] + [KCl]$	92·1–94·7
$[ZnCl_2] + [NaCl]$	83·9–89·9
$[ZnCl_2] + 1{\cdot}2\,[NaCl]$	89·6–91·2

Suchy[5] has determined the E.M.F. of the cell Zn | fused $ZnCl_2$ | Cl_2 at various temperatures, a figure which is identical with the decomposition voltage of the fused salt. Amongst other figures he obtained—

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[1] *Zeitsch. Anorg. Chem.* **39**, 434 (*1904*).
[2] *Zeitsch. Anorg. Chem.* **20**, 323 (*1899*).
[3] *Zeitsch. Anorg. Chem.* **39**, 389 (*1904*).
[4] Cf. p. 162.
[5] *Zeitsch. Anorg. Chem.* **27**, 152 (*1901*).

TABLE LXV

θ	E Volts
450° C.	1·643
500°	1·611
550°	1·576
600°	1·535
650°	1·494

Lorenz [1] has made a few direct determinations of decomposition voltage and obtained 1·49 volts at 500°–600°.

Technical.—Swinburne [2] has briefly described the electrolysis which constitutes the last stage of the Swinburne-Ashcroft process. In preparing his $ZnCl_2$, he boiled down and removed the residue of oxygen by a preliminary electrolysis, using cheap carbon anodes which were oxidised by the evolved gas. The main electrolysis took place in vessels internally heated by the current, between molten zinc as cathode and carbon anodes. These vats were built of firebrick cased with iron, and took about 3,000 amperes. This was considered a small load, and 10,000-ampere units were projected, but, if tested, there are no available accounts of their behaviour. Four volts were used, the current efficiency being nearly theoretical.

The same process has been described elsewhere [3] more fully. The final fusion of the $ZnCl_2$ took place in enamelled iron pans. 'With proper working, the amount of basic material formed is not great.' The preliminary electrolysis was carried out in a brick-lined iron vessel, the cathode being of molten zinc and the anode of cheap carbon blocks, and was continued until all the water and basic compounds were decomposed, a very pure product resulting. The energy thus expended was about 10 per cent. of that employed in the final electrolysis. This took place in a sheet-iron vessel lined with firebrick. The roof was of cast-iron, gas-tight, and provided with a charging port for $ZnCl_2$. Into it the carbon anodes were bolted, reaching almost to the bottom of the cell. The chlorine passed out through a suitably placed flue. The molten zinc cathode made connection with a small tank outside by means of a channel through the wall. A slight vacuum was maintained in the cell to prevent chlorine losses, and, working with pure material, the electrolysis is said to have proceeded very smoothly.

One interesting point is that the rule was to electrolyse a mixture of $ZnCl_2$ and NaCl, not $ZnCl_2$ only, the reason being that the resistance of the melt and also fuming were thereby diminished. This addition of an alkaline chloride has also, however, a favourable effect on the current efficiency. In the technical process NaCl was added until the melt contained 28 per cent. metallic zinc, whilst Lorenz and Grünauer [4]

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[1] *Zeitsch. Anorg. Chem.* **12,** 272 (*1896*).

[2] *Electrochem. and Metall.* **3,** 68 (*1903*).

[3] *Electrochem. Ind.* **3,** 63 (*1905*).

[4] P. 422.

obtained with a melt of about the same composition a 15 per cent. better current efficiency than when using the pure $ZnCl_2$. In the present case, almost theoretical current efficiencies resulted when using a well dehydrated melt. The current density was about 43 amps./dm.^{2} at the cathode, and the cell took about 4·5 volts. (Swinburne gave four volts.) The working temperature was 450°, under which circumstances the decomposition voltage is 1·64 volts. The energy efficiency was therefore—

$$98 \times \frac{1{\cdot}64}{4{\cdot}5} = 36 \text{ per cent.}$$

One ton of zinc would require

$$\frac{1000 \times 1000 \times 96540 \times 2 \times 100 \times 4{\cdot}5}{65{\cdot}4 \times 98 \times 3600 \times 1000} = 3750 \text{ K.W.H.}$$

One H.P. year would yield 1·75 tons of zinc.

Vogel[1] has described work on the electrolysis of fused $ZnCl_2$ in externally heated cells, the $ZnCl_2$ being previously prepared by the action of commercial HCl on crude ZnO. The chief point of interest here was the method employed for the preparation of the anhydrous salt—viz. evaporation *in vacuo*. By this means the water is removed more rapidly, more effectually, and at a lower temperature than when working under atmospheric pressure. The lower temperature is probably the most important factor. As in the case of $CaCl_2$, so also here the basic salt will lose its water far more readily if it is not heated too high in the process. The vacuum used was 26–27 in. of mercury, and allowed of satisfactory dehydration.

The electrolysis was carried out in an unglazed fireclay cell. After preliminary failures, a run of 250 hours was made, using 600 amperes and producing over 3 cwt. of zinc at 91·5 per cent. current efficiency. The temperature was kept at 450°–500°, and the voltage fluctuated between 4 and 5, of which over 1 volt was lost at the electrode contacts. The energy efficiency was consequently

$$91{\cdot}5 \times \frac{1{\cdot}63}{4{\cdot}5} = 33 \text{ per cent.}$$

The electrolysis voltage (allowing for the contact losses) was considerably less than that required by the internally heated cells previously described, and that in spite of the electrolyte consisting of the badly conducting $ZnCl_2$ with no admixture of salt. This was due to the small current density, apparently only about 16 amps./dm.^{2} (very low for a fused salt electrolysis), which in its turn was rendered possible by the external heating. Low current density, external heating, and absence of salt all combined to produce the rather low current efficiency.

The electrochemical conditions being favourable, it is not easy to

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[1] *Trans. Farad. Soc.* **2**, 56 (*1906*).

see why the above processes are not worked technically. The answer is that the problem of the complete dehydration of $ZnCl_2$ has not yet been fully solved on a large scale. The addition of HCl to the frothing mass just before the final fusion (as suggested by Lorenz) would be an exceedingly difficult and troublesome operation. The preliminary electrolysis is too expensive, both as regards power and also consumption of anodes; and the difficulties of satisfactory vacuum dehydration increase enormously with the size of the plant, owing to the multiplication of leaks. To really serve, the vacuum must be a very good one. Another disturbance encountered technically is due to the difficulty of preparing iron-free $ZnCl_2$ melts. Any iron present in such an electrolyte is deposited before the zinc.[1] Not only is the current efficiency thereby lowered and the purity of the product impaired, but the metal becomes viscous, which necessitates a rise of temperature and dislocates the working conditions.

5. Aluminium

The entire world's production of aluminium is now obtained electrochemically by the electrolysis of a solution of Al_2O_3 in fused cryolite (Na_3AlF_6). The two almost identical processes employed both date from the years 1886–1889. The Hall process is used in America, the Héroult process on the Continent and in Great Britain.

The Hall cell consists of a cast-iron box, thickly lined with carbon, of external dimensions 6′ × 3′ × 3′.[2] The internal dimensions are length 4½′ and breadth 2½′, and the actual depth of the electrolyte is 6″. The carbon lining acts as a cathode until sufficient molten aluminium has collected, whilst the anode system consists of a series of carbon rods, 3″ in diameter, and 15″–18″ long when new. Each bath contains 40–50 of these, arranged in four rows. They dip right down into the electrolyte, ending 1″ or so above the layer of aluminium at the bottom.[3] A tapping-hole is provided. The electrolyte consists simply of a solution of alumina (15–20 per cent.) in cryolite (J. W. Richards).[4] AlF_3 is present in excess, and CaF_2 is often added (Haber). During the electrolysis a layer of charcoal is kept on the surface of the melt. This tends to prevent loss of heat by radiation and loss of cryolite by vaporisation, and also minimises the burning away of the electrodes by the air at the points where they emerge from the bath. On the top of this charcoal is thrown fresh alumina, which is dried by the hot gases and stirred in when the bath needs replenishing. The

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[1] *Zeitsch. Anorg. Chem.* **39**, 461 (*1904*).

[2] Haber, *Zeitsch. Elektrochem.* **9**, 360 (*1903*).

[3] Later forms of the Hall cell are said to employ fewer electrodes of a much larger cross-section.

[4] *Electrochem. Ind.* **1**, 158 (*1903*).

AlF_3 Haber mentions is probably added to replace the slight vaporisation losses which occur.

The cryolite used needs no particular purification. It will contain small quantities of iron and silica, but these will soon be removed at the commencement of the electrolysis, and any subsequent additions need not be taken into account. But a pure alumina is essential. And this is generally prepared by the Bayer process from bauxite, a hydrated oxide of iron and aluminium, containing some silica and titanic acid. The crude material, after careful roasting to ensure that all the iron is in the ferric state, is digested with caustic soda under pressure, the alumina being thereby dissolved. After dilution and filtration to remove ferric hydroxide, the liquors are treated with some precipitated aluminium hydroxide made in a previous operation, when about 70 per cent. of the Al_2O_3 present in the super-saturated solution is precipitated. After washing and drying, it is ready for use, while the NaOH, after concentration, is utilised for treating a fresh quantity of bauxite.

A unit such as the one described takes about 10,000 amperes, 200–250 for each anode carbon, and absorbs 5·5 volts. The current density at the cathode, assuming the whole bottom of the bath but no part of its sides to be active, works out at nearly 100 amps./dm.^{2} At the anode it is perhaps 500 amps./dm.^{2} [1] The joule heat keeps the electrolyte liquid, but a solidified layer is allowed to form on the inside walls of the cell in order to protect them from corrosion. In the early days of the aluminium industry, when smaller units were employed, larger current densities were required to keep the bath molten—up to 250 amps./dm.^{2} at the cathode. A higher bath voltage was consequently necessary, 7–8 volts. This is now avoided.

Cryolite, according to J. W. Richards, melts at 800° ; according to Pyne [2] at 1000°, which is probably more correct. The former value may have been determined for cryolite with a considerable excess of AlF_3. The addition of Al_2O_3 lowers its melting-point—a mixture containing 5 per cent. Al_2O_3 melts at 915° (Pyne). Further addition of Al_2O_3 appears to raise the M.P., and a mixture with 20 per cent. Al_2O_3, roughly a saturated solution, melts at 1015°, higher than the temperature for pure cryolite. If, then, pure cryolite and Al_2O_3 alone are used, the electrolysis temperature cannot be much below 1000°. As a matter of fact it is kept as low as possible, and, according to Haber, fluctuates between 900°–1000°, and never exceeds 1065°. Richards puts it as 900°–950°. If we suppose the percentage of dissolved Al_2O_3 to be high, which it must be, or else the voltage increases, then these figures certainly indicate the presence in the melt of considerable quantities of substances other than cryolite and Al_2O_3—*e.g.* the AlF_3 and

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[1] In newer cells, *lower*.

[2] *Trans. Amer. Electrochem. Soc.* **10**, 63 (*1906*).

CaF_2 mentioned by Haber. The specific resistance $\left(\frac{1}{\kappa}\right)$ of the melt Richards states to be 3 ohms/cm.[3]

Neumann[1] has also described the aluminium bath as at present used, here presumably the Héroult type. It is round in section, not rectangular, and is made of wrought iron. The bottom is covered with carbon plates and serves as cathode at the beginning of the electrolysis. The anodes are distributed regularly over the whole surface of the melt. They are 40 cm. long and of large cross-section, 35 × 35 cm., the result being that the anodic current density is only 80–100 amps./dm.[2] The baths are built in, but space is left for the passage of a regulated current of air for the purposes of cooling their sides and of producing a solidified lining of electrolyte (Fig. 103).

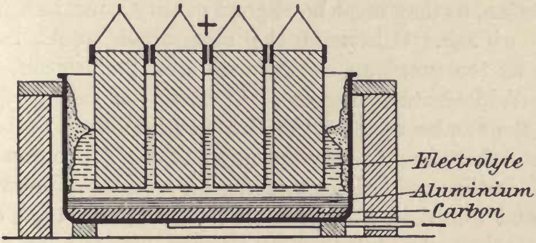

FIG. 103.—Héroult Aluminium Cell.

The greater part of the surface of the bath is also covered with a crust during working, and this must be broken through when necessary to add alumina. Of this the electrolyte contains 10–20 per cent., and some NaCl is sometimes added at the start to facilitate the fusion of the electrolyte. The working voltage is about 6 volts, but varies considerably with the distance apart of anode and cathode. The temperature is below 1000°. From statements from other sources we gather that an average unit carries 7000 amps. and absorbs 7 volts.[2]

The mechanism of the process is simple. The dissolved Al_2O_3 furnishes $Al^{\cdots}$ and O'' ions. The $Al^{\cdots}$ ions are cathodically discharged on the bottom of the bath, and the metal drawn off at suitable intervals. Calculating from the specific gravities of aluminium, cryolite, and alumina at room temperature, one would not expect the metal to

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[1] *Zeitsch. Elektrochem.* **16**, 230 (*1910*).

[2] At Dolgarrog, the Aluminium Corporation has baths taking 63·5 h.p. and containing ten anodes (baked at 1300°–1400°). The metal is tapped twice weekly, a cell yielding 7–7¼ cwts. per week (corresponding to 0·29 metric ton per h.p. year). 2 kilos. (almost) Al_2O_3, 0·1 kilo. cryolite, and 0·67 kilo. of anodes are consumed per kilo. of metal. The whole cell is lined with carbon, which is renewed every 6–8 months (Sept. 1912).

collect on the bottom of the cell, but rather to float on the surface. J. W. Richards[1] has, however, shown that fused aluminium is denser than fused cryolite, or the solution of Al_2O_3 in cryolite. Thus:

Substance	Specific gravity	
	Molten	Solid
Commercial aluminium	2·54	2·66
Commercial Greenland cryolite	2·08	2·92
Do. saturated with Al_2O_3.	2·35	2·90
Cryolite + aluminium fluoride ($Al_2F_6.6NaF + 2Al_2F_6$)	1·97	2·96
Do. saturated with Al_2O_3	2·14	2·98

The anodic oxygen does not leave the bath as such, but attacks the carbons, forming CO, which subsequently burns to CO_2 at the surface of the melt.

Anodes.—This loss of anodes is a heavy item in the cost of aluminium production, as they must be of good quality, containing a minimum percentage of ash. Otherwise the aluminium would become contaminated to too great an extent with iron and silicon. And they should not disintegrate during use. Clacher[2] has described the manufacture of the anodes used by the British Aluminium Co. Petroleum coke is first calcined up to temperatures of 2000° (?) to remove volatile matter. It is then pulverised, mixed with a suitable binding medium, moulded, and kilned in a furnace for five days at 1400°, after which the product is slowly cooled. The finished blocks have a section of 10″ square. For every pound of metal produced, 0·5–0·7 lb. of anode is consumed, approximately equivalent to the quantity of metal formed according to the equation $Al_2O_3 + 3C \longrightarrow 2Al + 3CO$. The anodes are also themselves directly attacked by atmospheric oxygen. This burning away of the anodes necessitates their continually being lowered deeper into the cell. It is as far as possible minimised by coating the surface of the electrode with some suitable material—*e.g.* whitewash.

The current efficiency obtained is about 75–80 per cent., though it can vary considerably. Haber quotes the following data:—

Voltage 5·5 volts.		Current 7520 amps.	
Yield of metal per 24 hours.	43·1 kilos.	Current efficiency 71 per cent.	
Energy consumption per ton metal	23,000 K.W.H.	1 H.P. year yields	0·28 ton.

The losses are chiefly due to the *metal-fog* phenomenon. Anode and cathode are only 3 cm. apart, and the aluminium is far above its melting-point (665°). There is therefore a continual regeneration of alumina at the anodes. Another loss that must not be overlooked (Haber) is that due to short circuits between anode and cathode.

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[1] *Zeitsch. Elektrochem.* 1, 367 (*1895*).

[2] *Metall. Chem. Engin.* **9**, 137 (*1911*).

This is to some extent inevitable with constant individual adjustment of the anodes. Our knowledge of the decomposition voltage of the cryolite solution is very scanty. No reliable experimental data exist. If we calculate according to the Helmholtz-Thomson Rule, as Richards has done, we get the following values :—

NaF	4·7 volts
AlF_3	4·0 volts
Al_2O_3	2·8 volts.

These values, though far from being absolutely correct, will stand in the right order, and we thus see that the Al_2O_3 will most easily undergo decomposition. When a very high current density is used at the cathode, the liberation of sodium has been observed. Fluorine can be formed anodically if the Al_2O_3 content of the electrolyte has become very low, or if the current density used is too high. In that case there is a marked 'anode effect,' and the voltage rises considerably. The correct decomposition voltage of Al_2O_3 will be less than the above figure. The value of 2·2 volts suggested by Richards is probably near the correct one, and we shall use it in the following calculation. (Richards further says that it can be regarded as 2·8 volts, the decomposition voltage of Al_2O_3 calculated as above, *minus* 0·6 volt, which corresponds to the heat of formation of CO from electrode and evolved oxygen. The coincidence is of course really very largely a chance one.) The energy efficiency is therefore, assuming a voltage of six volts—

$$75 \times \frac{2{\cdot}2}{6} = 27{\cdot}5 \text{ per cent.}$$

The study of the production of aluminium by this method has been the object of several laboratory investigations.[1] Haber and Geipert carried out three experiments with currents of 300–400 amperes, their cell consisting of a thick-walled carbon crucible hollowed from a carbon block. A carbon anode was used, its distance from the bottom of the crucible (0·5–1 cm.) being capable of exact regulation. The first experiment was carried out with 1000 grams artificial cryolite containing an excess of AlF_3 and 200 grams Al_2O_3. During the run of five hours, 885 grams more of cryolite and 927 grams of Al_2O_3 were gradually added. The average current was 310 amperes. The voltage started at 7·5 and gradually rose during the experiment to 10 volts. This increase was due to the progressive consumption of the anode, causing a rise in current density. The cathodic current density was about 3 amps./cm.^{2}, the anodic about 10 amps./cm.^{2} at the start, and rising continuously during the run. A current efficiency of 54 per cent. was obtained. The current density being considerably

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[1] Haber and Geipert, *Zeitsch. Elektrochem.* **8**, 1, 26 (*1902*). Thompson, *Electrochem. Ind.* **7**, 19 (*1909*). Neumann and Olsen, *Zeitsch. Elektrochem.* **16**, 230 (*1910*). Richardson, *Trans. Amer. Electrochem. Soc.* **19**, 159 (*1911*).

higher than that used technically, the voltage was accordingly also greater. The electrolyte was, further, too rich in Al_2O_3, and therefore too dense, and small particles of aluminium were seen to rise to the surface and re-oxidise. The second experiment was very similar. The cathodic current density and mean voltage were still higher—3·36 amps./cm.^{2} and 9·3 volts. The yield was 45 per cent. The third run was carried out with natural cryolite, containing a smaller percentage of AlF_3 and therefore melting less easily, but also being less volatile. The electrolysis proceeded much as before, the current efficiency being 43·5 per cent. The chief difficulty lay in bringing the anode sufficiently near to the bottom of the cell without short-circuiting.

Discussing the above results in a later paper,[1] Haber recommends 5 amps./cm.^{2} as the most suitable anodic current density, and 1 part alumina : 5 parts cryolite as the best electrolyte. To ensure a low voltage, anode and cathode should be as close together as possible. This, however, has the disadvantage of lowering the current efficiency. The alumina used must be easily soluble, otherwise a pasty mass settles down over the cathode, causing non-uniform current densities, raising the voltage, and probably assisting in the formation of short circuits. The consumption of the anode carbons was found to be almost equal to the weight of aluminium produced. As we have seen, it is far less in technical practice. The carbon anodes are the chief source of the small quantity of silicon in the product. Those used by Haber and Geipert contained 0·183 per cent. SiO_2.

Thompson used cell and anode of graphite and a current of 900 amperes. He could not satisfactorily reproduce the results of Haber and Geipert, chiefly because his current density was too high, 10 amps./cm.^{2} at the anode, his normal working voltage being about 10 volts. The alumina in the bath became rapidly exhausted, and a marked anode effect followed, due to the discharge of F' ions at a high current density. The voltage rapidly rose and the electrolysis was disturbed. The best current efficiency obtained was 49 per cent.

Neumann and Olsen used vessels of iron and hard carbon anodes, which do not disintegrate as Acheson graphite does. The anodic current density was lower, about 2 amps./cm.^{2}, and under these circumstances the electrolysis proceeded quietly and regularly. An ‘anode effect’ was rarely noticed unless the current density exceeded 4 amps./cm.^{2} The height of the anodes was regulated every half-hour, and the electrodes were kept 6 cm. or less apart. The average voltage was 9 volts. Current efficiencies up to 70 per cent. were obtained, but more often 60 per cent. Electrolysis with an anodic current density

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[1] *Zeitsch. Elektrochem.* **8**, 607 (*1902*).

of 1 amp./cm.^{2} or less (as in the Héroult process) required external heating. This is, of course, due to the fact that heat losses by radiation are far greater proportionally with a laboratory unit than with a technical one.

Richardson employed a cell of wrought-iron plates. The bottom (cathode) was graphite, the sides being of sand and asbestos and ultimately of solidified electrolyte. The anodic current density was 3 amps./cm.^{2}; the voltage varied very considerably, the mean value being 10–12 volts. He obtained average current efficiencies of 70–75 per cent., but they also showed great variations (46–93 per cent.). The working temperature and the composition of the electrolyte corresponded closely to those used in practice.

The results of these investigations point to the advisability of using low anodic current densities. Not only are 'anode effects' thereby excluded, but both voltage and anode consumption are less in the regular course of work. The excessive anode losses observed by Haber and Geipert are directly attributable to their very high current densities. There can be little doubt that the 'anode effect' which occasionally appears is not due to a layer of oxygen or oxides of carbon, but to one of fluorine gas, which is formed owing to the bath having become depleted of alumina. It thus falls into line with all other anode effects due to evolved halogens,[1] particularly with that noticed by Muthmann, Hofer and Weiss[2] in the electrolysis of pure molten cryolite, which was very marked at a current density of 4–5 amps./cm.^{2}

6. The Acker Process for Chlorine and Caustic Soda

This process,[3] the best conceived and most successful of those involving the electrolysis of fused NaCl, was worked for several years at Niagara on a considerable scale, but has not been re-started since the works were burnt down some years back. The difficulties met with were undoubtedly enormous.

The fused NaCl was electrolysed in a cell of cast-iron lined with magnesia bricks. The cathode covering the bottom of the cell was of fused lead. On this rested a 6″ layer of molten salt, into which dipped four graphitised carbon anodes, attached to carbon rods passing through the roof of the cell. These rods were coated with fireclay and cement to protect them from the hot gases. The lower (active) surface of an anode was 6·5 dm.^{2}, and at a current density of about 300 amps./dm.^{2} each anode took 2000 and each unit 8000 amperes. The anodes were not attacked under these conditions as might have been expected.[4] The chlorine was drawn off, together with about nine

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[1] P. 164.

[2] *Lieb. Ann.* **320**, 237 (*1901*).

[3] *Trans. Amer. Electrochem. Soc.* **1**, 165 (*1902*). *Electrochem. Ind.* **1**, 54 (*1902*). *Zeitsch. Elektrochem.* **9**, 364 (*1903*).

[4] *Electrochem. Ind.* **4**, 477 (*1906*).

times its volume of air (entering the cell through gaps in the walls), and converted into bleach. The cathodic lead-sodium alloy left the electrolysis cell and entered a smaller chamber where it was acted on by a jet of steam at 40 lb. pressure. This oxidised the sodium to NaOH and blew the mixture of lead and fused alkali over a partition into a third chamber. Here separation into a heavy layer of lead and a lighter layer of caustic took place. The former returned to the electrolysis cell by a suitable channel, and the latter continually flowed

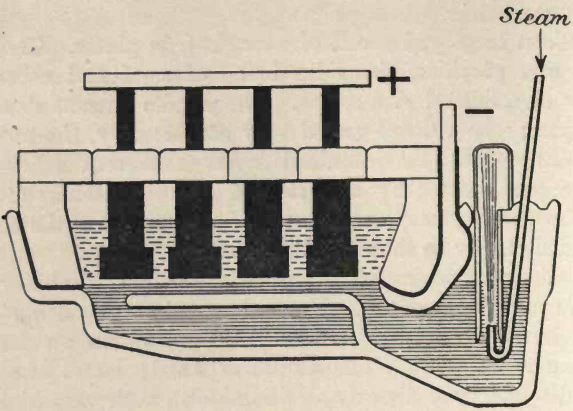

FIG. 104.—Acker Cell. Front Elevation.

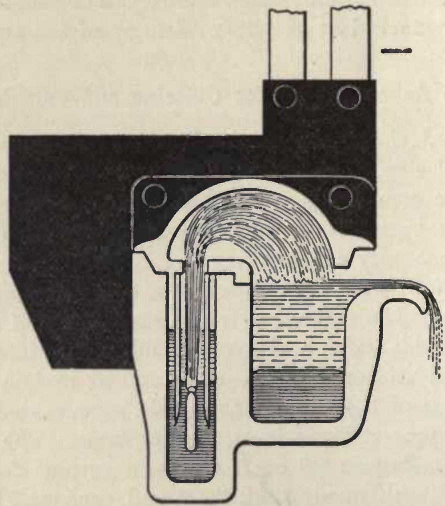

FIG. 105.—Acker Cell. Side Elevation.

off. The hydrogen burnt with a large flame at the mouth of this chamber.

It will be seen that the steam jet, besides separating the sodium from the lead, also circulated the latter. By means of a horizontal partition in the electrolysis cell it was arranged that the metal was always efficiently charged with sodium between successive treatments by the steam. Fig. 104 is a sectional front elevation of the cell, showing the electrolysis and steam chambers, whilst the side elevation (Fig. 105) shows the steam jet and the separating chamber.

The working temperature in the cell was about 850°, the melting-point of the salt used being 775° (impure). Each cell absorbed between 6–7 volts. The current efficiency averaged 93–94 per cent., rarely fell below 90 per cent., and often touched 100 per cent. Before being fed in through charging hoppers, the crude salt used was dried, but not otherwise purified. Calcium and magnesium salts present consequently appeared in the product as hydroxides. At the temperatures worked at the NaOH was always commercially anhydrous, even when using excess of steam. It was 98 per cent. pure after standing and packing, the 2 per cent. being mainly Na_2CO_3 and CaO.

Many difficulties were encountered in working out this process. At one time bleach could not be made satisfactorily owing to a little HCl in the chlorine, probably derived from aqueous vapour entering the furnace. Large quantities of chlorine used to escape into the air. The costs for repairs were very high. Crusts of insoluble salts forming over the surface of the lead cathode were a great source of trouble. At the beginning, too low current densities were used and gave bad results. What the exact reasons were that decided against the restarting of the process is not generally known.

The advantages of the process were the comparatively cheap first cost of plant and the avoidance of all evaporation charges. Against these points we must set the high power expenditure and cost of repairs. Assuming 6·5 volts and a 93 per cent. current efficiency, we calculate that

1 ton NaOH required

$$\frac{1000 \times 96540 \times 100 \times 6{\cdot}5}{93 \times 40 \times 3600} = 4700 \text{ K.W.H.}$$

1 H.P. year produced 1·39 tons NaOH.

Literature

Lorenz. *Die Elektrolyse geschmolzener Salze*, vol. i.

CHAPTER XXIV

ELECTROTHERMICS IN THE IRON AND STEEL INDUSTRY

General.—The introduction of electrochemical methods into iron and steel production has come comparatively late, and the recent great advances consequently appear the more striking. There is little doubt that in the near future the electrometallurgy of iron and steel will rank with electrolytic copper refining, the fixation of atmospheric nitrogen by the electric arc, and the electrolytic manufacture of potash and soda as a chemical industry of the first rank.

We can distinguish three separate fields in which electrothermic methods are employed. They are

(*a*) The production of pig-iron from ore;

(*b*) The production of refined steel from pig-iron, from steel of a poorer quality, or from scrap;

(*c*) The manufacture of ferro-alloys, for use in steel refining or in the production of alloy steels.

The historical order of development is the reverse of the above. It is a commonplace how the rise of the ferro-alloy industry about twelve years back resulted essentially from a crisis in the carbide industry, the works being compelled to use their plant in some other way or else to shut down. About the same time certain investigators were experimenting on electric steel production, their guiding idea being the fact that electric heat permits of far better utilisation than heat from fuel. The economic success of the electrothermic ferro-alloy industry undoubtedly acted as a stimulus, the result being the rapid development of electric steel refining which has taken place in the last decade. A circumstance which has already favoured, and which will favour still more in the future, the utilisation of these methods is the increasing demands made by modern conditions on all kinds of steel, whether for machine or tool work or for constructional purposes. Far greater strains and more severe usage generally must be borne than has hitherto been the case, and suitable high quality materials, whether carbon or alloy steels, are best prepared in the electric furnace. The subject of the electrical production of pig-iron has recently attracted serious attention, but only in certain countries where ore and water-power are plentiful and suitable fuel dear, and it is unlikely that the industry will find a footing elsewhere.

1. Pig-iron Production

The Blast Furnace Process.—The essential processes occurring in the ordinary blast furnace are as follows: The charge consists of ore (usually a hydrated Fe_2O_3 or magnetite with impurities), slag-forming materials (exact nature depending on the character of the ore), and fuel (generally coke). This fuel serves a double purpose. It is burnt to CO at the bottom of the furnace by air blown in through the tuyeres. The liberated heat liquefies the reduced iron and the slag, and preheats the descending charge, whilst the CO formed effects the reduction of the ore. In doing this, it is partly oxidised to CO_2, and the mixed gases, essentially nitrogen, CO, and CO_2, leave the top of the furnace. The ratio $\frac{CO}{CO_2}$ in this mixture is usually about 2 : 1. The heat carried by the gases is used for steam raising. Often the heat of combustion of the CO content is similarly utilised, the gases being burnt under steam boilers. In other cases, after filtering out the dust, they are burnt in gas engines.

The Electric Furnace Process.—In an electric pig-iron furnace the conditions are rather different. The charge—as before a mixture of ore, flux, and fuel—is fed down over an electric arc. No air is blown in. The reduction of the iron oxide takes place through the solid fuel, and the necessary energy required to effect this, together with the heat absorbed by metal, slag and gases, is provided by the current, not by the combustion of further quantities of fuel. As in the blast furnace, the fuel will partially give CO, partially CO_2. The obvious essential difference between the two methods consists therefore in the fact that the *energy absorbed by the reaction*

$$\text{iron oxide} + \text{carbon} \longrightarrow \text{iron} + \text{oxides of carbon}$$

is supplied in the one case by the combustion of more fuel and in the other by electrical energy.

Thermochemical Comparison.—An exact comparison of the two processes is only possible if certain specific conditions are assumed. Such calculations have been made by several authors.[1] We will here treat the problem on the broadest lines only. Suppose first the ore to be pure Fe_2O_3, and to be reduced by carbon with the formation of a gaseous mixture of two volumes CO : one volume CO_2. The equation will be

$$4Fe_2O_3 + 9C \longrightarrow 8Fe + 6CO + 3CO_2.$$

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[1] J. W. Richards, *Electrochem. Ind.* **5**, 165 (*1907*), and *Trans. Amer. Electrochem. Soc.* **15**, 53 (*1909*). Härdén, *Electrochem. Ind.* **7**, 16 (*1909*); Catani and Neumann, *Electrochem. Ind.* **7**, 153 (*1909*); Yngström, *Metall. Chem. Engin.* **8**, 11 (*1910*).

The approximate heats of formation at room temperature are

Fe_2O_3	201,000 Cals.	per kilo.-mol.
CO	29,200 Cals.	do.
CO_2	97,200 Cals.	do. ;

and we calculate that the formation of one ton of iron according to the above equation is endothermic, and requires

$$(804000 - 292000 - 175000)\,\frac{1000}{448} = 752000 \text{ Cals.}$$

at room temperature.

But both iron and gases leave the furnace at a high temperature. It is generally assumed that the iron would require 300 Cals. per kilo. for melting and heating to the tapping temperature. A ton therefore needs 300,000 Cals. Assuming that the gases leave the furnace at 800°, and that C_p (mean value) between 0° and 800° for CO and CO_2 is 6·9 and 9·1 respectively, we calculate that 123,000 Cals. are required per ton of iron. We must now take account of the impurities present, some of which are reduced and enter the iron, but most of which are slagged off. We can suppose 100,000 Cals. to be employed in this reduction (chiefly of silica). And we can roughly assume that 750 kilos. of slag are produced per ton of iron, and that each kilo. carries 500 Cals. This will be an outside figure, and we can neglect radiation losses, etc. The total energy which must be supplied is therefore

For reduction of iron	752,000 Cals.
For heating and melting iron	300,000 Cals.
For reduction of impurities	100,000 Cals.
For heating and melting of slag	375,000 Cals.
Carried by gases	123,000 Cals.
Total	1,650,000 Cals.

$$\text{equivalent to } \frac{1650000 \times 4{\cdot}19}{3600} = 1920 \text{ K.W.H.}$$

When, however, fuel is used, far more must be added than would be calculated from the above figure. The use of fuel means the use of air to burn it, and this involves the heating up of enormous quantities of dilute combustion gases. Assuming that this fuel also gives a mixture of $2CO : 1CO_2$, we have

$$3C + 2O_2 + 8N_2 \longrightarrow 2CO + CO_2 + 8N_2.$$

Taking C_p for nitrogen as equal to that for CO, we calculate

Heat liberated by CO_2 formation	97,200 Cals.
Heat liberated by CO formation	2 × 29,200 Cals.
Total	155,600 Cals.

Heat absorbed by gases $800\,[9{\cdot}1 + 10(6{\cdot}9)] = 62{,}500$ Cals.

Hence 36 kilos. of carbon only produce (155,600 – 62,500) Calories *net*. To get 1,650,000 Cals. we need

$$36 \times \frac{1650000}{(155600 - 62500)} = 640 \text{ kilos. carbon.}$$

Adding the 240 kilos. required for the reduction of the iron and 60–70 kilos. for carbonisation of the iron and for reduction of impurities, we arrive at a figure (940–950 kilos.) which agrees very well with the 1,000–1,100 kilos. of 90 per cent. coke required in modern blast furnace practice per ton of iron produced.

We must also take into account the difference between the calorific values of the furnace gases in the two cases. If we calculate from the above data the sum of the heat actually carried by the gases from the furnace and the heat which can be produced by the oxidation of their CO content to CO_2, we arrive at a value (per ton iron) of about 4,600,000 Cals. for a blast furnace and 1,150,000 Cals. for an electric furnace. The estimates of the respective proportions of these amounts of heat which are available for power production, after satisfying all the needs of the furnace, vary very widely. If we assume, however, that the surplus is greater in the case of the blast furnace by about 400 K.W.H. per ton of iron produced, we shall not be far wrong. Broadly speaking, then, the electric furnace will begin to compete with the blast furnace when 1,920 K.W.H. (or 2,300 K.W.H. if the furnace gases be taken into account) are cheaper than 0·7 ton coke. This calculation holds for the given conditions of ore and fuel only, assumes a very high electric furnace efficiency, and takes no account of questions of plant or metallurgical advantages and disadvantages.

Stassano's Experiments.—Stassano was the first worker in this field to build a pig-iron electric furnace of technical size. He experimented with several types of construction, and particularly endeavoured to produce a high-grade material (not an ordinary cast-iron) from the ore in a single operation. He managed, in fact, to produce a ductile iron containing a total of 0·35 per cent. of impurities. But this was only achieved by the use of exceptionally pure materials and by carefully watching the operation in a manner impossible under technical conditions.

The Haanel Reports.—In Canada there are enormous deposits of different iron ores, many very considerable undeveloped water-powers, and vast quantities of wood suitable for charcoal making, but comparatively little coal. These circumstances suggested to the Canadian Department of Mines that there would be a great future for electrical iron ore smelting in that country if it proved at all practicable technically. The immediate outcome has been the valuable series of reports compiled by Dr. Haanel, the director of the Department. A commission visited Europe in 1904 to report on the different electrothermal processes then used in the iron and steel industry. The most important experiments witnessed on electrothermal reduction of iron ores were carried out by Keller [1] at Livet. Although using a furnace really designed for ferro-chrome or ferro-silicon manufacture,[2] Keller was able, by suitable variations of the charge, to produce at will white or gray cast-iron, in all cases exceedingly low in sulphur. His furnace worked perfectly smoothly. The metal was further so hot that good castings could directly be made when tapping the furnace. The energy consumption varied rather considerably. The average was about 2,290 K.W.H. per ton (2·8 tons per H.P. year), whilst 310 kilos. of coke and 17 kilos. of carbon electrodes were also necessary.

An important series of experiments was next carried out at Sault Ste. Marie in Canada by Héroult.[3] Keller had shown that a good quality hematite could be reduced. It now remained not only to see whether Keller's results could be improved upon, but also to discover whether electrical methods were also applicable to Canadian conditions—to see, that is, whether magnetite and ores rich in sulphur but poor in manganese could be smelted, and whether charcoal could be used instead of coke as a fuel. Preliminary experiments were first made with different kinds of furnaces. In one case compressed air was blown in near the top in order to burn the CO, and thus preheat the charge, but the latter became sticky and tended to hang, and the electrode was rapidly consumed. The final type of furnace was exceedingly simple. A carbon crucible formed one electrode, the side walls being of firebrick, the whole enclosed in an iron casing and open at the top. The second electrode was also of carbon, suspended vertically in the middle of the furnace and adjustable by a pulley. Round this electrode the charge was heaped up. The furnace took about 5,000 amps. at 36 volts, its power factor being 0·92, considerably higher than that of Keller's furnace in Livet.

The results were very encouraging. Using hematite, the energy consumption was 1,700 K.W.H. per ton of product (1 H.P. year = 3·8 tons). Magnetite, with which difficulties had been anticipated on account of its high electrical conductivity, also smelted readily, the energy needed per ton of iron being about 1,900 K.W.H. (1 H.P. year = 3·4 tons). From sulphur-rich ores, magnetite and roasted pyrrhotite, a pig-iron very low in sulphur was readily obtained. The roasted pyrrhotite furnished a product containing 4 per cent. Ni at an energy consumption of 2,570 K.W.H. per ton (2·6 tons per H.P. year), a much more favourable result than was obtained by Sjöstedt [4] in his earlier experiments. Finally, an ore with nearly 18 per cent. TiO_2 gave a product with only 1–1·3 per cent. Ti, nearly all that metal entering the slag. The experiments also proved the suitability of charcoal

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[1] *Electrochem. Ind.* **2**, 280, 479 (*1904*).

[2] P. 466.

[3] *Trans. Farad. Soc.* **2**, 120 (*1906*).

[4] *Trans. Amer. Electrochem. Soc.* **5**, 233 (*1904*).

as a reducing agent. The material employed was of poor quality, and on that account, and also because large quantities burnt away at the top of the furnace, the actual amount consumed during the experiments has little significance. Haanel calculates 0·5 ton per ton of pig-iron under normal conditions, and 8 kilos. of electrodes. After the conclusion of the experiments the furnace was employed in the manufacture of ferro-nickel pig from roasted pyrrhotite. The smelting was stated to proceed very smoothly, but the power-consumption was greater (3,010 K.W.H. per ton) than that given by Héroult and Haanel, and the electrode consumption far higher.

Lyon Furnace.—The furnaces of both Keller and Héroult were of the type used for years in the ferro-alloy industry. Investigations have also been carried out with furnaces closely resembling the ordinary blast furnace in construction. The guiding ideas here are (*a*) the collection of the gases, and (*b*), by causing them to stream up through a long column of charge, the utilisation as far as possible of their heating and reducing properties before they leave the furnace. Such a shaft furnace, designed by Lyon, has been working some years in California.[1] The ore smelted is a very pure magnetite (68–70 per cent. Fe), and the reducing agent is charcoal, $\frac{1}{3}$ ton per ton of pig-iron. In general shape of hearth, shaft, and position of electrodes, the furnace resembles the one described below (Fig. 106). As to its exact behaviour we have only scanty data. It is fed with three-phase current, each phase (they are apparently not linked) having two electrodes, and taking 10,000–21,400 amps. at 35–75 volts, thus 750 K.W. The total power in the furnace is therefore 2,250 K.W. As the output per day is 25 tons (tapped 5 tons at a time), the energy consumption is $\frac{2250 \times 24}{25} = 2160$ K.W.H. per ton of pig (3 tons per H.P. year). This is a maximum expenditure, as we assume here $\cos\theta = 1$. More furnaces are being built.

The Domnarfvet Experiments.—The question was simultaneously studied in Sweden, and the furnace described below devised by Grönwall, Lindblad and Stålhane.[2] The figures given refer to a 600 K.W. unit at Ludwiga. The furnace body itself consisted of two parts, crucible and shaft. The latter varied in internal diameter at different heights (Fig. 106) very much as does an ordinary blast furnace. The reason of this form of construction is that the descending charge was then found not to fill up the crucible, but to lie in it at a definite angle—50°–55° to the vertical—and, by means of arching the crucible roof, a contact between wall, electrode and charge was avoided, there being always a ring-shaped layer of gas between the charge and the places where the electrodes passed through the roof; otherwise the

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[1] *Trans. Amer. Electrochem. Soc.* **15**, 39 (*1909*).

[2] *Trans. Farad. Soc.* **5**, 306 (*1909*); *Stahl und Eisen*, **29**, 1801 (*1909*); *Metall. Chem. Engin.* **8**, 11 (*1910*).

temperature became high enough to fuse the lining at those points. This lining was of magnesite, as were also the sides of the crucible. The shaft was lined with suitable firebricks, and its weight supported on cast-iron pillars (not shown). The three electrodes consisted each of two carbons 63″ × 11″ × 11″, the cross-section of each electrode being thus 242 inch^2. They were clamped in steel holders, passed through guides, and entered the furnace through water-cooled gas-tight stuffing boxes. Regulation was effected by a cable and pulley.

The furnace gases were collected and utilised. For this purpose the furnace was closed and provided with special charging arrangements, designed to avoid any possibility of an explosion on charging. Finally, an important feature was the means used to cool the roof of the crucible. A portion of the gas leaving the furnace throat was sucked off into a dust-catcher by means of a fan, and thence forced down into the crucible by three pipes or tuyeres (A). It entered at about 200°, abstracted much heat from the roof and the upper surface of the ore, gave it up to the descending charge, and was very effective in prolonging the life of the roof. The other exit for the furnace gases worked automatically when the pressure reached a certain figure. Three-phase current was used. Cos θ at 25 cycles was 0·8–0·9, at 60 cycles 0·7, and the furnace voltage was about 40 volts. During the tests described by Haanel, the current was very low, the furnace being worked at far below its full load.

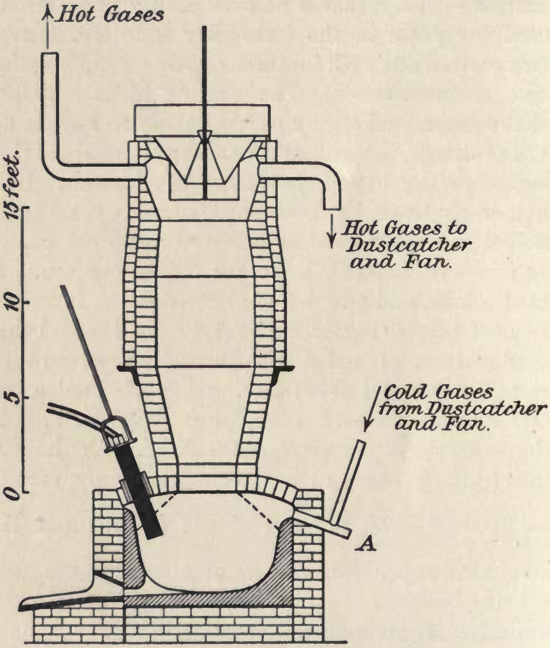

FIG. 106.—Domnarfvet Pig-iron Furnace.

Using a magnetite containing 60–63 per cent. iron, the energy consumption with this furnace averaged 3180 K.W.H. per ton of product (2·1 tons per H.P. year). The carbon consumption was low, the equivalent in coke or charcoal of about 280 kilos. of pure carbon per ton of iron. About 8 kilos. of electrodes were burnt per ton of iron, the total consumption amounting to 30 kilos. per ton. The furnace ran exceedingly quietly, and the electrodes needed no adjustment over long periods. The pig-iron obtained had occasionally 1 per cent. or less of carbon, but generally 2–3 per cent. The sulphur was exceedingly low; all the phosphorus entered the iron. The results of these trials were regarded as satisfactory, and a 2000 K.W. furnace of essentially the same construction was installed at Trollhättan. This furnace has run for six months uninterruptedly, yielding much improved results.[1] It takes two-phase current, the phase voltage varying between 50–90 volts, and is provided with four electrodes, each 2 metres long and 66 × 66 cm. in cross-section. These have an average life of 750 working hours, and the total electrode consumption per ton of iron (burnt and scrapped) amounts to only 10 kilos. The proportion of charcoal required is greater than with the smaller Ludwiga furnace, but the average energy expenditure per ton of iron has fallen to 2390 K.W.H. (2·7 tons per H.P. year).

The following table contains a summary of the results obtained in this field. The great differences apparent are largely to be ascribed to differences in composition of charge, etc., etc. The superiority of the Héroult-Haanel results (short runs) over all others is nevertheless remarkable.

TABLE LXVI

Furnace	Load of same	Ore used	K.W.H. per ton	Tons per H.P. year
Keller	400–700 K.W.	Hematite, — 69 per cent. Fe	2290	2·8
Héroult	170 K.W.	Hematite, — 62 per cent. Fe	1700	3·8
Do.	Do.	Magnetite, 55–59 per cent. Fe	1900	3·4
Do.	Do.	Pyrrhotite, 46 per cent. Fe + 2 per cent. Ni	2560–3010	2·2–2·6
Lyon	2250 K.W.	Magnetite, 68–70 per cent. Fe	2160	3·0
Ludwiga	600 K.W.	Magnetite, 60–63 per cent. Fe	3180	2·1
Trollhättan	2000 K.W.	Magnetite, 50–67 per cent. Fe	2390	2·7

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[1] *Zeitsch. Elektrochem.* **17**, 649 (*1911*).

Questions of fuel and energy apart, electrothermal methods of pig-iron production possess certain advantages dependent on the high temperature of reduction. Firstly, refractory ores can be treated which will not satisfactorily yield to ordinary metallurgical methods. The possibility of thus producing a good pig-iron from titaniferous ores has been repeatedly shown.[1] Secondly, a metal very low in sulphur is made as the result of a simple operation. It can be run directly into an electric steel furnace and refined under exceptionally favourable conditions. In spite of these facts, however, it is improbable that this industry will gain a footing in many countries. Blast-furnace reduction will be cheaper.

2. Electric Steel. General

The first workers on electric steel were chiefly concerned with making a product to compete with crucible steel. Because of the high costs of fuel and labour in this latter process, and because of the short life of the small units necessarily used, the field was essentially promising, and the electric furnace has achieved a very large measure of success therein. It has, in the last three or four years, commenced to invade other fields, and is likely to be largely used in the future for the production of a metal suitable for rail steel, etc.

The various methods of working which have been or are more or less used can be classified as follows :—

(*a*) Starting material pig-iron. Charged cold or in the fused condition from blast furnace or electric furnace. Then treated with fluxes and either with iron oxide (ore), by means of which the carbon is oxidised, or with scrap low-carbon steel or low-carbon iron, or with a mixture of the same. Product similar to open-hearth steel.

(*b*) Starting material steel from an ordinary Bessemer or acid converter and fluxes. Refined to steel of open-hearth quality, or further to crucible-steel quality.

(*c*) Starting material open-hearth (Siemens-Martin, Wellman) steel and fluxes. Refined to a crucible steel.

(*d*) Starting material scrap steel or low-carbon iron and fluxes. Refined to a crucible steel.

A ‘crucible steel’ can, of course, be either a carbon or an alloy steel. So far (*c*) and (*d*) have been most frequently used ; (*a*) and (*b*) not to such an extent. The United States Steel Corporation has refined acid converter steel in the Héroult furnace, the Kjellin furnace has been employed to produce high-grade steel from pig-iron and scrap or pig-iron and briquetted ore, and it is intended to use electric refining

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[1] Sault Ste. Marie experiments. Also *Electr.* **63**, 934 (*1909*) ; Gin, *Trans. Amer. Electrochem. Soc.* **11**, 291 (*1907*) ; Greene and Macgregor, *Trans. Amer. Electrochem. Soc.* **12**, 65 (*1907*).

in combination with the new electric iron furnaces to be erected in Sweden.

Thermochemical Relations.—The theoretical minimum of energy needed for the formation of a ton of steel under various given conditions has been calculated by Neumann,[1] using recently revised values for the specific and latent heats of iron. With a cold charge it is the sum of the heat required to heat the iron to its melting-point, to melt it, to heat the liquid metal to the tapping temperature and to reduce any iron oxide present. From this is subtracted the heat gained by the combustion of the carbon, silicon, etc., etc., which are removed. With iron or steel charged molten, the energy required is correspondingly less. The values given take no account of heat lost during the process by radiation and other causes. Neumann assumes that a pig-iron containing 3·6 per cent. C, 1·68 per cent. Si, 1·1 per cent. Mn, 0·62 per cent. P is refined to a product with 0·96 per cent. C and 0·28 per cent. Si, and calculates—

500 K.W.H. per ton of steel using cold pig-iron and iron ore.
190 K.W.H. per ton of steel using liquid pig-iron and iron ore.
460 K.W.H. per ton of steel using 670 kilos. pig-iron; 210 kilos. ore; 45 kilos. lime; 285 kilos. scrap—all charged cold.
230 K.W.H. per ton of steel using the same charge, the pig-iron being molten.
280 K.W.H. per ton of steel using 675 kilos. pig-iron; 350 kilos. scrap—both charged cold.
53 K.W.H. per ton of steel using the same charge, the pig-iron being molten.
330 K.W.H. per ton of steel using 365 kilos. pig; 650 kilos. scrap—charged cold.
210 K.W.H. per ton of steel using the same charge, the pig being molten.

For the further refining of *open-hearth steel*, he gives the theoretical energy consumption as 77 K.W.H. per ton.

Mechanism of Refining Processes.[2]—The actual mechanism of electrical steel refining is interesting. The raw material contains excess of carbon, sulphur, and phosphorus, which must all be eliminated. The metal is first submitted to the action of an oxidising and basic slag, either in an electric furnace or in an open-hearth furnace, before charging into the former. This slag generally contains Fe_2O_3, which oxidises the carbon to CO and the phosphorus to P_2O_5, the latter entering the slag. The metal, now low in carbon and phosphorus, still contains most of its sulphur and also dissolved oxides (chiefly iron). This sulphur is present as sulphides of manganese and iron, in equilibrium with the same sulphides dissolved in the slag. The ratio $\frac{\text{S in slag}}{\text{S in metal}}$ depends essentially on the temperature and basicity of the slag, becoming greater as these two factors are increased. The sulphur can only be

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[1] Article in Askenasy's *Einführung in die technische Elektrochemie*, vol. i. (1910).

[2] Geilenkirchen and Osann, *Electrochem. Ind.* **6**, 405 (*1908*). Amberg, *Electrochem. Ind.* **7**, 115 (*1909*).

completely removed from the steel by converting it into a sulphide insoluble in the latter. CaS is the only one we need consider. But as long as oxides of iron or other oxidising agents are present, formation of CaS is impossible. Either by direct interaction with the iron oxides, or else by oxidation to $CaSO_4$, and subsequent reduction by metallic iron, the final result is that CaO and FeS are produced, the latter dissolving in the steel.

All oxides of iron and manganese present, both in slag and in metal, must therefore first be reduced. The slag used for the purpose is made as basic as possible, and contains as reducing agent carbon and often ferro-silicon. When these oxides are removed, the metal becoming at the same time partly recarburised, the formation of CaS commences, *e.g.* thus :—

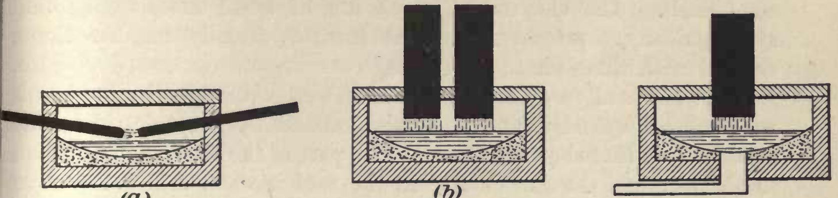
$$2CaO + 2FeS + Fe_xSi \longrightarrow SiO_2 + 2CaS + (2 + x)Fe.$$

The product is a steel containing very low percentages of phosphorus and sulphur and merely traces of dissolved oxides and gases, the last having full opportunity to escape at the high temperature at which the metal is 'killed.' Lastly, the steel can be further recarburised or a ferro-alloy added. The conditions essentially making for satisfactory desulphurisation in the electric furnace are the neutral or reducing atmosphere and the high temperature, which allows of very basic slags and rapid working. The frequent occurrence of CaC_2 in the slags of electric steel furnaces (particularly the Héroult type) shows that both these conditions are fulfilled. It is a mistake to assume, as has been done, that CaC_2 actually effects the deoxidation. When added, it has no marked action. Its formation simply witnesses to the reducing atmosphere and high temperature.

The technical furnaces at present used in steel refining are designed on one of two distinct principles. They are *arc furnaces* or *induction furnaces*. The latter can also be regarded as resistance furnaces, as the heating current is produced in and flows through the steel bath itself. Attempts made to construct resistance furnaces on any other principle have proved futile (*e.g.* those of the French electro-metallurgist Gin).

3. Arc Furnaces

In furnaces of this type the heating of the charge is effected by radiation from an arc or arcs playing immediately above the bath. These arcs can be arranged in several ways. We need here only consider in detail three arc furnaces, those of Stassano, Héroult, and Girod (Fig. 107). In the Stassano furnace (the simplest form) the arc passes between two almost horizontal electrodes. The Héroult furnace has two vertical electrodes and two arcs, passing between the electrodes and the surface of the bath. Later types have more arcs, but these are arranged on the same principle. In the Girod furnace the arc (or arcs) plays between one or more vertical electrodes and the surface of the slag, the current then passing through the steel bath and out through the bottom of the furnace.



(a) *Stassano.* (b) *Héroult.* (c) *Girod.*

FIG. 107.

Stassano Furnace.[1]—This furnace has assumed several forms. The fixed type, as existing in the Stassano Steel Works at Turin, consists of a thick-walled rectangular chamber with a slightly arched roof. Three pairs of electrodes are introduced through the two longer opposite sides. The raw material is charged in at the two ends. There are suitable tapping-holes for slag and steel, and the gas outlet is water-sealed.

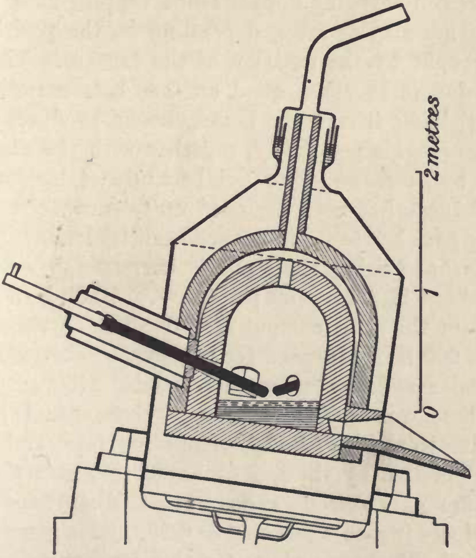


FIG. 108.—Stassano Steel Furnace.

The most usual type (Fig. 108) is, however, different. It is circular

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[1] *Electrochem. Ind.* **6**, 315 (*1908*). *Stahl und Eisen* **28**, 657 (*1908*). *Trans. Amer. Electrochem. Soc.* **15**, 63 (*1909*).

in plan, and is not fixed, but slowly rotates about an axis inclined 7° from the vertical. The melting chamber is lined with dolomite, the domed roof with magnesite bricks. These are surrounded by a thick layer of material of low conductivity, the whole being enclosed in a steel shell. The electrodes, which are of small cross-section and symmetrically arranged round the furnace, usually number three, are fed with three-phase alternating current, and connected $\triangle$-wise. Each is fastened to a metal rod which works through the head of a water-cooled cylinder, and is hand-regulated by a special hydraulic arrangement (not shown in figure). No part of the electrode is exposed to the air. As the gas outlet[1] in the roof is water-sealed, it follows that the atmosphere in the furnace is strongly reducing. Under these circumstances the electrode consumption is small, and far higher current densities can be used than would otherwise be possible. Stassano can work with 20 amps./cm.^{2} or more, 5–7 amps./cm.^{2} being the normal figure. Whether so to work is really advantageous is doubtful, judging from the considerations on pp. 175–179. The heat losses due to the electrodes are in all probability very high in this furnace.

There is a closed charging hopper and a tapping-hole, which serves to withdraw either slag or steel, depending on the position to which it has been brought by the rotation of the furnace. The purpose of this slow rotation is to effect good contact between steel and slag. Full charges yielding invariably homogeneous products are thereby made possible, and this possibility, together with the exclusion of all air, is claimed by Stassano as a special feature of his furnace.[2] The fixed type of furnace has been designed up to a capacity of 750 K.W. The rotating furnace has so far only been built for loads up to 200 K.W. A 140-K.W. furnace using three-phase current ($\triangle$ connections) at 80 volts takes about 1100 amperes per phase. A 200-K.W. furnace will be fed with about the same current at 110 volts. Stassano, however, has designed a 600-K.W. furnace for monophase current. There will be four electrodes and two arcs, each taking 2400 amps. at about 150 volts. These voltages, higher than those usual in other arc furnaces, are due to the long arcs Stassano employs, and these are in turn rendered possible by the quiet manner in which the arcs burn, with a minimum of electrode consumption, disturbance, etc. The power factor of the furnaces can rise to 0·95, but is generally lower.

Practically all the figures given for this furnace refer to the production of steel castings, tool steels, or special steels, starting with scrap steel and soft wrought-iron. The theoretical minimum quantity of energy necessary is 370–400 K.W.H. per ton of steel produced.

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[1] Present in earlier furnaces, as they were also intended for the reduction of iron ores; in recent furnaces entirely dispensed with.

[2] It, however, appears that the latest furnaces are no longer capable of rotation, but are tilted.

Stassano uses 700–900 K.W.H. in his 750-K.W. (5 ton) furnaces, 800–1000 K.W.H. in his 200-K.W. (1 ton) furnaces, and 1000–1300 K.W.H. in the 150-K.W. (0·7 ton) furnaces. The loss of metal is very small, averaging 2 per cent. The electrode consumption is about 10 kilos. per ton. Owing to the position of the arcs, roof and walls are more exposed than in other furnaces to their action. The hearth must be renewed every 3–4 weeks, the roof every 4–6 weeks. The furnace itself works very smoothly and regularly. According to Stassano, the various complications (rotation, method of cooling and regulating electrodes, method of attaching cables) are no serious disadvantage. The labour required is, however, disitnctly higher than with other furnaces.[1]

Héroult Furnace.[2]—This furnace (Fig. 109), so far more widely adopted than any other type, is of comparatively simple construction. It consists essentially of a shallow hearth, lined with calcined dolomite or magnesite, and roofed with silica bricks. This hearth slopes up in front towards a lip, through which the liquid steel can be discharged by tilting the furnace. This melting-chamber is surrounded by poorly conducting material, and the whole enclosed in a casing of sheet steel. The electrodes, two or three in number, enter vertically through openings in the roof, and project down to within one or two inches of the surface of the bath. They are water-cooled at the points where they pass through the roof, as well as at the cable connections. Regulation is automatically effected, utilising the voltage fluctuations. Towards the end of the refining, when conditions have become constant, a tight joint is made between electrodes and roof. In most cases, charging hoppers are provided at the ends of the furnaces. The charging otherwise takes place through the tapping-opening. The atmosphere in the furnace is strongly reducing, as is shown by the formation of CaC_2 in the slag.

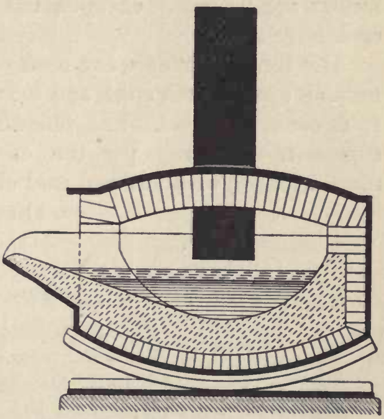

Fig. 109. Héroult Steel Furnace.

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[1] At Bonn, where two 1-ton rotating furnaces and a 2-ton tilting furnace are working, the metal roof to the furnace is dispensed with, the magnesite bricks being merely covered with a layer of sand. A run of about two weeks is usual before the hearth needs to be replaced. At variance with a statement made on p. 446, the arcs in these furnaces are not particularly long. (June 1912.)

[2] *Electrochem. Ind.* 5, 272 (*1907*). *Trans. Amer. Electrochem. Soc.* **15**, 139 (*1909*). For 15-ton furnaces, *Zeitsch. Elektrochem.* **16**, 853 (*1910*). *Metall. Chem. Engin.* **8**, 179 (*1910*). *Trans. Amer. Electrochem. Soc.* **19**, 205 (*1911*).

These furnaces have at present been built up to a capacity of 15 tons; 20-ton units are being constructed, and 30-ton furnaces are projected. In the smaller furnaces, two electrodes are used, fed with monophase alternating current. Thus a 3-ton furnace takes 4000 amps. at 100–120 volts. The larger 15-ton furnaces are supplied with three-phase current, and have three electrodes (section 2′ × 2′) arranged in star. At South Chicago each arc is fed by means of a 750 K.W. transformer. The maximum load it takes varies between 16,000 amps. at 45 volts and 12,000 amps. at 60 volts, corresponding in the latter case to a furnace voltage of 100 volts. Such a furnace consumes 2000 K.W. as a maximum, considerably less during a large part of the heat. Cos θ varies, according to the stage of the process, between 0·82–0·9. Electrodes of both carbon (current density 4–5 amps./cm.^{2}) and graphite (current density 15–16 amps./cm.^{2}) have been used. The former are naturally cheaper, but liable to breakages when made in such large sizes.

The Héroult furnace has been used for making steel from scrap, for refining open-hearth steel, and for making steel of open-hearth quality from converter steel. The following table contains the average consumption of energy per ton of product with furnaces of different sizes, working with hot and cold charges :

TABLE LXVII

Furnace	Molten steel	Scrap
1-ton (250 K.W.)	400 K.W.H.	1000 K.W.H.
3-ton (400 do.)	250–300 do.	800 do.
5-ton (700 do.)	180 do.	700 do.
15-ton (2000 do.)	150 do.	<700 do.

These values can fluctuate very considerably, according to the character of the charge and the exact degree of refining aimed at. The electrode consumption also varies considerably. If the charge is cold and the operation requires a long time, it is high (*e.g.* 30 kilos. per ton), far greater than in the Stassano furnace. But with a molten charge, rapidly refined, and with the furnace atmosphere of a reducing nature, after the first few minutes the consumption is only 5–7 kilos. per ton. The life of the lining depends also on the nature of the refining operation. With the smaller furnaces, the roof needs monthly renewal only, and the hearth lasts three months or longer. But with the 15-ton furnaces, in which 12–16 heats are worked per day, it is necessary to repair the roof weekly and to attend to bad spots on the hearth between each heat. The loss of metal is about 6 per cent. with a cold and 2–3 per cent. with a molten charge.[1]

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[1] Most of the new furnaces now designed, of capacity exceeding 3 tons, are circular in shape and fed with three-phase current. The largest of these (in fact the largest electric steel furnace so far existing) has been recently installed in the Deutscher Kaiser Works (Bruckhausen). It is about 18′ in diameter and has a capacity of 25 tons. (June 1912.)

The **Keller** furnace (I) needs no particular description here, as it does not essentially differ from the Héroult. An 8-ton unit has been working since 1905 in France, at Unieux.

Girod Furnace.[1]—This furnace is shown in Fig. 110. In its non-electrical parts (lining of hearth and roof, charging and discharging arrangements, etc.) it resembles the Héroult furnace. The electrode arrangement, however, is essentially different. Through the roof pass electrodes of one polarity (*sic*) only, and the current, supposing it to have thus entered the furnace, passes by means of an arc or arcs to the slag, through the steel bath, and finally leaves by a number of steel electrodes let in through the hearth. Thus, instead of having two arcs in series as in the Héroult furnace, there is only one, or (with more than one roof electrode) several arcs in parallel. The voltage of the Girod furnace is therefore approximately half that of the Héroult furnace, and, with furnaces of equal load, the current necessary is twice as great. Two-ton furnaces (300 K.W.) have one carbon and six steel electrodes; a 12–15 ton furnace (1200 K.W.) requires four carbon and sixteen steel electrodes. The depth of the steel bath is about 25–30 cm. In addition, the steel electrodes melt down to a depth of about 5–10 cm. When tapping, this molten part of course runs out, but is replaced by the next charge. Both sets of electrodes, carbon and steel, are water-jacketed, and the carbon electrodes automatically regulated.

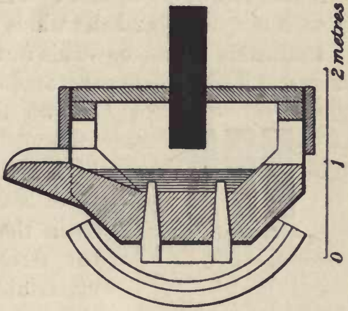

FIG. 110.—Girod Steel Furnace.

Girod furnaces have been built up to capacities of fifteen tons. Monophase alternating current is employed. The voltage varies between 55–75 volts. A 300-K.W. unit will take 5000–5500 amps. at 65–75 volts. Its power factor is 0·8–0·9. A 1200-K.W. unit works with 20,000 amps. at 70–75 volts. The current density in the carbon electrodes is about 5 amps./cm.^{2} These furnaces have been chiefly worked with cold mixed charges of various kinds of scrap. Girod claims that for such charges his furnace is undoubtedly the best, on account of the way the current is compelled to pass *through* the metal to be melted. About 800–1000 K.W.H. are required with a 2–2·5-ton furnace for 1 ton of molten steel, depending on the nature of charge and finished product. With a 15-ton furnace, 700–800 K.W.H. are

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[1] *Electrochem. Ind.* **6**, 428 (*1908*). *Trans. Amer. Electrochem. Soc.* **15**, 127 (*1909*). *Metall.* **6**, 673 (*1909*).

needed. If liquid steel is charged in, the energy consumption is 250–350 K.W.H. per ton, depending on circumstances. The electrode consumption is from 13–18 kilos. per ton with a cold charge. The metal losses are 6–7 per cent. The roof of the furnace requires repairs every one to two weeks. The rest of the lining is far more resistive.

Keller Furnace (II).—Keller has also designed a successful furnace resembling that of Girod in that it has hearth electrodes. They consist of a large number of 1″ iron bars attached to a metal plate connected with the source of current. The spaces between the bars are filled up with magnesia, and the whole conducting hearth is water-cooled.

Nathusius Furnace.—This furnace[1] (Fig. 111) should also be briefly noticed. Heat is here generated electrically (from three-phase current) in two different ways. Exactly as in the Héroult furnace, arcs pass between the steel bath and roof electrodes. But there are also three steel hearth electrodes which do not, as in the Girod furnace, make contact with the steel bath, but are embedded in the material of the hearth. Currents pass between these electrodes through this hearth material, and the latter, which conducts badly at low temperatures, but better at higher ones, is thus heated up. In this way the bath is heated from both above and below. We shall meet with this type of electrode arrangement again in the Röchling-Rodenhauser furnace,[2] when it will be more fully discussed. A 5-ton Nathusius furnace apparently consumes 550 K.W. at 100 volts in its upper electrode system, and 150 K.W. at a higher voltage in its hearth electrode system. Electrodes are connected in star. With a liquid charge of converter steel, 180–300 K.W.H. per ton are required for a very soft steel (0·05 per cent. C) as product. With a solid charge, 640–700 K.W.H. are needed. The electrode consumption is said to be only 2 kilos. per ton for a liquid, 4 kilos. per ton for a solid charge.

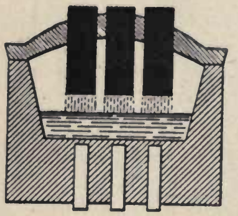

FIG. 111.—Nathusius Furnace.

4. Induction Furnaces

In these furnaces[3] an entirely different principle of heating is dopted, whereby the use of electrodes is avoided, together with the ompanying electrical and material losses and the possible contamina- of the steel by pieces of carbon entering the bath. That there are esponding disadvantages we shall see later. Briefly defined, an

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Metall. Chem. Engin. 9, 489 (*1911*).

ee p. 456.

ectrochem. Ind. 6, 438 (*1908*). Engelhardt, *Electrochem. Ind.* 6, 143 (*1908*). *Electrochem. Ind.* 7, 478 (*1909*). Hutton, *Engin.* 82, 779 (*1906*).

induction furnace is a step-down transformer with short-circuited secondary. A transformer is a machine by which a high-voltage alternating current can be changed into a low-voltage current (step-down transformer) or *vice versa* (step-up transformer), and is based on the following principles.

The Transformer.—A current, direct or alternating, passing through a coil of wire (*primary*), produces a magnetic field in its neighbourhood. If a soft iron core be pushed into the coil, the magnetic field is concentrated in this core. If alternating current be used, we have an alternating magnetic field in the core. Suppose now a second (closed) coil of wire be wound round the core. The turns composing this *secondary* winding cut a continually changing magnetic flux. It follows that an E.M.F. is induced in the coil, and as the flux changes in sign as well as in magnitude, this E.M.F. is an alternating E.M.F. The ratio of the primary voltage (neglecting the comparatively small amount used to overcome ohmic resistance) to the secondary E.M.F. is given by the ratio of the number of turns in the two windings. If, for example, there are twenty times as many turns in the primary as in the secondary, and the voltage in the primary is 5000, the voltage in the secondary will be 250. The current in the secondary is then determined by its resistance, its inductance, and the E.M.F. induced in it by the flux in the primary. The formula we have seen[1] to be $E = I\sqrt{R^2 + 4\pi^2 n^2 L^2}$.

Principle of Induction Heating.—In such an arrangement, with the exception of magnetic losses and joule heat losses in the primary, the whole of the energy absorbed by the transformer appears as the induced secondary current. If therefore cos θ is unity, the product IE in the two circuits (neglecting the losses) must be identical. And it follows that the ratio $\frac{\text{current in secondary}}{\text{current in primary}}$ must be equal to the ratio $\frac{\text{turns in primary}}{\text{turns in secondary}}$. If $\cos\theta < 1$, then $\frac{\text{current in secondary}}{\text{current in primary}} < \frac{\text{turns in primary}}{\text{turns in secondary}}$. The current in the primary in a step-down transformer is small, and determined essentially by the nature of the secondary winding. By making the ratio $\frac{\text{turns in secondary}}{\text{turns in primary}}$ small, and also making the resistance of the secondary turns low, enormous currents can be induced in the latter by applying a suitable E.M.F. to the primary. In the induction steel furnace there is only one turn in the secondary winding, and this consists of the steel to be refined, occupying, in the simplest form of furnace, a ring-shaped channel, through the

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[1] P. 181.

centre of which pass the primary and the core (Fig. 112). It is the heat produced in this short-circuited secondary of low resistance which effects the refining.

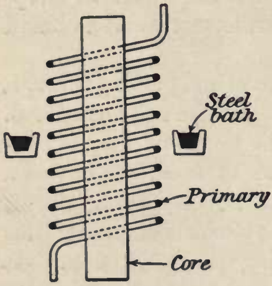

FIG. 112.

Losses. Power Factor.—Besides the heat losses common to all furnaces, induction furnaces are subject to magnetic and electrical losses. The former are due to hysteresis in the iron core. The electrical losses comprise eddy current losses in the core and joule heat losses due to the primary current, and in the latter case, with a constant primary voltage, depend on the power factor of the furnace. There are two main causes which tend to lower the power factor of induction furnaces. The first is that, owing to insulation and the necessity of cooling core and primary, it is impossible to bring primary and secondary so close together that all the lines of magnetic flux are cut by both of them. There is a certain leakage of lines which are only cut by the primary, and this means self-induction, instead of induction in the secondary. Secondly, the low value of the resistance of the secondary compared with its inductance leads to further lowering of cos θ. The consequence is that pure induction furnaces of high capacity, in which the secondary loop must either have a large cross-section, and therefore a low resistance, or else must be of wide diameter, in which case its inductance is high and there is a considerable magnetic leakage, tend to have very low power factors. We shall see how in the Röchling-Rodenhauser furnace this tendency has been largely overcome.

Circulation of Metal.—The fact that the secondary in the induction furnace is molten and flexible is the cause of several interesting phenomena observed in the steel bath. There is, firstly, a tendency for the secondary to assume a circular shape, and thus to enclose as many lines of magnetic flux as possible. The resultant of gravity and of this centrifugal pressure manifests itself in an upward and outward inclination of the surface of the steel bath (Fig. 113), together with a perpetual rolling motion of the steel round the longitudinal axis of the bath in the direction indicated by the arrows. As a consequence, the inner side of the lining of the channel in induction furnaces, which is more severely exposed to the action of the slag than the outer side, deteriorates more rapidly. Secondly, the whole molten ring rotates bodily round its containing channel in the direction of the longitudinal axis. With three-phase current, and therefore a rotating magnetic field,

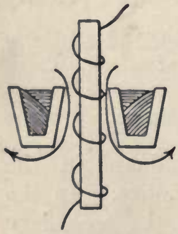

FIG. 113.

the cause of this behaviour is clear, but such a movement also apparently takes place to some extent with monophase currents, where the reason is less obvious. The combined effects of these two movements ensure excellent mixing of the metal and good contact with the slag.

Pinch Effect.—There is a further phenomenon often observed in induction furnaces, more particularly in those of small size—the 'pinch effect' described by Hering.[1] Two conductors carrying current in the same direction tend to attract one another, and the more strongly the greater the currents flowing. We can regard a liquid metal bath as composed of a large number of flexible parallel conductors in close contact, all carrying currents in the same direction, and at once see that there will be a radial pressure acting on the bath, tending to force in the liquid metal towards the centre and out at the ends, and thus to decrease the cross-section of the bath.

Fig. 114 (*a*) and (*b*) shows the effect of passing heavy currents through a series of parallel movable solid conductors and through a liquid conductor. At constant current this means an increase in current density at the point considered, and hence a still more powerful tendency to shrink together, an unstable state of things which may lead to complete rupture of the liquid conductor. In induction furnaces this tendency is partly counteracted by gravity. At the point where the pinch effect sets in (Fig. 114 *c*), the bath is in violent motion, metal continually running down the sloping surfaces and being forced back under them into the body of the melt. But if the current density be further increased, the influence of gravity is overpowered, and the ring is broken. The current at once stops, and the metal joins up again. If the current density be too high, this intermittent making and breaking may happen many times in succession, rendering it impossible to run the furnace, and finally the metal may become so cold that it no longer joins up again but solidifies, necessitating a complete stoppage.

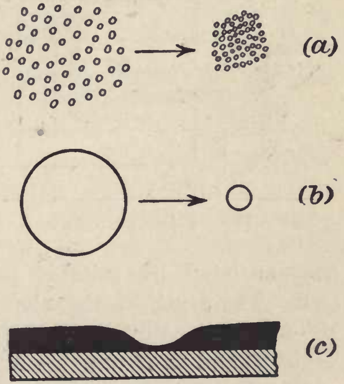

FIG. 114.—Pinch Effect.

To avoid this effect, the first condition is a channel of adequate cross-section. We have no exact data, but the limiting current density is probably about 500 amps./cm.[2] Secondly, the channel must be kept perfectly free from obstruction. Small pieces of solid slag, etc.,

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[1] *Trans. Amer. Electrochem. Soc.* **11,** 329 (*1907*); **15,** 255 (*1909*). Also Härdén, *loc. cit.*

might materially diminish the cross-section at a certain point, and thus start the effect. They will further collect in any initial depression in the metallic surface which forms, and increase the difficulty of remaking contact when once broken. If the pinch effect does appear, the power taken by the furnace must be immediately lowered. But in a properly-designed steel furnace, particularly in a three-phase furnace, there should be no danger of this. With smaller furnaces, such as are used to melt copper, brass, aluminium, nickel, nickel alloys, ferro-manganese, etc., the case is otherwise.

The first induction steel furnace was designed twenty-five years ago by Ferranti. Several others followed, but the first technically successful was that of Kjellin. Since then the greatest advance has been the introduction of the Röchling-Rodenhauser so-called ‘ combined induction and resistance ’ furnace.

Kjellin Furnace.[1]—This furnace, of essentially simple construction, is shown in Fig. 115. The core A is made of laminated sheets of soft iron, and, in order to minimise the stray magnetic flux, forms a closed circuit just like an ordinary transformer core. The primary B is of copper wire, insulated, and cooled, together with the core, by an air blast. Formerly it was of water-cooled copper tube. The ring-shaped channel C containing the steel bath is lined with calcined magnesite, and heat-insulated by suitable brickwork. The whole is sheathed in iron. The depth of the channel varies. In a large unit it will be 18″–2′. Originally it was U-shaped, but this was found inconvenient, and it is now V-shaped. It is covered above by a number of lids, D, through which the charging takes place, and is discharged through the mouth E by tilting. Fixed types are built provided with suitable tapping doors. When discharging, a certain quantity is always left in, so that on restarting the current can readily pass, and the cold charge is fed in on top of this.

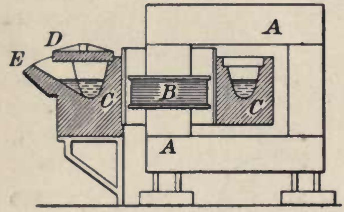

FIG. 115.—Kjellin Furnace.

Kjellin furnaces have been built of all sizes up to 8·5 tons capacity. The practical economic limit here reached (and perhaps passed) is determined by several circumstances. Firstly, large capacities mean low secondary resistances and a rapidly-decreasing power factor. Indeed, to keep the latter within workable limits it is necessary to use very low frequencies, involving expensive generating machinery.

[1] *Electrochem. Ind.* **3**, 294 (*1905*); *Trans. Amer. Electrochem. Soc.* **15**, 173 (*1909*).

[2] Cf. formula $\cos\theta = \dfrac{R}{\sqrt{R^2 + 4\pi^2 n^2 L^2}}$ (p. 182).

For $\cos \theta = 0{\cdot}6$, in itself low, a 2-ton unit must be worked with 15 periods, a 4-ton unit with 8 periods, and the 8·5-ton furnace with 5 periods per second. Further, the shape and small capacity of the channel are great disadvantages when the question is not one of making finest quality crucible steel from good raw materials, but rather of working up impure materials by the use of several slags to good quality steel. These reasons render it likely that the Kjellin furnace will in the future be applied more particularly to the manufacture of comparatively small quantities of highest quality alloy and carbon steels, and to the melting and casting of other metals and alloys.

A 2-ton furnace consumes about 170 K.W. It is fed with 3,000 volts in the primary, and this is transformed down to 30,000 amps. in the secondary. A smaller furnace will take 500 volts in the primary, and will have a secondary current of 20,000 amps. at 7 volts. (The ratios of transformation are of course different.)

Most of the work done with the Kjellin furnace has been with cold charges, either mixtures of pig-iron and pure briquetted ore or else of pig-iron and scrap. We find that the influence of the furnace capacity on the energy required is particularly great. Using cold pig and scrap, a 10 K.W. furnace would require 2,000 K.W.H. per ton of steel, a 100 K.W. furnace 1,200 K.W.H., a 170 K.W. furnace (2-ton) 750–850 K.W.H., and a furnace of 500 K.W. or over about 600 K.W.H. per ton. Working with briquettes and pig, a 2-ton furnace requires 1,000–1,200 K.W.H. per ton. With a charge of molten Bessemer or open-hearth steel, the largest unit needs 150–200 K.W.H. per ton. The furnace works very regularly. The heat losses are mostly due to radiation. The exposed surface per unit of volume is large, and the special cooling of primary and coil must have its effect. The actual electrical and magnetic losses in a well-designed furnace hardly exceed those of an ordinary transformer. Härdén[1] found them to amount together to only about 6 per cent., and that on a small 60 K.W. furnace. The metal losses are very low. The lining of the hearth has a life of two to three months, but it is not subjected to very severe slag treatment. In the absence of electrodes the roof lasts a long time.

Of other pure induction furnaces we may mention those of Colby,[2] Hiorth,[3] and Frick,[4] shown diagrammatically in Fig. 116. The Colby furnace has a double core and claims a higher power factor than the Kjellin furnace. In the Hiorth furnace, which has two circular secondary channels, there are also two sets of primaries, one being of water-cooled tubing embedded in the magnesite lining below the

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[1] *Electrochem. Ind.* **7**, 320 (*1909*).

[2] *Ibid.* **5**, 232 (*1907*).

[3] *Trans Amer. Electrochem. Soc.* **18**, 191 (*1910*).

[4] *Ibid.* **19**, 193 (*1911*).

channels. The Frick furnace has two primaries arranged as flat discs above and below the secondary channel. The power factor is stated to be very low. It does not appear that any of these works essentially better than the Kjellin furnace, and we need not consider them further.

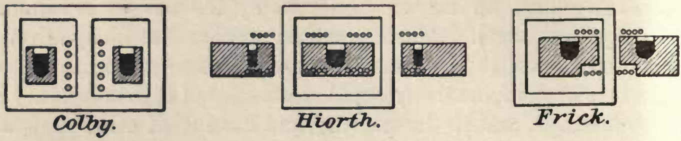

FIG. 116.—Induction Furnaces.

Röchling-Rodenhauser Furnace.[1] — The disadvantages of the Kjellin furnace—small capacity and low power factor—have largely been eliminated in the Röchling-Rodenhauser 'combined induction and resistance' type. Fig. 117 shows diagrammatically elevation and plan of the simplest form of this furnace, used with monophase current. A is the soft iron core, B and B′ are two primary windings, and C is the steel bath. So far the furnace is simply a double induction furnace, whose secondary has the shape of an 8, the middle part being a comparatively broad hearth allowing of convenient working and manipulation of slags. But to heat this central hearth sufficiently further means are necessary. These are provided by auxiliary

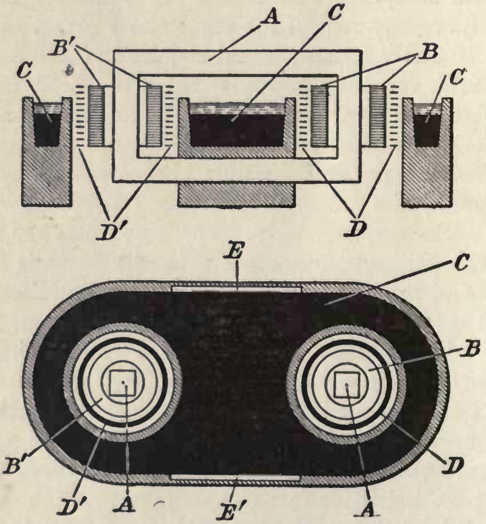

FIG. 117.—Röchling-Rodenhauser Furnace.

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[1] *Trans. Farad. Soc.* **4**, 120 (*1908*). *Trans. Amer. Electrochem. Soc.* **15**, **173** (*1909*). *Elektrotech. Zeitsch.* **31**, 903, 934 (*1910*).

secondary windings D and D′, consisting of a few turns of thick strip copper, separated from the primaries B and B′ by a small air gap only, and connected with so-called *pole-plates* E and E′ at the opposite ends of the centre hearth.

These pole-plates consist of plates of corrugated cast steel, embedded in the furnace wall[1] and covered with a thin layer of calcined dolomite, which also forms the lining of the whole hearth. At the high furnace temperature these oxide layers become conducting (cf. a Nernst lamp filament), and an extra current passes from D and D′ through the steel in the central hearth. The heat thus generated keeps this hearth at a high temperature, and permits of the use of refractory slags. The name 'combined induction and resistance furnace,' it is obvious, conveys a false idea of how the heating is effected. *All* the heat is generated from induction currents, but in the pole-plate secondaries a portion only of the circuit consists of fused steel. It may also be noted that, though the inventors object to their pole-plates being styled electrodes, they are nevertheless as much electrodes as are the steel conductors in the Girod furnace hearth.

About 0·25–0·35 of the total energy taken by the furnace is consumed in these pole-plate circuits. The greater part of this is generated in the oxide layer which covers the pole-plates. The resistance of fused steel is low $\left(\frac{1}{\kappa} = 0{\cdot}00014\text{–}0{\cdot}0002\right.$ at 1500°,[2] whilst for copper at 15° $\left.\frac{1}{\kappa} = 0{\cdot}0000017\right)$. As much heat will be generated in the copper windings as in the steel bath itself, but these amounts will probably be small compared with the heat produced in the pole-plate coverings. Of course a great proportion of this heat will enter the furnace, but much will be conducted away through the pole-plates and copper leads, which are at a lower temperature than the fused steel bath, and the losses in this circuit must be considerable.

The effect on $\cos\theta$ is twofold. The magnetic leakage, excessive in the Kjellin furnace, is minimised by the close proximity of the primaries and the auxiliary copper secondaries. And further, whilst the consumption of the furnace is raised by 30 per cent. or more through the introduction of the pole-plate circuits, this is achieved without any great increase in self-induction, as resistance is higher and inductance lower than in the two all-steel circuits.[3] The result is that whilst a 2-ton Kjellin furnace worked with 15 periods gives a power factor of 0·6 and a 15-ton furnace must be worked with 5 periods to attain the same result, a 3-ton monophase Röchling-Rodenhauser furnace

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[1] Cf. Nathusius furnace, p. 450.

[2] *Trans. Amer. Electrochem. Soc.* **15**, 215 (*1909*).

[3] Does the presence of the oxide layer introduce a capacity effect which tends to neutralise the effect of the self-inductance on $\cos\theta$? (Cf. p. 180.)

has $\cos \theta = 0{\cdot}7$–$0{\cdot}8$ when worked with 25 periods, and a 15-ton tri-phase furnace, fed with current of the same periodicity, has $\cos \theta = 0{\cdot}6$–$0{\cdot}7$. In a particular case, Rodenhauser states that a 1·5-ton three-phase furnace working with 50 periods had $\cos \theta = 0{\cdot}5$ before the pole-plate circuits came into play (in itself a much better result than the Kjellin furnace gives, and achieved by a more suitable dimensioning of the steel rings), and 0·8 after this happened.

A further great advantage gained in this modified induction furnace type is the possibility of refining steel in large quantities, using impure charges and several slags. We have seen how the small and inconvenient dimensions of the Kjellin furnace limit it in practice to the melting up of small quantities of pure raw materials.

Construction.—As in other furnaces, there is an outer shell of steel plate lined with non-conducting brick, and this again is lined with a stamped-in mass of calcined dolomite which serves as hearth. The roof is of refractory clay. There is a working door at each end of the central channel. From one of these the metal is discharged by tipping the furnace. Below them, under the surface of the bath, the pole-plates are embedded in the walls. The core consists of strips of soft transformer iron, isolated by paper. The copper secondaries and the primaries are so wound that all three current components in the central furnace channel flow in the same direction at the same instant. The coils are cooled by a strong air blast, filtered to remove steel particles. Monophase current furnaces have been built up to a capacity of 8·5 tons. Such a unit will consume 700–750 K.W. with a primary voltage of 4,000–5,000 volts. A 5-ton furnace takes up to 500 K.W., and a 3·5-ton furnace 300–400 K.W.[1]

Three-phase Type.—Recently furnaces adapted to three-phase currents have been built. Such a furnace has three soft-iron cores, connected above and below by yokes. Round each core is a molten steel channel, and these meet to form a central hearth. This is provided with three working doors, situated symmetrically between each pair of cores, and below the doors are the pole-plates. The copper secondaries are arranged in star. The soft-iron core itself is the neutral point, and to it one end of each of the secondaries is connected, the other ends being attached to the respective pole-plates. There are several advantages gained by the use of three-phase currents. Firstly, a possibility of a further increase in size (15-ton furnaces are contemplated); secondly, an economy in the generating machinery used; lastly, the very powerful circulation and mixing of the metal due to the rotating magnetic field. However, so far 1-ton and 2-ton units only have been built.

Röchling-Rodenhauser furnaces have been mostly used with a

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[1] A unit taking 14 tons and consuming 750 K.W. has recently been set in operation (June 1912).

charge of molten Bessemer steel or (at Dommeldingen, Luxemburg) with molten pig-iron. The energy consumption, as in the Kjellin furnace, varies with the size of the unit, and also, of course, with the degree of refining. If Bessemer steel be refined to open-hearth quality, about 120–160 K.W.H. per ton are needed. To lower sulphur and phosphorus still further (0·01 per cent.), 200–300 K.W.H. are required. Melting up cold scrap, as in the Kjellin furnace, needs 900 K.W.H. per ton in a small (2-ton) furnace. The refining proceeds regularly and quietly. When necessary, the hearth is repaired between the heats. In the latest furnaces built, slag is prevented from entering the narrow side channels, which are used solely for heating the steel. Damage to the less accessible parts of the lining is thus avoided. The roof has a long life. The pole-plate coverings do not suffer. Of course an excessive current passing through would tend to melt them. The steel losses are small.

5. Comparative

We have already discussed the nature of the advantages offered by electric heating. In the present case the first important point is the high temperature which is with ease attainable. In most furnaces it does not exceed 1550°–1600° through the whole mass, but this is already high enough to permit the use of difficultly fusible, very basic slags, which tend to quickly desulphurise the metal.[1] (In arc furnaces the temperature is much higher *locally*.) The high temperature also greatly increases the velocity of the different reactions, and, by rendering the charge more fluid, allows dissolved gases to escape easily. This high temperature is obtained at a much smaller cost than if fuel were used. The next point is the neutral or reducing atmosphere inside the furnaces. This is of the utmost importance, not so much in minimising the losses, as more particularly in assisting rapid desulphurisation.[2]

Then comes the question of size of unit and durability. Compared with the crucible steel process, the advantages are all on the side of the electric furnace. The units are much larger, labour is less, and so are repairs items. If, on the contrary, the products are of the nature of open-hearth steel or a little better, the comparison is not so one-sided. The units used in ordinary steel practice are larger, though this difference will probably disappear largely in the next few years. Secondly, as available figures show, the degree of refining arrived at can usually be more cheaply reached by ordinary metallurgical methods. However that may be, it is significant that the last few years have seen great progress in this direction, more particularly with the Héroult and the Röchling-Rodenhauser furnaces. With improved electrodes

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[1] P. 443.

[2] *Loc cit.*

and refractory materials we can in future expect increasing quantities of good quality steel to be prepared directly from Bessemer converter metal or even from molten pig-iron.

One feature indeed of electric steel furnace work is that it presents the possibility of turning impure raw materials at one operation into a high-grade exceedingly uniform product, with 0·01 per cent. of P and S, and any required quantity of carbon or alloyed metal. This is possible as the charge can be heated for a long time without danger of impurities entering from fuel gases.

Confining our attention now to the various *electric* furnaces used, the first obvious comparison is one between arc and induction furnaces. In the matter of power consumption there appears to be remarkably little difference between the two types. Working conditions vary so much that an exact comparison is not possible, but on the whole the induction type would appear to give the best results with a solid, the arc type with a liquid charge. The essential differences lie in other directions. The first advantage of the induction type is the elimination of electrodes. The power losses caused by electrodes are partly balanced by corresponding losses in induction furnaces. But the use of electrodes, apart from the somewhat over-estimated danger of impurities or pieces of carbon entering the bath, also involves a constant loss due to oxidation—an important point in all arc furnaces.

Further, as the heat in the induction furnace is produced in the metal, not in and above the slag, the furnace roof is much less severely attacked by radiation and by slag vapours. The absence of arc heating also keeps down the metal (vaporisation) losses. And a further advantage is the fact that external transformers and large cables are dispensed with. It is also claimed that the circulation and mixing in induction furnaces are far superior to those obtained in arc furnaces, but practical results show the advantage to be really illusory. The difficulties caused by electrode regulation and load fluctuations in arc furnaces have also been over-estimated, though induction furnaces certainly work more smoothly in this respect.

On the other hand, we have discussed the low power factor of induction furnaces, and what it entails. But the chief advantages of arc furnaces lie rather in the matter of temperature, and in their CO reducing atmosphere. The average temperature of arc furnaces (*e.g.* Héroult's) is probably higher than that of induction furnaces (even Röchling-Rodenhauser). The essential point, however, is that, while in the latter the large mass of metal is hottest, in arc furnaces the thin layer of slag and its surface of contact with the steel are the hottest parts of the bath, far hotter than in induction furnaces. Thus the refining takes place more quickly, and higher melting slags can be used. The fact that a region of maximum temperature lies immediately underneath the arc is a further advantage.

The presence of carbon electrodes, a drawback for other reasons, is responsible for the valuable reducing atmosphere. Arc furnaces then make it possible to remove impurities, particularly sulphur, more quickly than can be done in induction furnaces. This deduction, combined with the fact that large units can be more readily built, points to the conclusion that for large charges of comparatively crude material, such as liquid pig-iron or Bessemer steel, the arc furnace is the better, while for smaller charges of pure cold raw materials, particularly for alloy steels, the induction furnace has advantages.

A comparison of different furnaces is in some respects, particularly in the matter of power consumption, invidious. Not one of the furnaces above described has reached its final form, and improvements are constantly being made; whilst the numerous available figures of power consumption are not easily comparable owing to differences in raw material, size of unit, etc., etc. Nevertheless we can discuss comparatively some of the more obvious and fundamental features of design of the different furnaces. It may be noted in passing that much of the criticism which has appeared in technical journals is of an interested and frivolous nature, dealing with trivialities or imagined defects. The fact remains that all the furnaces above described are capable of regular and easy working, and of turning out with certainty high-class products.

Induction furnaces, and the special features of the Röchling-Rodenhauser furnace, have already been considered at length. There is little to add, except to emphasise the fact that the heat *unutilised* in the pole-plate circuits must form quite a considerable fraction of the total generated in these circuits. Exact data on this point would be interesting. The advantages of this type over other induction furnaces do not lie in the energy consumption per ton of steel, but in the possibility of using large units and cruder charges.

Of the different arc furnaces, the Héroult must be considered the simplest in construction, and therefore most suitable for continuous working up of large charges. Then comes the Girod furnace, whilst the Stassano furnace is the most complicated and requires most labour. And although these complications are unimportant when working up small charges of highest quality steel, it is unlikely, other considerations apart, that the Stassano furnace will ever be employed in the regular manufacture of large quantities of steel of open-hearth quality.

Walls and roof of the Stassano furnace are, in consequence of the peculiar position of the electrodes, more exposed to the heat of the arc than in the other types, but, as the arc does not directly play on the slag, less exposed to the action of slag vapours. Further, the roof is made of basic material (in the other furnaces of acid material), and we find its life comparatively long, that of the hearth being shorter than in other furnaces. The carbon (electrode) losses and the metal losses are also considerably less, as the hearth is so effectually closed in.

The Girod and Héroult furnaces must be regarded as equally reliable under regular working conditions. Experience has shown that the water-cooled steel electrodes in the former make no difference whatever to the durability of the hearth. Nor can we discriminate between them in the matter of efficacy of heating. Furnaces of equal load will have the same number of arcs, and will require the same carbon electrode section. The amount of heat abstracted from the furnace by the Girod hearth electrodes is very small—thus in a 3-ton furnace only about 1 per cent. of the total fed in.[1] The wear and tear of roof and hearth should also be about equal. The claims put forward in favour of the Girod furnace because the current passes through the bath must be regarded as unfounded. It cannot be too strongly emphasised that by far the greater proportion of heat produced in these furnaces is produced in the arcs—only a very small fraction is generated actually in the metal or slag. Far more is produced in the carbon electrodes.

6. Ferro-alloys[2]

A very important development in the steel industry during recent years has been the increased demand for alloy steels—*i.e.* steels which, besides carbon, contain another metal or metals as constituents. Such steels often have very favourable mechanical properties, and are now indispensable for the manufacture of high-speed tools, machinery exposed to severe usage, armour-plate, projectiles, etc. At first these steels were prepared by the addition of the metal itself or of ferro-alloys produced in the blast furnace, but ferro-alloys produced electrothermally are now generally used. For nickel steels, metallic nickel is used; for manganese steels, the ferro-manganese employed is still made in the blast furnace, the high temperature of the electric furnace causing too great volatilisation losses. But ferro-silicon, the most important product of all, as well as ferro-chromium, ferro-tungsten, ferro-molybdenum, and ferro-vanadium, are chiefly[3] prepared by electrothermal methods, by far the best at the high working temperatures necessitated by the difficultly reducible oxides used. The products are also purer than those made by other methods, containing much less carbon, phosphorus, sulphur, etc.

The chemistry of these processes is simple. It consists essentially in the interaction at high temperatures of as pure a form as possible

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[1] *Zeitsch. Elektrochem.* 17, 773 (*1911*).

[2] *Electrochem. Ind.* 2, 349, 395, 449 (*1904*); 5, 9 (*1907*); *Zeitsch. Elektrochem.* 9, 362 (*1903*).

[3] Certain amounts of the pure metals are made by the Goldschmidt Thermite process.

of the refractory metal oxide, carbon, and iron, CO and the ferro-alloy resulting. Occasionally a pure iron oxide is used instead of the iron. But as this necessitates energy consumption for the reduction of the iron oxide as well as for the reduction of the refractory metal oxide, this procedure is but seldom followed. As, instead of difficultly fusible pure metal, a more or less rich low-melting iron alloy results, it follows that the energy needed per unit weight of reduced substance is less than that necessary if the latter were produced in the pure state. The reaction takes place at a lower temperature. Thus Greenwood[1] found that the reaction in a finely divided intimate silica-carbon mixture commenced at 1460°, but when iron was added the temperature could be as low as 1200°.

The total energy absorbed during the reaction is composed of that needed to reduce the refractory oxide *minus* that produced by the burning of the carbon (both at room temperature) *plus* that necessary to heat the product to its tapping temperature. The heat effect of the alloying of the iron and second constituent must be neglected as probably insignificant. We will carry out the calculation in detail for a 50 per cent. ferro-silicon.

The melting-point — per cent. composition diagram of the system iron-silicon has been mapped by Tammann and Guertler.[2] From their results we gather that the 50 per cent. alloy melts at about 1370°. Suppose it to be tapped at 1600°. The CO will impart much of its heat to the fresh charge, and we will assume it leaves the furnace at 1000°. The equation is

$$SiO_2 + 2C \longrightarrow Si + 2CO.$$

The heat of combustion of a kilogram atom (28·3 kilos.) of Si to SiO_2 at room temperature is 180,000 Cals. The heat of combustion of 2 kilogram atoms of carbon to CO is $2 \times 29200 = 58400$ Cals. Hence the production of 28·3 kilos. silicon at room temperature requires $180000 - 58400 = 121600$ Calories, *i.e.* 2,148,000 Cals. for 500 kilos. The specific heat of silicon between 0° and 1600° we will set at 0·21. For the heating of 500 kilos. to 1600° are therefore necessary $1600 \times 500 \times 0{\cdot}21 = 168000$ Cals. For the heating and melting of 500 kilos. of iron are necessary about $310 \times 500 = 155000$ Cals. We will set the mean molecular specific heat of CO between 0°–1000° at 7·0, and calculate that the heating up of the CO needs 247,000 Cals. The total is

	Cals.
For chemical reaction	2,148,000
For heating the silicon	168,000
For heating and melting the iron	155,000
For heating the CO	247,000
	2,718,000

The theoretical quantity of energy necessary for the production of 1 ton of 50 per cent. ferro-silicon is therefore

$$\frac{2718000 \times 4{\cdot}19}{3600} = 3160 \text{ K.W.H.}$$

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[1] *Electrochem. Ind.* **7**, 120 (*1909*).

[2] *Zeitsch. Anorg. Chem.* **47**, 163 (*1905*).

The theoretical minimum values for other ferro-alloys can be similarly calculated.

Ferro-Silicon.[1]—This is the most important of the ferro-alloys, largely used for deoxidising steel during refining, in making steel castings, and for regulating the silicon content of cast-iron. When made in the blast furnace, the silicon percentage seldom exceeded 15 per cent., whilst the first electrothermal products were mostly 30 per cent. Far richer alloys can now be made, and there is a tendency to produce three grades only—25 per cent., 50 per cent., 75 per cent.—the relative demand for the richer products steadily increasing.

The raw materials for ferro-silicon manufacture are silica, carbon, and iron. (Iron oxide is still used, but only very occasionally.) They must be very carefully selected, particularly from the point of view of impurities. If these enter the product they lower its value for steel refining. In particular, if phosphorus is present, then the ferro-silicon is liable to evolve PH_3,[2] which has been the cause of several poisoning cases. Apart from that, the impurities tend to form more or less infusible slags, which disturb the working of the furnace. Formerly the charge contained lime as a flux, but with pure materials this is usually unnecessary. As silica, 95–98 per cent. quartzite is used. A lower percentage material is apt to cause disturbances. The chief impurities are Al_2O_3, MgO, and CaO, which form the slag. Sand is usually too impure, and contains too much moisture. The carbon is present as charcoal, anthracite, or a high-grade coke. Generally, the less dense the variety of carbon and the lower the ash, the more suitable it is. Unfortunately, most cokes contain too much sulphur and phosphorus, and both coke and anthracite suffer from their high content of ash. Phosphorus and sulphur also debar the use of cast-iron, and shavings, etc., of soft iron and steel are usually employed. In small furnaces the charge should not contain pieces greater than 1″ diameter; in large furnaces bigger pieces are permissible.

All ferro-silicon furnaces are of the mixed arc-resistance type. The current passes as an arc between electrode and charge, through the charge, and then to the other electrode, sometimes by means of a second arc, sometimes not. The part played by resistance heating depends on the arrangement of electrodes and composition of charge. The

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[1] Many of the details in this section, particularly those dealing with the charge used and with the results obtained with large three-phase furnaces, are taken from the article by Helfenstein in Askenasy's *Einführung in die technische Elektrochemie*, vol. i. (*1910*). See also Conrad, *Electrochem. Ind.* **6**, 397 (*1908*). Further *Metall. Chem. Engin.* **8**, 133 (*1910*).

[2] Recent investigations indicate that only those grades which tend to disintegrate behave thus—*i.e.* alloys containing 30–65 per cent. Si. Richer or poorer products are innocuous, and the alloys prepared in large modern furnaces are stated to be much freer from all such impurities. *Metall. Chem. Engin.* **8**, 133 (*1910*).

more heat produced this way, the higher the voltage and the lower the current for a hearth working at constant power.

We can distinguish three types of furnace. The first (Fig. 118), of which many are still working in France, has a hearth electrode like the Girod steel furnace. The working of a furnace of this type (the **Rathenau** furnace) has been fully described by Pick.[1] Such furnaces consist essentially of a hearth or crucible of electrode carbon surrounded by a wall of acid firebrick, the whole contained in a strong iron sheath. The lining must be very carefully constructed, for if the ferro-silicon penetrates to any extent between the bricks, and there solidifies, it will thrust them asunder and destroy the furnace. A protective layer of solidified ferro-silicon forms the best furnace lining. A 250-K.W. unit has a crucible 1 metre in diameter and 40 cm. deep. The hearth forms one electrode, contact being made with a steel plate by stamping in a mixture of graphite or carbon and pitch. The other electrode enters the furnace from above, and can be regulated. The furnace is uncovered, and the charge simply shovelled in, and heaped up on top round the electrode. The ferro-silicon is tapped every one or two hours into carbon moulds, and the process occasionally stopped to remove the viscous slag. Direct current can be used, but alternating current is preferable.

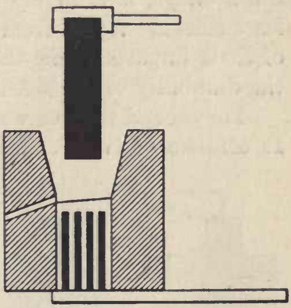

Fig. 118. Rathenau Ferro-Silicon Furnace.

Such furnaces usually take 200–600 K.W., but in the Ugine works 1,350-K.W. units are stated to be working. A 200-K.W. furnace takes about 5,000 amperes at 40 volts, and generally the voltage of a single hearth varies between 35–50 volts, the furnaces of bigger capacity taking larger currents. The kind of carbon used somewhat affects the current-voltage relations. With the feebly-conducting charcoal, the ratio $\frac{\text{voltage}}{\text{current}}$ is higher than with coke or anthracite, the current density in the electrode carbons showing corresponding variations between 3–7 amps./cm.^2 Owing to the small size of the units, and to the fact that, being uncovered, the volatilisation losses are very great, the yield of ferro-silicon with these furnaces is low. Pick's figures for a 200-K.W. unit, using charcoal, are

1 kilo.	25	per cent.	alloy	requires	5 K.W.H.
„	50	„	„	„	16 K.W.H.
„	70	„	„	„	34 K.W.H.

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[1] *Dissertation* (Karlsruhe, 1906).

The losses of silica were respectively 42 per cent., 54 per cent., and 69 per cent.; of carbon, 47 per cent., 43 per cent., and 73 per cent.

With larger units (*e.g.* 500 K.W.) better results are usually obtained. Thus Helfenstein gives 1 kilo. 50 per cent. alloy = 9·2 K.W.H. using charcoal, and 12 K.W.H. using coke or anthracite, where the difference results from the larger currents in the second case causing great vaporisation losses, heat losses also arising from the high ash content of the fuel. The silicon losses vary from 20–25 per cent. The electrode consumption can amount to 100 kilos. per ton for the 50 per cent. alloy, or even more; for the 25 per cent. alloy, up to 60 kilos. per ton. This necessitates renewals every few days. As we shall see, later types of furnaces give far better results, and though, owing to the smaller quantities made, this type of furnace may be retained for other alloys, it is highly improbable that new ones will be built for ferro-silicon. Apart from other considerations, the bottom electrode, of little importance in the Girod steel furnace, here seriously affects the durability of the hearth.

The second furnace we must notice is the **Keller** furnace (Fig. 119). It consists of two vertical shafts, through which the electrodes and charge (anthracite is used) are introduced, and a horizontal channel connecting them. Here the ferro-alloy collects, being tapped every two hours. Usually the shafts are large enough to contain several electrodes connected in parallel, each independently regulated. The slag can be tapped, and the furnace run for months continuously. Units have been constructed up to 900 K.W. A 500-K.W. unit requires 3·5 K.W.H. per kilo. 30 per cent. ferro-silicon. The consumption of electrodes is small, owing to their being much better protected than in the first type. They usually last two to three weeks. The losses of material amount to 10 per cent.

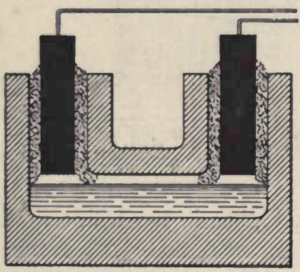
FIG. 119.—Keller Ferro-silicon Furnace.

The third and latest type of ferro-silicon furnace (Fig. 120) is derived from the Héroult type. The hearth is neutral, all the electrodes being introduced from above. The great advance, however, is the increased load. In its latest form, the furnace is fed with three-phase current, and takes from 4,000–9,000 K.W., divided between three hearths. The voltage can vary within wide limits, depending on the amount of resistance heating. This in its turn is chiefly determined by the composition of the charge. For the largest units, the normal figure using anthracite is 75–90 volts per hearth, and to this corresponds a current of 40,000 amps. (star connections), cos θ being 0·8 and the electrode current density some 7 amps./cm.[2] But higher voltages (120–130 volts) can be employed almost as easily. Such a furnace can produce 1 kilo. 50 per cent. alloy per 6·9 K.W.H., the losses being 15–20 per cent. and the electrode consumption 40 kilos. per ton. Using charcoal, in which case the hearth voltage is higher, the current lower, and the vaporisation less, the energy required is 5·3–6·0 K.W.H. per kilo. and the losses 10 per cent. With still larger furnaces of Helfenstein's pattern,[1] still better results may be expected. The more refractory the alloy made, the poorer is, of course, the yield, and to obtain satisfactory results the larger must be the load of the working hearth.

These large modern furnaces are very simply constructed of fire-brick, lined with carbon. They are cooled by air or often by water, so that a crust of solidified material forms the actual lining. For purposes of tapping a hole is melted in this wall by means of a pointed rod, serving also as an electrode. Current passes from the rod through the lining to one of the electrodes, and the liberated heat effects the fusion. Slag is occasionally removed through a larger hole bored at the right height. Except when tapping, the load is exceedingly constant. The regulation of the electrodes is done by hand, guided by voltmeter readings.

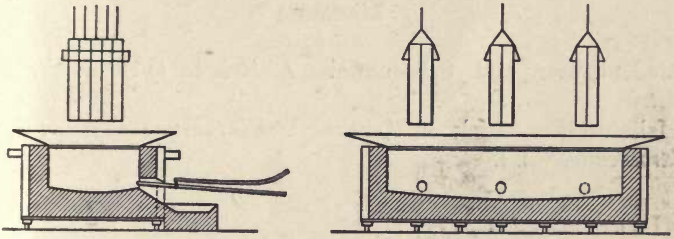

FIG. 120.—Large Modern Ferro-silicon Furnace.

Ferro-chromium is largely employed for making chrome steels, which are exceedingly hard and extensively used for armour-plate, projectiles, high-grade castings, high-speed tools, the best cutting tools, etc. Little is known of the manufacture of ferro-chrome. It is prepared in the works of Girod, Keller, and Héroult, and therefore in furnaces similar to those described in the last section. Grades are made containing 50 per cent. and 65 per cent. chromium. The carbon content varies considerably, but by suitable refining can be brought down to 0·25–0·5 per cent. In the Héroult furnace this is done by lining the bath with a chromium ore and using a slag containing Cr_2O_3. Haber[2] briefly describes the manufacture in America of a 71 per cent. alloy containing 23 per cent. iron and 5·2 per cent. carbon.

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[1] Fig. 47.

[2] *Zeitsch. Elektrochem.* **9**, 362 (*1903*).

The furnaces were small, averaging 300 K.W. and of the Girod type. A chromium ore containing iron oxide was directly reduced without the addition of any metallic iron. One kilo. of alloy needed 8 K.W.H. The furnaces employed by Girod himself at Ugine are somewhat larger, 400–600 K.W.

Ferro-tungsten is employed for making very hard steel used for high-speed cutting tools. Nothing is known of its manufacture. Girod makes grades containing up to 85 per cent. W. **Ferro-molybdenum** is stated to be even more effective than the last two alloys as an addition in the manufacture of steel for high-speed tools, large guns, rifle barrels, etc. It is made as an 80 per cent. alloy. No details are known of its manufacture, and the same statement holds of **ferro-vanadium,** prepared as a 50 per cent. alloy very low in carbon, and said to greatly increase the strength of steel without at all impairing its ductility.

Literature

Rodenhauser and Schoenawa. *Elektrische Öfen in der Eisenindustrie.*

Helfenstein. Article in Askenasy's *Einführung in die technische Elektrochemie*, vol. i.

CHAPTER XXV

CALCIUM CARBIDE AND CALCIUM CYANAMIDE

1. Carbide. General and Theory

ALTHOUGH previously discovered, our essential knowledge of calcium carbide dates from Moissan,[1] who in 1892 prepared the substance in quantity and comparatively pure by the interaction of lime and sugar charcoal in an arc furnace. Willson chanced to rediscover it independently in America about the same date. As soon as its valuable property of generating acetylene by interaction with water was recognised, its commercial manufacture was started and developed in Europe chiefly by Bullier and others, in America by Willson and Bradley. It was the earliest of the electrothermal industries. Owing to injudicious speculation and over-production, a severe crisis was experienced in Europe in 1899. Many companies failed, and others were compelled to manufacture other products, such as ferro-silicon. Present conditions and prospects are far better. Business reorganisation, considerable technical improvements, a purer and more reliable product causing a greater demand, and the rise of the cyanamide industry [2] have all played a part.

Calcium carbide is produced in the electric furnace according to the reversible reaction

$$CaO + 3C \rightleftarrows CaC_2 + CO.$$

This reaction is endothermic. At high temperatures the tendency is for carbon and lime to interact, furnishing carbide and carbon monoxide. At low temperatures the equilibrium moves in favour of the left-hand side of the equation. To each temperature corresponds a definite CO equilibrium pressure,[3] which must be exceeded before CaC_2 can be converted into lime and carbon. The higher the temperature

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[1] *The Electric Furnace*, p. 203.

[2] Together with minor applications of acetylene, *e.g.* for cutting and welding metals.

[3] See p. 479.

the greater this pressure. But CaC_2 can also decompose in the absence of CO, dissociating into graphite and calcium vapour, as follows:

$$CaC_2 \rightleftarrows Ca + 2C.$$

The calcium dissociation pressure is higher the higher the temperature. These two reactions are connected by a third, the reduction of lime by carbon to metal and CO. So that we must finally consider the three following equations, the right-hand side of each being favoured by increased temperature:

$$\begin{aligned} &(a) \quad CaO + 3C \rightleftarrows CaC_2 + CO; \\ &(b) \quad CaC_2 \rightleftarrows Ca + 2C; \\ &(c) \quad CaO + C \rightleftarrows Ca + CO. \end{aligned}$$

Several attempts have been made to measure the CO equilibrium pressure corresponding to the first equation. Rothmund,[1] Lampen,[2] and Rudolphi[3] heated together lime and carbon to different temperatures, and observed the temperature necessary for the resulting product to give acetylene on treatment with water. Rothmund found 1620°, Lampen 1700°–1725°, and Rudolphi 1810°. Assuming that the gaseous phase consisted of nitrogen and CO produced by the atmospheric oxygen, we have as a result that the equilibrium temperature corresponding to a CO pressure of about 250 mm. is between 1620° and 1810°.

These measurements, however, were very approximate. Results of greater value were got by Thompson,[4] working with an Arsem[5] vacuum electric furnace, and using a 78 per cent. pure carbide, the residue being lime and carbon. He found that between 1700° and 2000°, where the CO pressures would have been easily measurable, no readings were possible. The CaC_2 dissociated, the calcium vapours burnt in the CO (equation *c*), and a deposit of lime formed on the sides of the furnace. He was therefore compelled to work below 1500°, and finally, owing to experimental difficulties, to heat the carbide in an atmosphere of a neutral gas. Hydrogen was used, the equilibrium not being appreciably disturbed thereby. Analysing large quantities of gas, he obtained the pressures

0·44 mm. at 1445°,
0·82 mm. at 1475°.

He calculated the heat absorbed in the formation of CaC_2 according to the above equation as $121000 - 3{\cdot}3\ \theta$ Cals., where θ is the difference

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[1] *Zeitsch. Anorg. Chem.* **31**, 136 (*1902*).
[2] *Jour. Amer. Chem. Soc.* **28**, 850 (*1906*).
[3] *Zeitsch. Anorg. Chem.* **54**, 170 (*1907*).
[4] *Metall. Chem. Engin.* **8**, 279, 324 (*1910*).
[5] *Trans. Amer. Electrochem. Soc.* **9**, 153 (*1906*).

between the working temperature and room temperature. At 1460°, Q is 116,000 Cals. Working as on p. 24, the ratio $\frac{p_{1475°}}{p_{1445°}}$ becomes 1·79, whilst he had found $\frac{0·82}{0·44} = 1·86$. The agreement justified a further extrapolation, and Thompson gives as mean values for the equilibrium pressures

0·50 cm. at 1575°,
2·53 cm. at 1675°,
10·7 cm. at 1775°,
40·5 cm. at 1875°,
133 cm. at 1975°.

Rudolphi's figure (25 cm. at 1810°) shows the best agreement. The others are undoubtedly too low.

The melting-point of pure CaC_2 is unknown. The commercial product always contains much lime together with other impurities, often including carbon, and consequently melts lower. The temperature at which it collects in the furnace is probably about 2000°, perhaps lower. From Thompson's figures we see that under these circumstances a CO pressure of 100–150 cm. would be necessary to convert it into lime and carbon. As the gas leaving a carbide furnace averages 75 per cent. CO, corresponding to a pressure of 57 cm., there is at these temperatures no fear of such a reverse action taking place. At lower temperatures, however, this is possible. But it is unlikely to assume any importance. The CaC_2 is produced at higher temperatures in the neighbourhood of the arc, and falls in the liquid state to the bottom of the furnace, the arc still playing on its surface. For re-formation of carbon and lime, contact with CO is necessary, and the area presented to the action of the gas is small.

The quality of the carbide somewhat affects its stability. The poorer it is, the lower the temperature to which it can be brought under a given CO pressure *without* the reverse reaction commencing. Commercial carbide is usually about 85 per cent. pure, a better material than Thompson's, and therefore more liable to be decomposed than the latter. But, apart from any interaction with CO, there is no doubt that carbide whilst in the furnace must continually dissociate into its elements, giving graphite and calcium vapour (equation *b*). The latter, as it passes away, will be oxidised by the CO, giving finely-divided lime and carbon dust (equation *c*), which will be largely carried off by the issuing gases. This fact is responsible for a large proportion of both the power and the lime losses. If carbide were not formed in the arc far more quickly than it dissociates, there would be none at all produced in the furnace. It should be added that a certain re-formation of carbide also probably takes place in the melt itself between the graphite resulting from the dissociation and the excess of lime always present.

Heated CaC_2 can also undergo another change.[1] If kept at 1000° for some time it slowly separates carbon (its colour turning from grey to black), and apparently forms a lower carbide. This new product gives no acetylene with water, but can absorb nitrogen, forming cyanamide. The change is accelerated by the presence of certain substances such as CaF_2, etc. No equilibrium is observed. This change, which has not yet been fully studied, is obviously of the greatest interest. Apart from other reasons, it is probable that it forms a preliminary stage in the conversion of carbide to cyanamide by nitrogen.[2]

In calculating the theoretical energy expenditure for the production of one ton of carbide, we will assume with Haber that it is tapped at 2000°, and that the gases leave the furnace at 2500°. Then the energy necessary to produce 64 kilos. of carbide is the sum of

(*a*) The energy necessary at room temperature for the reaction

$$CaO + 3C \longrightarrow CaC_2 + CO$$

using amorphous carbon;

(*b*) The energy necessary to heat 64 kilos. of carbide from 0°–2000°.

(*c*) The energy necessary for the heating up at constant pressure of one gram. molecule CO from 0°–2500°.

We have—

(*a*) 114,550 Cals.

(*b*) The specific heat of CaC_2 between 0°–2000° can be taken roughly as 0·28. From that we calculate an expenditure of $0{\cdot}28 \times 64 \times 2000 = 35840$ Cals.

(*c*) C_p (mean) for CO between 0°–2500° is about 7·4. The necessary heat expenditure is therefore $7{\cdot}4 \times 2500 = 18500$ Cals.

A total of 169,000 Cals. is therefore necessary for the production of 64 kilos. of carbide. We have then—

1 ton requires
$$\frac{169000 \times 1000 \times 4{\cdot}19}{64 \times 3600} \text{ K.W.H.}$$
$$= 3100 \text{ K.W.H.}$$

2. Carbide. Technical[3]

Raw Materials.—These are essentially lime and carbon. The question of their purity is important. If they contain too large quantities of impurities, then, with small furnaces, thick crusts are formed which are a great hindrance to regular and effective working. With larger furnaces a viscous melt results, not easily tapped. But usually all the impurities dissolve in the carbide, and the question becomes —which of these lower the value of the product?

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[1] Erlwein, Warth, and Beutner, *Zeitsch. Elektrochem.* 17, 177 (*1911*).

[2] P. 481.

[3] Many details in this section, particularly those dealing with the charge and with the large three-phase furnaces, have been taken from Helfenstein's article in Askenasy's *Einführung in die technische Elektrochemie*, vol. i. (1910). See also Conrad, *Electrochem. Ind.* 6, 397 (*1908*).

It is of prime importance that the phosphorus content should be at a minimum. Subjected to the strongly reducing action of the carbide furnace, any phosphorus present will be as phosphide, from which water liberates PH_3. It is well known that in the impure state this gas is spontaneously inflammable, and there is little doubt that many of the earlier explosions with acetylene lamps and generators were caused by it. Less likely to be present, but equally harmful, is arsenic. Sulphur, though not dangerous, should also be avoided. These impurities are likely to occur in the raw materials as $Ca_3(PO_4)_2$, $CaSO_4$, pyrites, arsenical pyrites, etc., and must not exceed a certain low limit. From the point of view of regularity and ease of furnace working, both magnesia and alumina must be kept low, as it is they which thicken the carbide and form crusts. Silica, alkali, iron, etc, the other constituents of the lime or of the fuel ash, are of quite minor importance.

The lime used, besides being of good quality chemically, must also have a certain mechanical strength, and not tend to crumble into dust. The carbon can be used, as in the ferro-silicon furnace, as either charcoal, coke, or anthracite. Charcoal is usually more expensive and a larger quantity is needed, but its purity and voluminous structure render it the best form. Coke is often used, but its high ash content is a disadvantage. Anthracite is perhaps most often employed. It can be got with a low ash content (3 per cent.), and fairly free from sulphur and phosphorus. Its dense structure renders it less reactive than charcoal or coke, and though this decreases the combustion losses, it is otherwise not an advantage in the furnace process. Lime and fuel are mixed and charged in pieces up to a few inches diameter, depending on the size of the furnace.

Furnaces.—Carbide furnaces are essentially of two types, those in which the carbide leaves the furnace as a solid block, and those from which it is tapped as liquid. Considerable difficulties retarded the development of this second type of furnace, owing to the hardness of the solid carbide, its high melting-point, and the viscosity of the fused mass. These have now been overcome, and the disappearance of the 'block' furnaces is only a matter of time. All carbide furnaces are arc furnaces. Resistance heating also takes place, its extent depending on the conductivity of the carbon used, and current and voltage are somewhat affected thereby. But the essential part of the heating comes from the arc. Coke-fed furnaces, because of the higher conductivity of the charge, have more resistance heating than others.

The simplest type of carbide furnace is the low power **discontinuous block furnace** with hearth electrode, still much used in France. A box (Fig. 121) of iron plate mounted on wheels is lined with electrode carbons. The bottom of this lining is connected electrically with one of the terminals of the generator or transformer, and the current passes through it, through the layer of carbide in the crucible, and then as an arc to the carbon electrode, fed in from above. The furnace is provided on top with a funnel-shaped sheet-iron extension, lined with a refractory. The charge is shovelled into this and heaped up round the electrode. During a run the electrode must be gradually raised as the carbide collects in the crucible, and this is done by hand. When sufficient material has collected (the furnace can be almost filled), the current is stopped, the hearth electrode disconnected, the furnace wheeled away, and the whole allowed to cool for a few hours. The block formed is then lifted out, and, after further cooling, separated from the large quantities of adhering lime and carbon, broken up and packed.

Such a furnace does not consume much power. The first ones made only took 100 K.W. King describes early furnaces at Niagara working with 65–70 volts and 1,700–2,000 amperes. The units now generally used are of 200–250 K.W., requiring 40–70 volts. Several such furnaces are connected up and run together. The block produced can weigh up to 400 kilos., and is taken out after a four-hour run. To a very great extent (50 per cent. or more) it consists of substances other than carbide, chiefly lime and fuel, but also containing crusts of impurities and half-converted material. The removal of these impurities is a great source of loss in the block process. As far as possible, of course, all is returned to the furnace, but much burns away or is lost as dust. Then large quantities of fuel are burnt away and lime vaporised during the process itself. We must further add the lime losses due to dissociation of CaC_2. The heat losses are high, both because of the small size of the furnace and because of the fact that, after each block has been taken out, the furnace itself and the unchanged material removed from the block must both be reheated. There are usually further large losses resulting from bad electrical contacts, particularly at the hearth electrode, which is disconnected after each run.

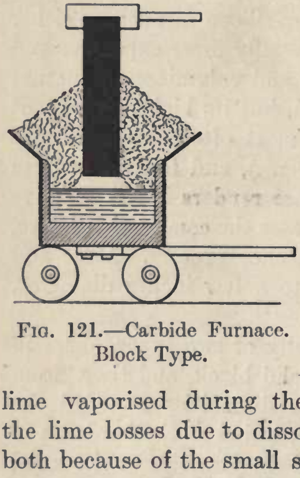

FIG. 121.—Carbide Furnace. Block Type.

In view of the above it is not surprising that, for the production of 1 ton of 85 per cent. commercial carbide, 0·8–1·5 tons of fuel (depending on its nature) and 1·08–1·2 tons of lime are necessary (Helfenstein). The theoretical figures are 0·75 ton lime and 0·48 ton carbon, assuming that all the energy for the reaction is supplied by the current. The energy consumption amounts to about 6–7 K.W.H. per kilo. of 85 per cent. carbide. The energy efficiency is therefore

$85 \times \frac{3 \cdot 1}{6 \cdot 5} = 40$ per cent. Apart, however, from low energy efficiency and high consumption of raw materials, the discontinuous block process has other disadvantages. Of these the chief is the high labour charge entailed in the frequent uncoupling of the furnaces, removal and cleaning of the blocks. The output of the plant is also small for its size, and the whole method of working cumbersome. On the other hand, the furnace itself is simple and easy to repair, and, if the power available happens to be very small, is the only kind which can be used.

Continuous Block Furnace.—The Union Carbide Co. works a continuous block process at Niagara, employing the Horry furnace (Fig. 122). In appearance this furnace resembles a large vertical wheel. It consists essentially of two broad disc-rings of sheet-iron. These are placed in a vertical position, parallel to one another and 3′ apart. By means of two drums, AA′ and BB′, on the circumferences, these are combined together into a ring-shaped box. The inner drum BB′ is continuous and connected with the axle on which the furnace revolves. The outer drum is not made in one piece, but consists of a number of segmental plates about 1′ in length (and naturally 3′ broad). These are bolted on to the outside edges of the two rings. A fixed vertical shaft C fits into the box tangentially at one of its horizontal diameters. It is clear that when the furnace revolves (in the direction indicated by the arrow) the plates forming the outer periphery of the box must be removed before the corresponding segment comes opposite to the shaft. In practice these plates are only kept bolted on to what is at any time the lower half of the furnace, the upper half being always open.

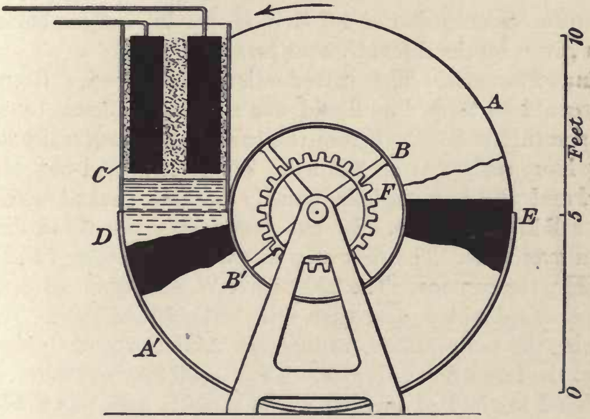

Fig. 122.—Horry Carbide Furnace. Continuous Block Type.

Two electrode bundles are placed in the shaft C, and the raw materials charged in above. The current passes from one electrode to the surface of the carbide and back to the other electrode. On starting the current and slowly revolving the furnace, a continuous block of carbide (sausage-shaped) is produced in the middle of the box, surrounded with unchanged raw material. By the time it has reached the other side of the furnace it is sufficiently cooled, and is withdrawn. During the process the outer segmental plates must be continually bolted on at D and taken off at E. The regulation and rotation of the furnace are effected by a screw working in the cogwheel F, and controlled automatically by voltage fluctuations in the hearth.

According to Haber,[1] the furnace revolves once in three days. It is fed with 110 volts and consumes 150–250 K.W. The electrodes are each a bundle of four rods (1 m. × 10 cm. × 10 cm.). The current density in the carbon is about 5 amps./cm.^{2} J. W. Richards [2] states that the load is 375 K.W., and that 2 tons carbide are produced daily. This means a consumption of 4·5 K.W.H. per kilo., a far better result than that given by the discontinuous furnace.

Tapping Furnaces.—The introduction of furnaces from which the CaC_2 could be tapped as liquid was rendered difficult by the very high temperature necessary before the carbide becomes really fluid, not viscous. Most early attempts failed. The melt flowed out with great difficulty, and the tapping-hole quickly became choked with a hard mass of solidified carbide. In the last few years these difficulties have been overcome. The first step was a large increase in the power consumed by the furnace. The 200–250-K.W. unit of the discontinuous block type was doubled, and then still further increased. The effect was to raise the temperature, to increase the fluidity of the melt, and to prevent the formation of crusts. The second improvement consisted in a modified method of tapping. The tapping-hole was made larger than before, and closed with a large iron plug whilst the carbide was still flowing freely out. The formation of a thick resistive wall of solidified carbide was thus prevented. Further, when necessary, the Helfenstein method of tapping with the aid of an auxiliary electrode [3] was adopted.

By these means, and by the general use of purer raw materials, the tapping of liquid carbide has been rendered easy, considerable advantages being thereby secured. There is a great saving in labour. The furnaces are no longer uncoupled every few hours, and there is no block to be cleaned. Then there is a considerable economy in heat and material losses. The furnaces being larger, the relative heat losses become less. And after each batch of carbide has been removed, it is

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[1] *Zeitsch. Elektrochem.* **9**, 357 (*1903*).

[2] *Electrochem. Ind.* 1, 22 (*1902*).

[3] See p. 467.

no longer necessary to heat up the furnace and a large quantity of raw material which has already been once heated. The wastage of carbon and lime resulting from the cleaning of the blocks is avoided, and the losses in the furnace due to burning and vaporisation are relatively less.

We can distinguish two types of furnace from which the carbide is tapped, those with a hearth electrode and one electrode only above, and the larger new three-phase furnaces with either three or six distinct arcs. Of the former type the **Bullier** furnace was one of the earliest, and of similar design to the simple ferro-silicon furnace of Fig. 118. A unit consumed 200–250 K.W., taking about 3,000 amps. at an electrode current density of 4–5 amps./cm.² An excess of lime was used to lower the melting-point of the product, and the tapping difficulties were thus evaded at the cost of making a lower grade material. The energy consumption was 6–7 K.W.H. per kilo., thus no lower than that necessary with the small block furnace. But there was a considerable saving of raw material.

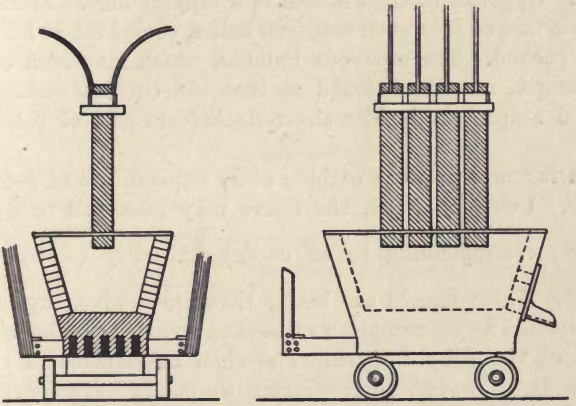
Fig. 123.—Alby Carbide Furnace.

As a type of the modern furnace with hearth electrode the **Alby** furnace may be taken (Fig. 123). The hearth consists of a steel grating into which a mixture of carbon and tar is compressed. The electrical contact is permanent and water-cooled. The sheet-iron side walls have a comparatively thin refractory lining. The tapping-hole is in one of the end walls. A single unit usually consumes 750–1,200 K.W. At Odda[1] the furnaces take 28,000 amps. at about 50 volts. The electrode bundle consists of five carbon electrodes, each of section 40 × 40 cm., corresponding to an electrode current density of 3·5 amps./cm.² The furnaces are tapped every 45 mins. into special ladles, and yield carbide at an expenditure of

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[1] *Electrochem. Ind.* 7, 212, 309 (*1909*).

4·2–4·5 K.W.H. per kilo. For every ton of product some 900 kilos. of lime (poor in MgO and Al_2O_3) and 600 kilos. anthracite (3 per cent. ash) are used.

The large three-phase carbide furnaces are very similar to that in Fig. 120. They have been built for loads up to 9,000 K.W., 3,000 K.W. per phase and per hearth. Above that limit it was found impossible to go, owing to heat and fumes, but a larger furnace was built by including two separate three-phase systems in one furnace channel. The resulting unit contains six electrode bundles, and consumes 18,000 K.W. at $\cos \theta = 0{\cdot}8$ (about). Such furnaces consist of rectangular iron boxes lined with a thin layer of refractory, and with a hearth of carbon (water-cooled). A layer of solidified carbide coats the inside of the walls, and the electrode bundles are so spaced that a bridge of solid carbide separates them. The arcs all pass between electrode and carbide. Opposite to each hearth is a tapping-hole. From these the carbide is tapped into open cast-iron ladles, cooled for 24 hours, broken up and packed. The electrode bundles, which may each carry up to 45,000 amps., are dimensioned so that the current density does not exceed 6 amps./cm.^{2} [1] The electrode holders are, of course, water-cooled.

Such furnaces produce carbide at an expenditure of 4–4·2 K.W.H. per kilo. Using charcoal, the figure may even fall to 3·8 K.W.H. per kilo., corresponding to an energy efficiency of $85 \times \frac{3{\cdot}1}{3{\cdot}8} = 69$ per cent. These figures are better than those given by other types of furnace. The consumption of lime and carbon is almost the same as that of the Alby furnace. The chief advantages of these large furnaces is, however, their greater simplicity of construction and working. With the introduction of the Helfenstein closed furnaces,[2] these advantages will be still further extended.

3. The Nitrogen Problem [3]

The last decade has seen an enormously increased demand for combined nitrogen in available form, a demand resulting from the wider appreciation of the value of artificial manures for crop-raising. The only two sources of combined nitrogen for this purpose until very recently have been the Chile deposits [$NaNO_3$] and the distillation of coal [$(NH_4)_2SO_4$]. The world's consumption of the former substance is now over 2,000,000 tons per annum, of the latter about 1,200,000

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[1] Thus a 7,000 H.P. three-phase furnace takes 45,000 amps. at 80–100 volts per phase, $\cos \theta$ being about 0·75 and the electrode current density 5 amps./cm.^{2}

[2] Fig. 47.

[3] Guye, *Jour. Soc. Chem. Ind.* **25**, 567 (*1906*); Haber, *Zeitsch. Angew. Chem.* **23**, 684 (*1910*).

tons, and the demand is likely to continue rapidly to increase. On the other hand, the Chile deposits are becoming exhausted, and, even including the less pure material which has yet hardly been touched, will probably not last out for more than fifty years, assuming a normal rate of increase of consumption. The production of $(NH_4)_2SO_4$ is limited by the coal consumption, and although far more nitrogen might be obtained from this source if a greater proportion of the coal were gasified in low temperature gas producers, yet the amount available will never be capable of coping with the present increasing demand. In the future it is indeed possible that the enormous dissipation of the combined nitrogen of sewage which takes place may be checked, but at present there is nothing to expect in that direction.

Under these circumstances it has become imperative to secure fresh sources of combined nitrogen. The atmosphere furnishes a practically unlimited supply in an uncombined state; the problem is therefore the conversion of this nitrogen into a useful form. Three methods of doing this are in the field. The first, which has been worked technically for some years and which we shall presently discuss, consists in separating pure nitrogen from air and allowing this to act on CaC_2, when calcium cyanamide ($CaCN_2$) results. This product can either be used directly as a fertiliser, or its nitrogen readily converted into ammonia.

The second method has been recently worked out by Haber and Le Rossignol, and is being developed by the Badische Anilin und Soda Fabrik. It consists in the direct synthesis of ammonia from nitrogen and hydrogen at relatively low temperatures under pressure, using a suitable catalyst, and will probably assume considerable importance in the near future.

The third method consists in passing an electric discharge through air. Nitrogen oxides result, and by absorption in water or in alkaline solutions are converted into HNO_3, nitrates, or nitrites. We shall consider this method in detail in Chapter XXVII.

4. Cyanamide. General[1] and Theory

It was early discovered that, on strongly heating a mixture of carbon and an alkali or alkaline earth in nitrogen, the latter was absorbed, giving cyanides or similar substances from which ammonia could be obtained. Many investigators attempted to carry out this reaction technically, but without success. Thus Erlwein heated the charge under pressure in a resistance furnace. At best he got a product with 20 per cent. nitrogen, but generally only half as much was absorbed and the power costs were high. Frank suggested in 1895 the action of nitrogen on CaC_2 previously prepared, and, with Caro, succeeded

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[1] *Trans. Farad. Soc.* **4**, 99 (*1908*); *Zeitsch. Angew. Chem.* **22**, 1178 (*1909*).

finally in developing a successful commercial process on these lines. Finely-divided technical carbide rapidly absorbs nitrogen at 1000°, giving calcium cyanamide, according to the equation

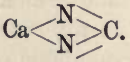
$$CaC_2 + N_2 \longrightarrow CaCN_2 + C.$$

This product can be used directly as a fertiliser with great success, except in certain abnormal soils. Steam gives ammonia almost quantitatively (97 per cent.); and, by suitable treatment, cyanides and products such as urea and guanidine salts can be made. The heating necessary during the nitrogen absorption was at first carried out in gas-fired retorts. This method has now been replaced by electric heating.

The chemistry of the relations between CaC_2, $CaCN_2$, and connected substances is complex, and by no means yet cleared up, in spite of the work recently devoted to the subject. Two formulæ have been proposed for $CaCN_2$, viz.:

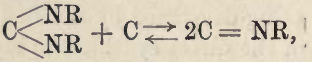
$$Ca = N - C \equiv N,$$

and



$$Ca\begin{matrix} <N> \\ <N> \end{matrix}C.$$

The first corresponds more closely to the name of the substance, the latter renders its relation to $Ca(CN)_2$ more apparent. Thus we can write the general equation



$$C\begin{matrix} NR \\ NR \end{matrix} + C \rightleftarrows 2C = NR,$$

where R is an atom of a monovalent (alkali) metal or a half-atom of a divalent (alkaline earth) metal.

According to this equation, carbon and a cyanamide can react, giving a cyanide, and *vice versa*. It is found experimentally that, if R be an alkali metal, the right-hand side of the equation is favoured. Thus $CaCN_2$ heated with carbon and NaCl or KCl as a flux gives large quantities of NaCN or KCN. If $CaCl_2$ be used instead, only quite small quantities of $Ca(CN)_2$ result. The equilibrium in that case lies over in favour of the left-hand side of the equation. A barium salt gives a mixture of cyanide and cyanamide in more or less equal proportions. In all cases the higher the temperature the larger the proportion of cyanide.

Commercial CaC_2 and BaC_2 commence to absorb nitrogen appreciably at about 700°. CaC_2 gives almost entirely cyanamide, BaC_2 also large quantities of cyanide, corresponding to the above statement. Until quite recently it was assumed that the reaction between the nitrogen and the carbide took place according to the equation

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

without the formation of any intermediate product. On that view there should be a definite nitrogen equilibrium pressure corresponding to each temperature. If that be exceeded, any carbide present must be azotised; if the pressure be kept below that value, cyanamide and carbon must react (or tend to react) and reproduce carbide and nitrogen. As the absorption of the nitrogen is strongly exothermic, rise in temperature should favour the left-hand side of the equation.

According to Caro,[1] the equilibrium temperature corresponding to one atmosphere pressure is 1360°. Matignon[2] calculates it under certain assumptions to be 1100°. Attempts have been made to measure this equilibrium, *e.g.* by Le Blanc and Eschmann.[3] The investigators have attributed their non-success to a variety of causes; viz. (*a*) disturbance of the equilibrium by sublimation of the cyanamide; (*b*) gradual alteration in the properties of the carbon present ('ageing'); (*c*) impurities which may take part in the reaction; (*d*) chemical inertness of the nitrogen. But the results of Erlwein, Warth, and Beutner[4] indicate a still more fundamental cause, *i.e.* that the above equation does not fully express the azotisation of CaC_2. Two consecutive reactions are probably involved, the decomposition of the CaC_2 by heat into carbon and a lower carbide, and the absorption of nitrogen by the latter. Assuming, for example, CaC to be formed, we should have

(i) $$CaC_2 \longrightarrow CaC + C;$$

(ii) $$CaC + N_2 \longrightarrow CaCN_2.$$

Any equilibrium involving nitrogen would then correspond to equation (ii), and it is clear that its investigation must be preceded by a thorough study of the change undergone by CaC_2 when heated.

It is true that Thompson and Lombard[5] claim to have measured true equilibrium values (1 atmosphere at 1700° [extrapolated]). But it is an unlikely assertion. The straight line relation they give connecting pressure and temperature between 1050°–1450° necessitates an enormous and improbable variation of heat of reaction with temperature, and their criteria of equilibria are not quite free from objection. Further, one interesting experiment confirms the work of Erlwein, Warth, and Beutner. A sublimed sample of cyanamide was mixed with graphite and heated. Much gas (assumed to be nitrogen) was given off at 1287°. But *no carbide resulted.* They suppose oxygen to have accidentally entered their furnace. It is more likely that the cyanamide simply decomposed thus:

$$CaCN_2 \longrightarrow CaC + N_2.$$

Carbide would first be formed at a far higher temperature.

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[1] *Zeitsch. Angew. Chem.* **22**, 1178 (*1909*).
[2] *Ann. Chim. Phys.* [viii], **14**, 51 (*1908*).
[3] *Zeitsch. Elektrochem.* **17**, 20 (*1911*).
[4] *Zeitsch. Elektrochem.* **17**, 177 (*1911*), and p. 472.
[5] *Metall. Chem. Engin.* **8**, 617, 682 (*1910*).

We must next deal with the dynamics of the reaction. Moissan showed that pure CaC_2 is quite inert towards N_2 at 1200°, and that pure BaC_2 only absorbs traces. That commercial CaC_2 absorbs nitrogen comparatively easily and below 1200° is due to the fact that it contains 10–15 per cent. lime and other impurities. But even then the action is not rapid. Foerster and Jacoby[1] investigated the rate at which the gas is absorbed at different temperatures, and Fig. 124 contains their results. The maximum nitrogen content possible with the sample of carbide used was 25·5 per cent. One notices that the temperature must be at least 1000° for complete and rapid absorption. At lower temperatures an apparent saturation limit is reached, beyond which the percentage of nitrogen very slowly rises. But these are not true equilibria, for carbide azotised at 1100° loses no nitrogen when heated for four hours at 900°. The above absorption velocities hold for nitrogen at atmospheric pressure. The rate of azotisation is proportional to the pressure up to about two atmospheres; above that limit, further increase of pressure makes little difference.[2]

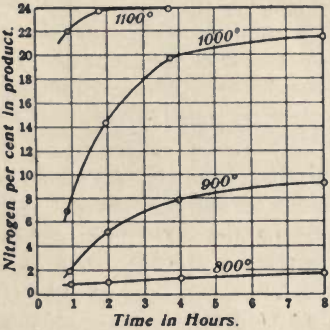

FIG. 124.

Under technical conditions, using large quantities of carbide, the heat liberated during the initial stages of the absorption serves to heat the charge up to 1000°–1100°, *i.e.* to the temperature necessary for satisfactory absorption. A product with 20–22 per cent. nitrogen usually results. External heating is required only for raising the charge to the initial reaction temperature, and for compensating subsequent conduction and radiation losses. It has been found that various substances admixed with the carbide are capable of lowering this minimum initial reaction temperature, and their technical use has been proposed. It was claimed that, as the reaction takes place at a lower temperature, the heat losses during the azotisation would be less, and less energy would be required for the initial heating up of the charge. The best known of these additions are $CaCl_2$ (Polzenius) and CaF_2 (Carlson).

This subject has been investigated in detail by a number of workers, including Bredig, Fraenkel, and Wilke,[3] Foerster and Jacoby,[4] and Rudolphi.[5] A very large number of substances have been found to

[1] *Zeitsch. Elektrochem.* **13**, 101 (*1907*).

[2] Pollacci, *Zeitsch. Elektrochem.* **14**, 565 (*1908*).

[3] *Zeitsch. Elektrochem.* **13**, 69, 605 (*1907*).

[4] *Loc. cit.*, and *Zeitsch. Elektrochem.* **15**, 820 (*1909*).

[5] *Zeitsch. Anorg. Chem.* **54**, 170 (*1907*).

thus facilitate azotisation. Such are CaO (which accounts to a large extent for the properties of the technical carbide), $CaCO_3$, Na_2CO_3, NaCl, LiCl, $AlCl_3$, K_2CO_3, etc., etc., as well as $CaCl_2$ and CaF_2. With the exception of LiCl, $CaCl_2$ is by far the most effective addition. Thus, Bredig heated a sample of carbide at 800° for two hours and obtained the following results :

TABLE LXVIII

Addition.	Per cent. nitrogen absorbed.
———	3·2
10 per cent. CaO	4·0
10 per cent. Na_2CO_3	8·5
10 per cent. NaCl	13
10 per cent. $CaCl_2$	22

Rudolphi found that a carbide which only took up 1·4 per cent. nitrogen during two hours at 800° absorbed 13·05 per cent. when 18·7 parts $CaCl_2$ were added to 62 parts CaC_2. Foerster showed that, under his working conditions,[1] CaC_2 with 15 per cent. $CaCl_2$ absorbed in two hours at 700° seven times as much nitrogen as pure CaC_2 did at 800°. At 900° the effect of 10 per cent. CaF_2 during a two-hours experiment was equal to that of 15 per cent. $CaCl_2$ at 800°.

The effect of the *quantity* added is very irregular in the initial stages of the absorption. With $CaCl_2$, the maximum effect at 800° is produced with 30 per cent. $CaCl_2$ in the reaction mixture ; with CaF_2 the best proportion is 5 per cent. at 800° and 2 per cent. at 900°. With K_2CO_3 the best effects are produced with 4 per cent. added. But in some cases (*e.g.* CaF_2—Foerster) these differences disappear in course of time, the tendency being for a constant percentage of the carbide to be azotised, whatever the *amount* of addition present. This only determines the velocity of absorption. The final limit differs in different cases. Thus, with CaF_2, the limit at 860° is 14·9 per cent. nitrogen, as compared with about 5 per cent. without the CaF .

The ultimate cause of the effect produced by these additions (including the lime always present in commercial carbide) appears to be connected with the lowering of melting-point brought about. Other possible explanations were eliminated by Bredig and his co-workers. Both with and without any special addition, the azotised mass is found to have sintered (*i.e.* to have undergone surface fusion). The immediate cause is more obscure, but is probably connected with the rate of decomposition of the CaC_2 to carbon and that lower carbide which, as we have seen, is probably the substance that actually absorbs the nitrogen.

It has already been indicated that technically these additions are

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[1] Differences in composition of starting material and in degree of fineness of division account for the discrepancies between the results of the different experimenters.

not used. Foerster and Jacoby were able to show that, in the case of $CaCl_2$, though the reaction commenced at a lower temperature, the heat liberated soon raised the mass to 1000°. Thus the gain would be limited to the small amount of energy required to heat up the charge to the reaction temperature. But with CaF_2 the reaction took place more slowly and the temperature remained at about 900°. The heat losses would in that case be somewhat lower, but it is doubtful whether the advantage would amount to much. The energy consumed in the cyanamide furnaces is small in any case.

5. Cyanamide. Technical[1]

The published details concerning this process are somewhat scanty. The carbide is first finely ground in an air-tight apparatus filled with pure dry nitrogen, and then transferred into a number of drum-shaped retorts. These are of iron, take from 300–500 kilos. carbide, and are provided with a central resistance in the shape of a carbon rod (or several in series). These retorts are now placed in position in the 'furnace,' which consists of a gas-tight horizontal channel, the roof of which can be removed to allow of the handling of the retorts, and the carbon resistances of the latter are connected electrically to suitable permanent terminals in the furnace. Pure nitrogen is then admitted into the channel under a slight *plus* pressure in order to overcome any tendency of air to enter. This nitrogen is usually prepared by fractional distillation of liquid air (Linde process), but can also be made by passing air over heated copper. It must be as free as possible from O_2, H_2O, CO, CO_2. Thus O_2 should on no account exceed 0·4 per cent. These substances act on the carbide and lower the nitrogen content in the final product.

When all air has been expelled, the current (usually alternating) is switched in. Each retort takes some 65–75 volts. It is probable that the amperage is low (*e.g.* 20 amperes), and that a number of units are connected together in parallel. The process lasts 30–40 hours, longer with the larger units. During this time the temperature rises to about 1000°. When this value has been reached in the outermost layers of the retort (*i.e.* those furthest from the resistance) the current is stopped, and the reaction allowed to complete itself. The end of the process is indicated by a manometer in the nitrogen pipe-line. After cooling the retorts, the coke-like mass, which has somewhat shrunk and sintered together, is crushed and packed. It usually contains 20 per cent. nitrogen, sometimes a little more, sometimes only 15 per cent. if the quality of the carbide is bad.

The use of the small units described is necessary because of the

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[1] *Zeitsch. Elektrochem.* **15**, 820 (*1909*); *Electrochem. Ind.* **7**, 212, 309, 360 (*1909*); *Metall. Chem. Engin.* **9**, 100 (*1911*).

difficulty of otherwise getting a reliable product, which demands uniform conditions, particularly of temperature. The electric method of heating avoids the difficulties otherwise arising from the strong sintering of the material, particularly its adhesion to the sides of the externally-heated clay retorts. The energy consumption is small. According to Caro, the total energy necessary for the fixation of one ton of nitrogen by this method, including the production of the carbide, azotising, machine driving, grinding and crushing, mechanical charging and air liquefaction, amounts to $<$ 3 H.P. years. The share of the cyanamide furnaces in this amount must be of the order of 0·1 K.W.H. per kilo. of product (0·5 K.W.H. per kilo. of nitrogen).

Literature

Helfenstein. Article in Askenasy's *Einführung in die technische Elektrochemie*, vol. i.

CHAPTER XXVI

OTHER ELECTROTHERMAL PRODUCTS

In this chapter we shall treat certain electrothermal products relatively less important than those already discussed. They include:

(*a*) Carborundum and allied substances;
(*b*) Graphite;
(*c*) Alundum: fused silica;
(*d*) Carbon bisulphide: phosphorus: zinc.

1. Carborundum and Allied Products

When silica is reduced by carbon at high temperatures, it is possible by varying the conditions to obtain a number of different products. We can distinguish at least four: (*a*) silicon monoxide ('monox'), SiO; (*b*) metallic silicon; (*c*) silicon carbide, SiC ('carborundum'); (*d*) an oxycarbide of rather indefinite composition, but approximately Si_2C_2O ('siloxicon'). Silicon and carborundum are technical products, and attempts have been made to put monox and siloxicon on the market.

The two conditions chiefly determining the product are temperature and the composition of the charge. According to Greenwood,[1] an intimate mixture of SiO_2 and carbon first evolves CO at 1460°, and in absence of further knowledge we can suppose that at this temperature the reaction

$$SiO_2 + C \rightleftarrows SiO + CO$$

becomes appreciable. At higher temperatures the course of the reaction depends on the proportion of carbon present. If this is not in excess, the SiO will be reduced to metallic silicon only; with sufficient carbon present, siloxicon or carborundum will result. The latter can also directly arise from the action of silicon vapour on carbon, and, at still higher temperatures, will dissociate, liberating its silicon

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[1] *Electrochem Ind.* 7, 119 (*1909*).

as vapour and leaving a grpahite residue. The corresponding equations are

(a) $SiO_2 + C \rightleftarrows SiO + CO$;
(b) $SiO + C \rightleftarrows Si + CO$;
(c) $2SiO + 3C \rightleftarrows Si_2C_2O + CO$;
(d) $Si + C \rightleftarrows SiC$;
(e) $SiO + 2C \rightleftarrows SiC + CO$;
(d) $SiC \rightleftarrows Si + C$ (graphite).

All are reversible. CO passed over silicon or carborundum at suitable temperatures gives carbon and silica. Our knowledge of the temperatures corresponding to these different reactions is, however, scanty. We know that the preparation of silicon demands a furnace of high power and a high temperature, exceeding that necessary for the production of 50 per cent. ferro-silicon, which we have assumed to be tapped at 1600°. Lampen and Tucker[1] have investigated the temperatures of production and dissociation of carborundum. At 1600° the first signs of siloxicon formation were observed. Between 1600° and 1900° more and more was produced. At 1920° its conversion to carborundum commenced, and was complete at 1980°. The longer the charge was heated and the higher the temperature, the larger were the crystals produced. Finally, at 2220° dissociation into graphite and silicon commenced, and was complete at 2240°. Gillett[2] investigated the matter more accurately. He gives 1540° ± 30° and 1820° ± 20° as the temperatures of formation of siloxicon and carborundum respectively, and 2220° ± 20° as the temperature of dissociation of the latter. The first two values are lower than those of Lampen and Tucker, the last agrees well. These figures give us some idea of the necessary technical conditions.

Silicon Monoxide (Monox).—It is unnecessary to consider this substance at length. A red-brown powder, its use as a pigment, as a reducing agent, and for polishing purposes, was suggested by Potter, who discovered it.[3] For a short time it was on the market, but met with no great success, and its technical production soon ceased.

Silicon.—The production of this substance (95 per cent. pure) has been developed both by the ferro-silicon and the carborundum manufacturers. The former look on it as essentially a high-percentage ferro-silicon, whilst the latter regard it as one of the products of the reduction of silica by carbon. Indeed the first attempts[4] to make it took place in a resistance furnace (such as is used in the manufacture of carborundum (p. 489). This consisted of a vertical cylinder of

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[1] *Jour. Amer. Chem. Soc.* **28,** 850, 853 (*1906*).
[2] *Jour. Phys. Chem.* **15,** 213 (*1911*).
[3] *Trans. Amer. Electrochem. Soc.* **12,** 223 (*1907*).
[4] Tone, *Trans. Amer. Electrochem. Soc.* **7,** 243 (*1905*).

firebrick, open at the top, and containing a vertical carbon core as resister. The charge was a thoroughly incorporated mixture of 5 parts silver sand + 2 parts finely-ground coke. It is stated that various silico-carbides were first obtained and subsequently decomposed, giving drops of silicon, which gradually collected in the bottom of the furnace, from which the melt was tapped off. If this view is correct, it follows that the temperature of formation must have exceeded 2200°, the silicon vapours condensing in the cooler parts of the furnace.

This method evidently worked unsatisfactorily, as we learn[1] that the Carborundum Co. now uses an arc furnace, apparently similar to the large furnaces used in Europe for the same purpose and for the manufacture of high-percentage ferro-silicon.[2] The unit employed consumes 1200 H.P. and is constructed of firebrick lined with carbon. It has two vertical electrodes, dipping well down into the charge of coke and sand. A pig of 250–350 kilos. is tapped every few hours. It is 90–97 per cent. pure, the impurities being iron and aluminium, with some carbon. The yield (per K.W.H.) is small, and in Continental practice the furnaces are larger—at least 1500 H.P.—with a very high electrode current density. The tapping offers difficulties, and the electrical method is invariably used. The product is a dense crystalline substance with a dark silver lustre. According to Tone it melts at 1430°, but at this temperature, and probably for a good deal higher, it will certainly be very viscous. It is used for making silico-steels, etc.

Carborundum.[3]—This substance is the most important of the interaction products of silica and carbon. It was discovered in 1891 by Acheson, who was attempting to dissolve carbon in molten clay, hoping that on cooling it would crystallise out. Instead of diamonds he obtained hard blue crystals, and, believing their constituents to be carbon and alumina, coined the name 'carborundum' from 'carbon' and 'corundum.' The product was quickly marketed as an abrasive, and its importance in this direction has since continually increased.

Carborundum is prepared by heating a suitable charge of carbon and sand in a resistance furnace. As carbon is used anthracite or good quality coke, containing not less than 85 per cent. carbon. The ordinary impurities do not seriously affect the process, but sulphur is unpleasant on account of the SO_2 produced, and iron and aluminium appear to catalyse the dissociation into graphite and silicon. Moisture is as far as possible avoided. The finely-ground fuel is mixed with silver sand (98–99·5 per cent. pure). The proportions of the constituents correspond roughly to the equation $SiO_2 + 3C \longrightarrow SiC + 2CO$.

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[1] *Electrochem. Ind.* 7, 189 (*1909*).

[2] P. 466.

[3] *Electrochem. Ind.* 1, 50 (*1902*); 7, 189 (*1909*).

A slight excess of coke is used. In addition some sawdust and some salt are added. The purpose of the sawdust, which, of course, soon decomposes, is to increase the porosity of the charge and thus allow the evolved CO to stream away more easily. The salt attacks the oxides of some of the metallic impurities and forms volatile chlorides (*e.g.* $FeCl_3$, $AlCl_3$), which distil away from the reaction zone. One ton of charge contains

	(Fitzgerald) Ton	(Tone) Ton
Sand	0·522	0·544
Coke	0·354	0·351
Sawdust	0·106	0·070
Salt	0·018	0·035

The construction of the furnace is as follows: The two ends are permanent stout brick walls (Fig. 125), lined with refractory carborundum bricks. Through them enter the electrode bundles. Each bundle consists of a number of rectangular carbon blocks *aaa*, firmly gripped in an iron frame set in the end wall. Between the electrodes are copper strips, which pass through the iron frame and make connection externally with the cables. As the technique of making *large* carbon electrodes improves, this electrode construction will be considerably simplified. A shallow firebrick channel connects these two ends, and the sidewalls consist of firebrick, mounted in sections in curved iron frames (convex side outwards) to facilitate their easy removal. Like the furnace bed, they are not strongly heated, and merely serve to keep the charge in position. The charge *c* is filled into the furnace to the lower level of the electrodes. Then the *heating core d* is introduced along the length of the furnace. It consists of granulated coke, the pieces having a diameter of about an inch. As far as possible the material of an old core is used, which very largely consists of graphite, and has therefore a much higher conductivity than fresh coke. To secure good contact between core and electrodes, the intervening space is filled with finely-divided coke powder (*e*), well pressed down. Finally more charge is heaped in all round (not too tightly, as gases must escape), and the core is covered above by a thick layer of material. There is no roof of any kind. In consequence of the curved sides the furnace has a roughly circular cross-section.

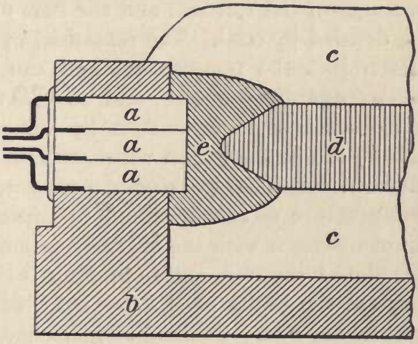

FIG. 125.—End of Carborundum Furnace.

Furnaces have been built taking up to 2,000 H.P. Their dimensions and the relative sizes of electrodes, core, etc., vary correspondingly. A 2,000-H.P. furnace is 30′ long and 10′ in diameter. The core is 3′ in diameter. When current first passes the resistance of the furnace is high. A 2,000-H.P. unit requires about 230 volts (alternating current), and will therefore take some 6,000 amperes. As the core heats up its resistance decreases, and, the furnace being worked at constant power, voltage will fall and current rise. At the end of the process some 20,000 amperes will be flowing at 75 volts. Not all will traverse the core —some will pass through the graphite and carborundum surrounding it. In a 2,000-H.P. furnace we can assume the maximum core current density not to exceed 3 amps./cm.^{2} In the electrodes it will be still lower, and this fact, together with the absence of air, accounts for their long life.[1]

These relations of current density, size of furnace, and disposition of charge are of the utmost importance in determining the efficient working of the furnace, and the best proportions in any case can only be decided by trial. The reason is, of course, that the current density determines the temperature and the rate at which the heat travels outwards from the core, and as the temperatures of formation and dissociation of carborundum lie comparatively close together (1820°–2220°) the limits within which current density, etc., can be varied are narrow. In ideal working the mass of charge which has reached the temperature of carborundum formation must be as large as possible in comparison with the quantity which has reached the temperature of graphite formation, and in practice it is found that if the current varies beyond the limits of ± 3 per cent. of the most favourable value the results are bad. Collins has published some interesting considerations on this point.[2]

An enormous quantity of CO is liberated during the process, and is burnt at the sides and top of the furnace. At the same time a considerable contraction takes place, and Amberg states that to allow for this it is usual to build the core sloping up somewhat from the two electrodes towards the middle of the furnace. When the requisite amount of energy has been passed in, the current is cut off and the furnace rapidly dismantled. Immediately surrounding the core is a ring of graphite. The carbon has been first converted to carborundum by the vapours of SiO or silicon, and this has subsequently dissociated. Then comes a layer of carborundum, the crystals being larger the nearer they are to the core, and this passes imperceptibly into a region of siloxicon. Finally there is the half-converted and unchanged material, its amount minimised by the circular furnace cross-section. The outermost layer of this is caked together owing to the fusion of the salt present,

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[1] Their connections with the copper leads are water-cooled.

[2] *Trans. Amer. Electrochem. Soc.* **9**, 31 (*1906*).

much of which has distilled out from the interior of the furnace. The thickness of the carborundum layer in a 2,000-H.P. furnace is some 18″–20″.

The different products are carefully separated, and the carborundum is broken up, sieved, and the best grades washed free from graphite, metallic oxides, etc. Five furnaces are worked together, being at different stages of heating, charging, discharging, etc. A large modern furnace requires some 8·5 K.W.H. per kilo. of purified carborundum, and produces a comparatively small proportion of siloxicon. The smaller earlier furnaces gave less favourable results.

We can calculate the theoretical quantity of energy necessary for carborundum production as follows. The equation is

$$SiO_2 + 3C \longrightarrow SiC + 2CO.$$

We have

$$[Si,O_2] = 180000 \text{ Cals.}$$
$$[Si,C] = 2000 \text{ Cals.}$$
$$[C,O] = 29200 \text{ Cals.}$$

Hence the production of one kilo.-mol. (40·3 kilos.) of carborundum at room temperature requires $180000 - 2000 - 58400 = 119600$ Cals. We will assume that the mean temperature to which the carborundum is heated is 2100°, and that the CO, while usefully warming the next layer of charge, cools down *on an average* to 1400°. (Although it doubtless leaves the furnace at a much lower temperature, much of the heat it gives up is unutilised.) Then as C (mean) for carborundum between 0°–2100° is about 11·3, and C_p (mean) for CO between 0°–1400° about 7·1, we have

Heat required to heat up carborundum

$$= 11{\cdot}3 \times 2100 = 23700 \text{ Cals.}$$

Heat required to heat up CO

$$= 2 \times 7{\cdot}1 \times 1400 = 19900 \text{ Cals.}$$

Hence, total amount of heat required

$$= 119600 + 23700 + 19900 = 163200 \text{ Cals.},$$

and 1 kilo. carborundum requires

$$\frac{163200 \times 4{\cdot}19}{40{\cdot}3 \times 3600} = 4{\cdot}7 \text{ K.W.H.}$$

This is the necessary irreducible minimum. Under technical conditions there are radiation losses, losses due to vaporisation of salt, reduction of impurities, to heating up unchanged charge, to producing graphite and siloxicon, to heating up the core, and also in the electrodes. Further, the material must be kept at a high temperature for a long time to facilitate the formation of large crystals.

Pure carborundum is white. The commercial material has generally an iridescent surface coloration, due to a trace of oxidation. If this be removed, the colour is seen to be usually a dark green. Its exceedingly resistive chemical properties, particularly to oxygen, are well known. It is practically unattacked below its dissociation temperature. All acids are without action on it. Chlorine attacks it with difficulty, but fused alkalies and alkaline carbonates, and certain metallic oxides and salts, such as $PbCrO_4$, dissolve it. Its extreme hardness makes it a very important abrasive, both for grinding and polishing. It is used as a top-dressing for pavements and stairs, etc. Its indifference to oxygen and to fused metals and its infusibility render it a valuable refractory.

It has also a high electrical conductivity, and its use in electrical cooking apparatus, etc., has often been suggested. Recently a special modification suitable for this and other purposes, and called **silundum,** has been prepared by Bölling.[1] This material is apparently a solid solution of silicon in carbon of variable composition, and is formed by the action of silicon vapour on carbon. Articles of silundum are prepared by shaping them out of graphite, embedding them in what is practically the charge of a carborundum furnace, and subjecting them to the action of silicon vapours. The extent of the silicification depends on the duration of heating. It can be either superficial or extend through the whole mass. The article produced retains its original shape, cohesion, and strength, and possesses the hardness, resistivity, and electrical conductivity of carborundum. All kinds of vessels and tubes can be made, and its power of conducting currents at high temperatures renders it particularly serviceable for electrical cooking apparatus.

Siloxicon was also discovered by Acheson, and some is always obtained in the manufacture of carborundum. The so-called 'amorphous carborundum' is merely a variety of siloxicon. It is a greyish-green powder, approximating to the composition Si_2C_2O. How far it is a definite compound is not clear. Like carborundum, it is exceedingly refractory, and makes a very useful furnace lining if the atmosphere is of a reducing nature. But it is much more readily oxidised than carborundum, and this naturally restricts its application.

2. Graphite

The successful development of the artificial production of graphite we also owe to Acheson. It was a direct outcome of his carborundum work. Carbon exists in three forms. Two are crystalline—diamond and graphite. The third is amorphous and unstable at all temperatures with respect to one of the other two. Of the two crystalline forms the diamond is stable at low temperatures, graphite at high temperatures, the former changing into the latter on heating. The exact temperature above which this change tends to occur is unknown, but may be as

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[1] *Zeitsch. Elektrochem.* **15**, 725 (*1909*); *Electrochem. Ind.* **7**, 24 (*1909*).

low as 450°. Below this temperature, whatever it is, amorphous carbon will *tend* to slowly change into diamond, above this temperature into graphite. The rate of change into diamond is immeasurably slow, and, unless the temperature be high, the rate of change into graphite is slow also. We know, however, that furnace electrodes of carbon heated to high temperatures become gradually graphitised, as also do the tips of arc lamp carbons.

It has already been mentioned that, after a carborundum furnace run, the conducting core is found surrounded by a ring of graphite, which has resulted from decomposition of previously formed carborundum. Acheson followed up this point, and soon found that the rapid conversion of coke or anthracite into graphite does not necessitate the presence of sufficient silica to form carborundum with all the carbon present. A far smaller quantity suffices, and, moreover, other oxides are active, some more, some less so than silica.[1] Al_2O_3, Fe_2O_3 and B_2O_3 are examples. The more oxide present up to a certain limit, the lower the temperature at which the reaction velocity becomes measurable.

It is evident that the function of the oxide is catalytic. The exact way in which it acts is less clear. The most natural assumption is that the stability of the metallic carbide is intermediate between the stabilities of the systems metal + amorphous carbon and metal + graphite, and that when the metal has been liberated from its oxide by the carbon it first forms carbide, which subsequently decomposes, giving graphite. The metallic vapour liberated forms more carbide with the amorphous carbon, and the process continues. When all the amorphous carbon present has become graphite, the metal simply volatilises away. This hypothesis agrees with the fact that, *after* complete graphitisation, the charge can be almost entirely freed from impurities by further heating.

Graphite[2] is produced in two forms, as powder and as finished articles, ready for use. These include bars and plates, lamp carbons, electrodes, brushes for electrical machinery, metallurgical crucibles, etc. The furnace used for the production of graphite powder is similar to the carborundum furnace. It has the same permanent end walls and arrangement of electrodes, a shallow firebrick bed, and movable side-walls of carborundum bricks. When charging, a layer of carborundum is first placed on the bed to protect it from fusion. Then the charge is filled in to the lower edge of the electrodes. Its nature depends on the quality of the product required. Usually it consists of anthracite ground to the size of rice, but far larger pieces can be used. The anthracite contains 5–15 per cent. ash, and the silica, alumina, and Fe_2O_3 present suffice to catalyse the reaction. For the finest quality

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[1] Borchers and Mögenburg, *Zeitsch. Elektrochem.* 8, 743 (*1902*); Borchers and Weckbecker, *Metall.* 1, 137 (*1904*).

[2] *Electrochem. Ind.* 1, 52 (*1902*).

of lubricating graphite, petroleum coke is used with 1–2 per cent. Fe_2O_3 added. The core consists of graphite, originally coke. It is longer and of smaller cross-section than in a carborundum furnace of equal load. This is due to the far higher conductivity of the charge. Finally, more charge is heaped around and above the core, and the furnace covered with a siloxicon layer.

A 1,000-H.P. unit (the largest constructed) is 30′ long, and has an internal cross-section 2′ in diameter. When starting, 200 volts are used. The current varies, and is comparatively low. As the temperature rises the resistance decreases. The voltage is kept constant until the current has so increased that the furnace is taking its maximum power—*i.e.* until the current is about 3,700 amperes (assuming $\cos \theta = 1$). Then the voltage gradually falls with simultaneous increase in current, the final values being 80 volts and 9,000 amperes. The total duration of a run is 20–24 hours. At its conclusion the furnace is allowed to cool sufficiently, carefully dismantled, and the graphite ground and sieved or otherwise graded.

During a single run a 1,000-H.P. furnace will convert 90 per cent. of a 6-ton charge into graphite. The energy used is consequently about $\frac{750 \times 24}{5400} = 3{\cdot}3$ K.W.H. per kilo. This will be a maximum figure. The theoretical energy expenditure necessary for the formation of one kilo. of graphite (assuming a mean temperature of 2200°) is equal to the amount required to heat up the graphite to 2200° minus the heat evolved at room temperature by the graphitisation of the amorphous carbon. Taking c (mean) for graphite as 0·45, the former figure is $0{\cdot}45 \times 2200 = 990$ Cals. The heat evolved during the transformation of amorphous carbon into graphite is 236 Cals. per kilo., and hence the total heat needed is $990 - 236 = 754$ Cals., equivalent to 0·88 K.W.H. per kilo. The low efficiency of 27 per cent. (probably somewhat higher) is the result of the long duration of heating, the large radiating surface of the furnace, the reduction and volatilisation of impurities, electrode losses, etc., etc. As in carborundum manufacture, several furnaces are run together, being at different stages in the process at the same moment.

The product got from anthracite has 5–10 per cent. ash, that from petroleum coke 0·5 per cent. or less. The physical properties of the graphite—colour, consistency, etc.—depend largely on the duration of heating and manner of cooling, and on the kind of carbon and the catalyst used. Material intended for lubricating purposes is treated with particular care. The other grades are used extensively in electrotechnics, for cleaning purposes, for pigments, and to some extent in pencils. Recently emulsions in oil and water, known as 'oil-dag' and 'water-dag,' have been marketed. They are used respectively as a lubricant and as an anti-corrosion metal paint.

For the preparation of graphite articles, such as electrodes and motor-brushes, finely-powdered petroleum coke is used. This is compressed and moulded with the aid of some tar or pitch, the necessary amount of a suitable oxide being added as catalyte. The furnace used by the Acheson Co. is again of 1,000 H.P., and externally very similar to the carborundum and powdered graphite furnaces (Fig. 126). It is shorter than the latter, however, and differs from both in having no core. The space between the end electrodes is instead filled with the objects to be graphitised, arranged transversely across the furnace at right angles to the flow of the current, each article being surrounded and separated from its neighbours by a layer of granulated coke. This arrangement increases the resistance of the furnace, and ensures gradual and regular heating. This is necessary in order that the gases may escape from the interior of the articles without damaging them. The greater part of the heat production takes place in the coke interlayers. The furnace is finally covered with a layer of siloxicon.

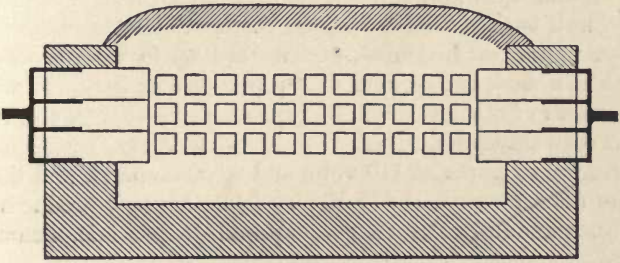

Fig. 126.—Graphite Electrode Furnace.

The duration of a run is about the same as with the powdered graphite furnaces, and voltage and current vary similarly. The production of graphite articles is 3–3·5 tons per run. Owing to the purity of the raw material, the product has only 0·1–0·6 per cent. ash.

Another method—that of Girard and Street—has been to some extent used for making graphite electrodes and rods. The moulded carbon article (B_2O_3 being the catalyst) is drawn by rollers through a horizontal arc passing between carbon electrodes in a closed chamber filled with an indifferent gas. This treatment graphitises them sufficiently for certain purposes. It is stated that the energy used is 7·36 K.W.H. per kilo. of graphite, a considerably higher figure than that of the Acheson process.

3. Alundum. Silica

Alundum.[1]—This is the name given to the fused alumina manufactured by the Norton Emery Wheel Co. at Niagara, and extensively

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[1] *Electrochem. Ind.* 1, 15 (*1902*).

used as an abrasive, for grinding and drilling, and recently for making firebricks, muffles, etc. A similar product made at Rheinfelden is called 'diamantin.'

The raw material consists of the purest bauxite obtainable. Before use it is washed free from various impurities, dried and calcined. At Niagara the fusion takes place in an arc furnace devised by Higgins. It consists essentially of a circular hearth of carbon blocks and a movable wall. This wall is of sheet-iron, water-jacketed throughout. In shape it is a truncated cone, which fits into a groove on the outside of the fixed hearth. Two carbon electrodes, introduced from above, convey the alternating current to and from the furnace. The alumina is charged in above, much as in carbide furnaces. The fused material falls to the bottom, and the current passes from one electrode to the melt and back to the second electrode, the furnace thus containing two arcs. As the alumina collects, the electrodes are presumably raised. When sufficient has been fused, the current is stopped, the electrodes lifted out, and the whole furnace allowed to cool for 3–4 hours. The movable wall is then raised, and the block of alundum removed. It is broken up, crushed, graded, and worked up in various ways. In colour it is a dark brown, due to the presence of iron. It may also contain traces of other substances, present in the charge, and reduced by the carbon electrodes.

Each furnace works at 110 volts and 2,500 amperes, and therefore consumes (at a maximum) 275 K.W. In 24 hours it produces about 7,000 lbs. alundum. The energy expenditure per kilo. amounts to $\frac{275 \times 24 \times 2{\cdot}2}{7000} = 2{\cdot}1$ K.W.H., about one-fourth that required for an equal weight of carborundum. The raw material is, however, more expensive, and there must be a considerable electrode consumption.

Fused Quartz Ware.—We can only deal with this subject very briefly here. Fused quartz glass is made in England by the Thermal Syndicate and in Germany by the Deutsche Quarz-Gesellschaft of Beuel a.Rh.[1] The process of the former is based on work of Hutton's,[2] developed later by Bottomley and others, and the Quarz-Gesellschaft uses practically the same methods.

The principle employed is as follows: Pure silver sand (99·5 per cent.) is fused by a current passing through carbon rods or plates embedded in it. Its melting-point is 1800° to 1900°, but it must be heated to about 2000° before it flows easily enough for it to be worked, and at this temperature it is already readily volatile. When we remember that carbon and silica commence to

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[1] Both these companies make the translucent material. Small transparent quartz vessels are manufactured by the firm of Heraeus.

[2] *Trans. Amer. Electrochem. Soc.* **2**, 105 (*1902*).

give siloxicon at 1540° and carborundum at 1820°, we see that there are possibilities of complicating side-reactions. It must be remembered, however, that the area of contact between the carbon and silica is comparatively small, and moreover that a thin, dense, protective layer of siloxicon or carborundum probably forms on the resistor. If the temperature of the latter exceeds 2220°, this layer will decompose, leaving graphite and evolving silicon vapours. When sufficient sand has been fused the carbon resistor is withdrawn, and, by utilising the hole left in the interior of the melt, the latter is blown out and moulded to the desired form.

This is done in various ways. Air is blown in. Or some chalk, green wood, or similar material is placed in the space left by the resistor, the ends of the semi-solid mass pushed together and closed, and the whole put inside a suitable mould.[1] In this way evaporating dishes, muffles, etc., are produced. To make tubing, a wooden twig is pushed into the interior, and the mass drawn out with great rapidity. On the speed with which this is done depend the thickness and diameter of the tubing. Sometimes the resistor consists of a perforated carbon tube. When the fusion is finished, the tube is not taken out, but compressed air is forced into its interior, and the mass thus blown into a mould.[2] Hutton made quartz tubing by simply passing a current through a carbon pencil embedded in sand. This fused round the pencil, and after cooling a tube resulted, from which if necessary the carbon could be removed by burning out.

The crude articles thus obtained are subsequently trimmed and polished, use being made of the oxyhydrogen flame, the sand blast, and various abrasives.

4. Distillation Products. Carbon Bisulphide. Phosphorus. Zinc

The purely chemical manufacture of the remaining substances which are here discussed—carbon bisulphide, phosphorus, and zinc—suffers in each case from certain common disadvantages. The reacting mass is distilled at a high temperature, and the retorts or muffles used must be small in order to allow of conduction of heat into the interior (in the case of CS_2 to diminish the danger resulting from a possible accident). The results are high labour charges, and, owing to the temperatures to which the retorts are externally subjected and the frequently corrosive nature of the charge or products, high costs for depreciation and repairs. Phosphorus and zinc also give poor yields, due to the difficulty of reaching a sufficiently high temperature and to the strongly reactive nature of the product. We have already seen[3] that such circumstances favour the development of electrothermal processes, and we find accordingly that

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[1] *Zeitsch. Angew. Chem.* **23**, 1376 (*1910*).

[2] *Metall. Chem. Engin.* **9**, 226 (*1911*).

[3] Pp. 4, 168–171.

the whole of the CS_2 used in North America and the greater part of the world's supply of phosphorus are so produced. With zinc the case is different. No process hitherto proposed has proved so successful commercially as to be widely adopted.

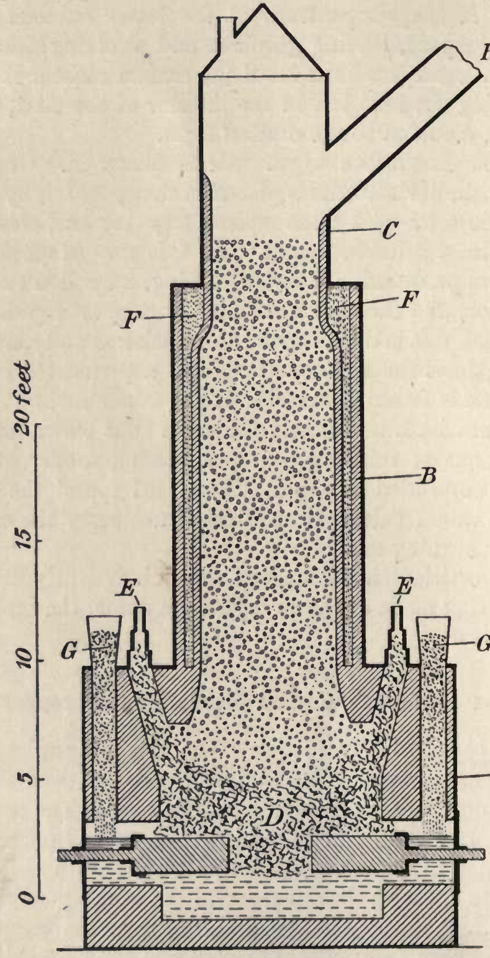

FIG. 127.—Taylor Bisulphide Furnace.

Carbon Bisulphide.—The electrothermal production of CS_2 was worked out by E. R. Taylor, and, as stated, his works at Penn Yann (U.S.A.) supply the whole demand of North America. A resistance furnace is employed[1] (Fig. 127) of very ingenious construction. It

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[1] *Zeitsch. Elektrochem.* 9, 399 (*1903*).

consists of three parts, all circular in plan, the hearth A, the shaft B, and the head C. The whole is constructed of firebrick, enclosed in a stout iron sheath. The carbon electrodes number four, placed horizontally and symmetrically around the hearth. They enter through suitable plates and stuffing-boxes, and are insulated with mica and asbestos. They appear somewhat squat in shape, being 4′ long and 20″ square in cross-section. The resistor consists of pieces of coke or broken electrode carbons, D, which are introduced through four channels, EE, in the hearth walls above the electrodes. Carbon in this form is only slowly attacked by sulphur under the conditions prevailing in the furnace. The electrodes also have a long life. Of the two reacting substances, the charcoal enters at the top of the furnace by means of a charging arrangement similar to that in the ordinary blast furnace. The sulphur enters the hearth below the electrodes through channels in the walls of hearth and shaft. The latter are visible in the diagram (FF); the former are situated between the electrodes, with the exception of GG, by means of which sulphur is introduced behind the electrodes. The CS_2 leaves the furnace at H, is condensed under water, and redistilled.

The furnace construction would seem to permit of an excellent heat utilisation. The charcoal is heated by the escaping vapours during its descent to the reaction zone (immediately above the core), which is at a bright red heat. The greater part of the heat, which would otherwise be lost as radiation, serves to melt the sulphur charged in at FF and GG, and much of the heat usually lost in the electrodes is here utilised, as, instead of water being used for cooling, sulphur is employed which afterwards enters the hearth. The regulation of the furnace is effected from the generators used, by varying the bulk of the carbon resistor, and to a certain extent automatically by the entering sulphur. When the furnace becomes too hot the sulphur melts rapidly, rises above the level of the electrodes, and, being a non-conductor, decreases the current.

The furnace is fed with two-phase alternating current. The phase currents generally pass between opposite electrodes, but, if necessitated by a stoppage, can be easily made to pass between adjacent electrodes. Owing to the small amount of the water-power available, the furnace usually takes 240 K.W. (60 volts; 4,000 amps.), and seldom more than 330 K.W. It could easily take 500 K.W. The energy consumption amounts to about 1·15 K.W.H. per kilo. CS_2.

The theoretical amount necessary is readily calculated. According to Haber the vapours leave the furnace at about 100°. We can suppose the CS_2 to be formed at 20°, to be heated in the form of liquid to 100°, and at that temperature to be vaporised. The formation of one mol. (76 grams) CS_2 at 20° requires 19,030 cals. For liquid CS_2 between 20°–100°, c (mean) is 0·245. L (vaporisation) at 100° is 72 Calories.

The heat necessary for the production of one kilo. CS_2 is therefore $\frac{19030}{76} + (0{\cdot}245 \times 80) + 72 = 342$ Calories, equivalent to 0·4 K.W.H.

The thermal efficiency of the Taylor process would thus be about 35 per cent., an unexpectedly low figure. The reasons for this are not clear. A certain amount of sulphur is vaporised with the CS_2, thus absorbing heat. Perhaps the product really leaves the furnace at a temperature considerably exceeding 100°. The electrode losses may be far greater than is assumed. Finally, though the fusion of the sulphur in the wall-channels must considerably lower the radiation losses, these may be much greater than they appear. The radiating surface is very large in comparison with the load of the furnace.

The furnace works exceedingly smoothly and without explosions. It can run for a year without cleaning. The supervision and labour required are small.

Phosphorus.[1]—The old chemical methods for the preparation of phosphorus involved the reduction of HPO_3 or of an acid calcium phosphate with charcoal. The disadvantages were great, particularly in the second case, where corrosive calcium silicate was produced, and where the temperature never sufficed to drive off all the phosphorus. From various causes the yields were exceedingly low, an 8 per cent. phosphorus recovery being considered good (Herrmann), and a preliminary H_2SO_4 treatment was always necessary.

For some years past much phosphorus has been prepared electrothermally, and the proportion so manufactured steadily increases. The published details concerning the processes used are most meagre. It appears, however, that all methods employed are based on the original Readman and Parker patents. Readman electrically heated bone-ash or crude HPO_3 with powdered coal or charcoal and sand. Natural calcium phosphate could be used if first calcined. At 1150° the reaction commences, and phosphorus and CO distil off.[2] It is complete at 1450°. According to the Parker patent, wavellite ($AlPO_4$) is treated with H_2SO_4 to remove the aluminium, and the HPO_3 liquors mixed with coal and reduced in the electric furnace.

At the present time, bone ash, calcined mineral calcium phosphate or calcined wavellite are mixed with carbon and sand without any preliminary treatment with acid, and reduced electrothermally. One form of furnace is a large gas-tight iron cylinder, lined with refractory, and containing in its upper part two large carbon electrodes, between which an arc passes. The charge receives the heat by radiation. Phosphorus distils off, and collects under water in copper vessels, and the calcium or aluminium silicate slag is drawn off intermittently.

[1] *Electrochem. Ind.* 5, 407 (*1907*); *Elektrochem. Zeitsch.* 17, 91 (*1910*).

[2] Hempel and R. Müller, *Zeitsch. Angew. Chem.* 18, 132 (*1905*).

The charging is continuous. A solidified layer of slag protects the lining. The percentage of phosphorus recovered rises to 92 per cent. and is usually 80–90 per cent. At Oldbury it is said to be 86 per cent. For these favourable results the iron content of the charge must be low. Landis has worked out a similar process. The arc passes between vertical carbon electrodes and carbon bricks in the lining. The flues must be constructed of non-absorbent material, or else much of the phosphorus is lost. The furnace is water-sealed at all the joints. The slag is drawn off every 3–4 hours.

According to J. W. Richards,[1] the furnaces working at Niagara in 1902 consumed only 50 H.P., and produced 170 lbs. of phosphorus daily. Assuming them to work continuously, we calculate that one kilo. requires $\frac{50 \times 24 \times 3 \times 2{\cdot}2}{4 \times 170} = 11{\cdot}6$ K.W.H. The electrode consumption is always small.

Zinc.[2]—As ordinary metallurgical processes for the winning of zinc furnish very unsatisfactory results, much attention has been devoted to different electrochemical methods. We have seen that neither the electrolysis of aqueous solutions[3] nor that of fused melts[4] has met with great success, and up to the present the same statement holds applied to electrothermal processes. But future prospects are distinctly more favourable. In the ordinary processes of zinc distillation, the charge of calcined ore and carbon is heated in small externally-fired clay retorts, holding 20–40 kilos. The reaction commences at about 1030°, but to expel all the zinc the retorts must be heated to a white heat for perhaps 20 hours. The thermal efficiency of the process is very low, 4–12 per cent., depending on the size of the retort and the nature of the ore. About 2·5–4 tons of coal are used per ton of zinc produced. Particularly in the later stages of the distillation is the thermal efficiency so low.

Many kinds of ore cannot be conveniently treated at all. A low-grade ore must first be concentrated. An ore with much iron and lime forms a corrosive slag which attacks the retorts. Mixed ores containing silver and lead furnish an impure zinc and corrode the retorts. If smelted as lead ores in a small blast furnace, infusible slags result, the furnace becomes choked up, and the zinc is lost. The retorts themselves are strongly attacked, by hot gases outside and by zinc vapours and slags inside. Their average life is 4–7 weeks. The cost of renewals is therefore high, as also the cost of labour, owing to the small size of the units. The product is not always of a reliable and regular

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[1] *Electrochem. Ind.* **1**, 17 (*1902*).

[2] Brown and Oesterle, *Trans. Amer. Electrochem. Soc.* **8**, 171 (*1905*); Johnson, *Trans. Amer. Electrochem. Soc.* **11**, 265 (*1907*); **19**, 311 (*1911*); Côte and Pierron, *Electrochem. Ind.* **7**, 468 (*1909*).

[3] P. 281.

[4] P. 421.

composition. Finally, the zinc recovery is poor. Any sulphur in the calcined ore keeps back twice its weight of zinc (hence the calcination must be very thorough), zinc vapours diffuse through the retorts and pass through the cracks, and considerable losses are incurred in the necessary concentration of the low-grade ores. The sum of these losses amounts to 10–25 per cent., under exceptional conditions even 35–40 per cent.

A successful electrothermal method would mean the employment of larger and more durable units, and lower costs for labour and repairs. The thermal efficiency would be higher, and some of the sources of loss of zinc would disappear. If, further, it were found possible to treat low-grade, impure, mixed, and uncalcined ores, a great advance would have been made. Experiments have shown that all these advantages can actually be secured by using electrothermal methods. Two main causes have, however, prevented their general adoption. The first is the cost of the large quantity of energy necessary; the second is the difficulty of condensing the zinc vapours to liquid metal instead of to zinc dust.

This difficulty is universal in zinc distillation, but appears to be particularly troublesome in electric-furnace processes.[1] The two chief causes of the zinc-dust formation are probably as follows. (*a*) The zinc vapours are too dilute or the cooling is too rapid, and they become supercooled. When the point is reached at which they condense, the temperature is already below the melting-point of the metal, and a fine powdery dust results. (*b*) The small globules of condensed zinc are superficially oxidised by the gases present (CO_2, H_2O, O_2, CO under some conditions), or are perhaps coated with dust or slag vaporised from the furnace. In that case they are unable to coalesce. Recent reports from both Europe and America state that this condensation difficulty has been largely overcome.

The different processes proposed are divisible into two classes, according to whether the uncalcined ore (generally a sulphide) is directly treated, or whether the calcined ore (oxide) is used.

Brown and Oesterle have investigated on a small scale the electrothermal reduction of zinc blende. Using equimolecular quantities of ore (59·6 per cent. zinc), lime, and coke, they successfully produced zinc and a melt of CaS containing only 0·13 per cent. Zn. The equation is

$$ZnS + CaO + C \longrightarrow CaS + CO + Zn.$$

Attempts to form simultaneously CaC_2 and CS_2 by using excess of carbon proved unsatisfactory, as would be anticipated. Snyder has devised commercial furnaces for a similar purpose, but the only process technically working is that of Côte and Pierron, which has been for some years in operation in a small plant in the Pyrenees.

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[1] See for example, Snyder, *Trans. Amer. Electrochem. Soc.* **19**, 317 (*1911*).

The furnace consists of a closed chamber with a graphite hearth, from which an electrode projects upwards, and an arched roof lined with magnesia, through which a second electrode enters. An arc passes vertically between the electrodes, and the charge of blende, lime, and carbon is heaped around it. Suitable openings are provided for charging, for tapping slag and any lead produced, and for the exit of the zinc vapours. Difficulties are evidently experienced in the condensation, as the zinc is now generally completely burnt to ZnO and collected as such. The method of heating doubtless causes much slag vapour and dust to accompany the zinc to the condensers.

The electrothermal reduction of zinc from calcined ores has also been much studied. In America, Johnson has designed several furnaces, one type being provided with a gas- or coke-fired preheater, in which the first part of the reduction takes place, electrical heating being only used for the later, high temperature, stages. In a 25-H.P. experimental arc furnace of another type, he has produced zinc at the rate of 2 tons per H.P. year, 70–80 per cent. of it condensing as liquid. The furnace vapours pass through a layer of heated charcoal before reaching the condensers. In this way any CO_2 present is removed and the condensation facilitated. But, again, only one furnace is in technical operation, that of **de Laval**, which is working in three Swedish plants, and said to be using some 6,500 K.W. It is an arc furnace in which the heat is transferred to the active mass entirely by radiation, as in the Stassano steel furnace and the phosphorus furnace. The consequence is that the reduction proceeds much more quietly, without overheating and vaporisation of slag and impurities. Ores containing large quantities of lead and silver furnish a very pure zinc. The de Laval furnace has been used, indeed, to extract zinc from impure spelter, and the zinc-silver alloy[1] which results from the Parkes lead desilverisation process could be also treated.

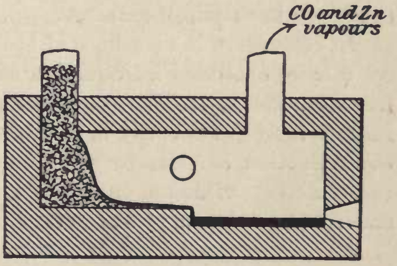

Fig. 128.—De Laval Zinc Furnace.

The furnace is shown in Fig. 128, and is of very simple construction. It consists of a closed, suitably-lined, thick-walled chamber, with provision for tapping off molten lead, slag, etc. The zinc vapours and CO escape through a flue in the roof. The charge, consisting of roasted ore, carbon, and fluxes, enters through a sealed charging shaft. A hopper and screw feed has also been used. The arc passes between carbon

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[1] See p. 284.

electrodes inserted in the walls (at right angles to plane of paper). Owing to the reducing atmosphere, the consumption of these is low. Furnaces are of moderate capacity, taking up to 100 K.W. As about 50 volts will be used, the amperage may rise to 2,000.[1] The utilisation of the heat is naturally not very good. One arc placed between two banks of charge would be better. A kilo. of zinc requires about 4·8 K.W.H. (1·37 tons per H.P. year). This is not as favourable as Johnson's figure. The zinc losses in the slags are small, and, as low-grade ores can be treated, the losses due to concentration are avoided. The metal recovery amounts to at least 95 per cent., and the product is of excellent quality. Two samples contained

Pb	0·06 per cent.	0·03 per cent.
Fe	0·01 per cent.	0·01 per cent.
S	0·00(3) per cent.	
Cd, As	Absent.	

Such a metal can be used for the best qualities of brass, such as are employed in cartridge-making.

In conclusion it may be said that the next few years will probably see a more extended introduction of electrothermal methods into non-ferrous metallurgy. There are great latent possibilities, for the induction furnace more particularly in refining and alloying, for the arc furnace in the reduction of refractory or low-grade ores. Hansen has already mentioned experiments on copper ; Härdén has described the electro-smelting of tin ores ;[2] and nickel ores have also been treated.[3]

Literature.

Amberg. Articles in Askenasy's *Einführung in die technische Elektrochemie*, vol. i.

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[1] Assuming cos $\theta = 1$.

[2] *Metall. Chem. Engin.* **9**, 453 (*1911*).

[3] *Metall. Chem. Engin.* **8**, 277 (*1910*).

CHAPTER XXVII

THE OXIDATION OF ATMOSPHERIC NITROGEN

1. Theoretical

THE fixation of atmospheric nitrogen by electrical discharges has now become an established industry. Much laboratory and technical experimental work has been devoted to the problem, and three entirely different processes are now in successful technical operation, all using some form or other of the *high-tension arc discharge.* We have already[1] discussed the mechanism of chemical transformation in the electrical discharge, but it will be interesting to consider at this point the earlier work done on the oxidation of nitrogen and the different ideas put forward. Crookes was the first to notice the formation of nitrogen oxides in a high-tension arc discharge in air. Rayleigh[2] was the first to study the process from the point of view of the economic production of HNO_3. He used an apparatus consuming 0·8 K.W., a $N_2 - O_2$ mixture with 36 per cent. N_2, and had an excess of alkali continually present. Twenty litres of gas were absorbed per hour. Assuming nitrite to be formed, a probable assumption as the rate of absorption was rapid, 1 K.W.H. fixes $\frac{2}{5} \times 25$ litres of nitrogen, equivalent to 56 grams HNO_3.

The next investigators were McDougall and Howles.[3] They carried out extensive experiments, passing the gas continuously through an arc burning between two horizontal electrodes in a large earthenware vessel. From air they obtained a maximum yield of 34 grams HNO_3 per K.W.H., whilst the mixture used by Rayleigh yielded 67 grams per K.W.H. The increased yield in the latter case they attributed to mass action. They also found that neither yield nor concentration of nitrous gases could be raised by indefinitely increasing the current. The excess of electrical energy was simply dissipated as radiation and conduction. The NO formation therefore appeared limited by some kind of equilibrium condition. This view was clearly expressed by

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[1] Chap. XIV.

[2] *Trans. Chem. Soc.* **71**, 181 (*1897*).

[3] *Manch. Mem.* (iv.) **44**, No. 13 (*1900*).

Muthmann and Hofer.[1] They regarded the process as essentially a *thermal* one. At low temperatures NO is really unstable, its equilibrium concentration in presence of nitrogen and oxygen being exceedingly small. The reaction $N_2 + O_2 \longrightarrow 2NO$ is endothermic, absorbing 43,100 Cals. at room temperature. It follows that at higher temperatures the formation of NO is favoured, and that at very high temperatures its equilibrium concentration in presence of nitrogen and oxygen may be quite considerable.[2]

Nernst, Jellinek, and Finckh[3] have experimentally determined the equilibrium concentrations of NO in air at several temperatures, and from their figures other values can be calculated. In Fig. 129 absolute temperatures are plotted against per cent. NO in the equilibrium mixtures. According to the thermal theory, the incoming gases are heated to the temperature of the arc, and NO produced in equilibrium concentration. On leaving the flame the mixture is more or less rapidly cooled, during which time the tendency will be for NO to decompose into nitrogen and oxygen in accordance with the lower equilibrium concentrations at lower temperatures. The more effective the chilling, the quicker the gases will pass through the range of temperature in which the velocity of decomposition is appreciable, and the higher then will be the concentration of NO or its oxidation products in the cooled gases. The two points to be aimed at are consequently (*a*) a high temperature in the discharge ; (*b*) very rapid cooling of the gases.

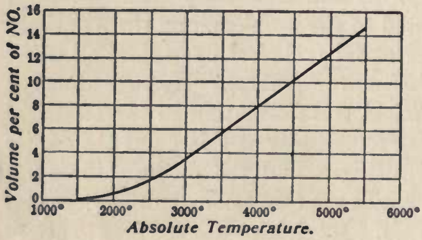

FIG. 129.

Muthmann and Hofer worked very similarly to McDougall and Howles. They obtained concentrations of 3·7–6·7 per cent. NO in the end product, the figure being higher the smaller the arc, and therefore, as they argued, the higher the temperature. Starting with NO, they found that approximately the same final concentrations were reached, a strong support for the thermal theory. The concentrations they obtained would correspond to temperatures of 2800°–3400° C. They estimated the minimum temperatures of their arcs at 1600°–1800°. The actual ones were probably several hundred degrees higher. The work of Nernst and his pupils on the $NO - N_2 - O_2$ equilibrium had not then been published, so the theory of Muthmann and Hofer was generally accepted, and their experimental work regarded as supporting

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[1] *Ber.* **36**, 438 (*1903*).

[2] P. 24 and fig. 2.

[3] *Zeitsch. Anorg. Chem.* **45**, 116 (*1905*) ; **49**, 213, 229 (*1906*).

it. Brode,[1] working with a similar apparatus, but chilling the gases by a water-cooled tube, reached a concentration of 8 per cent. NO, which would correspond to 3700° C., assuming the formation to be purely thermal. These calculated temperatures are of course all minimum values. A certain amount of decomposition is unavoidable. Brode accepted the thermal explanation. The arc he used, distorted by the passage of gases through it, consisted of three distinct zones, and according to him each zone corresponded to a distinct stage in the reaction. In the one, NO and ozone were formed, in the second ozone decomposed, and in the third NO dissociated.

The results of these three researches all supported the thermal conception of NO formation, even if the concentrations obtained seemed rather high. But in 1906 it was conclusively shown by Warburg and Leithäuser[2] and by Berthelot[3] that nitrogen oxides could be directly produced from air by means of the silent discharge, and Warburg[4] expressed the opinion that electrical phenomena would doubtless also play a part in the formation of NO in the arc discharge. Next appeared the valuable work of Grau and F. Russ.[5] In order more certainly to obtain equilibrium conditions in their arc, they caused the latter to burn vertically between platinum electrodes in a tube of silica or water-cooled glass. The distortion of the arc to a flame, inevitable with the horizontal arrangement of the previous investigators, was thus avoided, and steadily burning arcs up to several cm. long resulted. From these the gases were sucked off through a water-cooled platinum capillary, the equilibrium thus being rapidly frozen. With a 3-cm. arc a product with 5 per cent. NO resulted, and with a longer arc a gas with 5·6 per cent., concentrations corresponding to temperatures of 3000° C. and 3100° C. respectively. Sucking the gases off a few mm. away from the arc gave much lower concentrations, *e.g.* 2·65 per cent., indicating that decomposition had already largely taken place. Their yields were high. A 3-cm. arc gave 454 kilos. HNO_3 per K.W. year (52 grams per K.W.H.), and a 5-cm. arc 539 kilos. per K.W. year (62 grams per K.W.H.). With longer arcs they anticipated even better results. Grau and Russ clearly recognised the possibility of the arc having some specific electrical effect, but did not nevertheless discard the thermal hypothesis.

We owe to Haber and Koenig[6] the considerations and the work which finally showed that electrical phenomena without doubt play an

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[1] *Über die Oxydation des Stickstoffes in der Hochspannungsflamme* (1905).

[2] *Drud. Ann.* **20**, 743 (1906); **23**, 209 (*1907*).

[3] *Ann. Chim. Phys.* (viii.), **8**, 9, 145 (*1906*).

[4] *Zeitsch. Elektrochem.* **12**, 540 (*1906*).

[5] *Experimentaluntersuchungen über die Luftverbrennung im elektrischen Flammenbogen* (1906).

[6] *Zeitsch. Elektrochem.* **13**, 725 (*1907*); **14**, 689 (*1908*); (with Platou) **16**, 789 (*1910*).

exceedingly important part, and that thermal effects are probably simply superposed on them, and of a secondary nature. They critically examined the experimental researches just described, more particularly comparing the temperatures deduced from the NO concentrations with the temperatures which appeared probable for other reasons. Concentrations of 7 per cent. NO, such as were obtained, correspond with temperatures of 3500° C., and from their considerations they conclude that such temperatures were probably never reached, even supposing that the conditions in the arc remained constant with respect to time and position. But they certainly do not in a high-tension alternating current discharge. At every half-period the arc is extinguished, there will be great local cooling and reheating, and consequently all parts of the arc will be in constant rapid motion. There is little doubt that the composition of the arc gases must vary very considerably with respect to time and place, and that the mean temperature calculated from the NO concentration obtained has no real significance or application. Further, it would seem absolutely impossible to cool down NO from a temperature such as 3500° so rapidly as to avoid extensive decomposition. Thus Jellinek[1] has calculated that even at 2800°, pure NO at one atmosphere will be half decomposed in 2×10^{-9} minutes.

The experimental work of Haber and Koenig was decisive. They burnt a vertical arc inside a narrow tube, cooled outside with water. Various electrodes were used—platinum, iron and Nernst filaments. In order to keep the arc burning steadily, the gases were introduced and withdrawn between and not behind the electrodes. Gas pressure, current, and voltage were varied. A few typical results will suffice.

TABLE LXIX

Original gas	Pressure in mm. of Hg.	Current in amps.	Arc voltage	Litres passing per hour	Per cent. NO	Electrode material
Air	94	230×10^{-3}	4800	8·5	9·5	Iron
Air	51	205	2050	1·0	5·2	Iron
Air	86	350	3700	1·0	9·8	Nernst filament
Air	180	290	5400	35·1	7·5	Platinum
$50N_2 : 50O_2$	103	360	4800	0·8	14·4	Nernst filament
$18N_2 : 82O_2$	62	360	2100	0·9	11·1	Nernst filament
$25N_2 : 75O_2$	99	320	4600	0·75	12·8	Nernst filament

These investigators, using cooled arcs, could thus produce NO at concentrations corresponding to temperatures up to 4750° C., and, moreover, without making any attempt to rapidly chill the gases, which simply passed slowly through the arc.[2] The results obtained

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[1] *Zeitsch. Anorg. Chem.* **49,** 229 (*1906*).

[2] The *yields* obtained were very low.

depended on the gaseous pressure, and different concentrations were given by mixtures $\frac{1O_2}{4N_2}$ and $\frac{4O_2}{1N_2}$. If the reaction were a thermal one, simply depending on the law of mass action and the temperature, these two results would be impossible. That the concentrations obtained really represented an equilibrium, though not a thermal equilibrium, they showed by starting with NO, and getting the same mixture as they obtained from $\frac{1O}{1N_2}$. The decomposition of the NO took a measurable time, and this in itself proves that the temperatures were not very high. From certain other observations, they calculate them to be about 2000°–2200° C.

Accounts have also been published[1] of experiments with a short direct-current arc, using a cooled anode.[2] Gases containing up to 9 per cent. NO were obtained from air. The temperature of the arc was about 2700° C., corresponding to an equilibrium concentration of NO in air of about 4 per cent. only. The highest yields of NO were about 90 grams per K.W.H. At 60 grams per K.W.H. the NO concentration was 3·5–4 per cent. In technical work it seldom exceeds 2 per cent.[3] This difference is easily explained under the electrical theory, as in technical arcs the voltage gradient hardly exceeds 10 $\frac{\text{volts}}{\text{cm.}}$, whilst in the arcs used by Holwech it was about 200 $\frac{\text{volts}}{\text{cm.}}$. The ionisation should be much greater in the latter case.

Certain chemists still believe the thermal theory to be tenable. Thus Briner and Durand[4] suggest that, as our knowledge of the $NO - N_2 - O_2$ equilibrium at high temperatures rests only on an uncertain extrapolation of values experimentally obtained at lower temperatures, it is possible, assuming the thermal theory, that the high NO concentrations obtained by Haber and Koenig may in reality not correspond to such excessively high temperatures. Further, above 3000° there may be considerable dissociation of N_2 and O_2 molecules into N and O *atoms*, and these may partly combine on cooling to give NO instead of entirely N_2 and O_2. Guye is of a similar opinion. In this connection may also be mentioned the recent work of Strutt,[5] who, by submitting pure

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[1] Morden, *Trans. Amer. Electrochem. Soc.* **14**, 113 (*1908*); Holwech, *Zeitsch. Elektrochem.* **16**, 369 (*1910*); Holwech and Koenig, *Zeitsch. Elektrochem.* **16**, 803 (*1910*).

[2] In some cases the cathode was specially heated, but this made little difference.

[3] There are two difficulties in applying these results to technical work. Firstly, the apparatus would be exceedingly complicated. Secondly the series resistances necessary with the direct current would involve a loss of power, not merely a lowering of cos θ.

[4] *Jour. Chim. Phys.* **7**, 1 (*1909*).

[5] *Proc. Roy. Soc.* A. **85**, 219 (*1911*).

nitrogen at low pressure to the action of a high-voltage intermittent jar discharge, has produced a gas containing a small fraction of an *active* nitrogen, with very remarkable though fleeting properties, which have no connection with the presence of charged particles or ions. Strutt supposes nitrogen atoms to be present. This active nitrogen is destroyed by oxygen, but no NO results. It seems that though further investigation of this very interesting point may perhaps throw fresh light on the subject of the production of NO in the high-voltage arc, yet Strutt's results, obtained with quite extraordinary electrical means, cannot be regarded as affecting the views of Haber and Koenig.[1]

These depend for their justification on the experimentally ascertained fact that high NO concentrations are best obtained by slowly drawing gases through a low-temperature discharge, not by rapidly sucking them off from a very high-temperature arc, as the thermal theory would demand. Confronted by this direct evidence, one is compelled to accept the electrical theory of NO formation as sketched on pp. 190–192. In the ordinary technical arcs, as in some of the arcs used by experimenters prior to Haber and Koenig, thermal effects doubtless play a very important part in causing the decomposition of NO into nitrogen and oxygen, but *it is a secondary one.*

2. Early Attempts at Technical Apparatus

The designers of technical apparatus have been chiefly guided by the following considerations. Assuming the thermal theory to be true, they have wished to get very high temperatures with subsequent sudden cooling. Then it was early found that, as the consumption of electrical energy in a given space increased, the NO concentration did not increase as quickly, but soon reached a limit, and any further increase in the energy used was wasted. Hence inventors have avoided short thick arcs, and have tried many devices for making long thin stable arcs which would come into contact with a large quantity of air. Then, to get good NO concentrations, it is advantageous for all the gas fed into the furnace to pass through the discharge, avoiding 'false air' as much as possible. Finally, units of large capacity, consuming much energy, are of importance.

Naville and Guye worked on this subject for years, and devised many pieces of apparatus. In some the air enters through one of the electrodes, which is hollow. In others a direct-current arc passes between electrodes of various shapes, and this is rotated rapidly by means of a rotating magnetic field. Just like any other conductor carrying a current, the electric arc is deflected by a magnetic field.

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[1] Professor Haber has kindly informed the author that this is essentially his view.

With such an apparatus, up to 400 kilos. of HNO_3 per K.W. year has been obtained.

Bradley and Lovejoy[1] proceeded on the principles that, for a given quantity of energy, as much air as possible should come under the influence of the discharge, and that the gases should be cooled very quickly. They employed an apparatus containing a multitude of thin arcs, which were rapidly extinguished and restarted. Through the wall of a vertical iron cylinder were inserted large numbers of electrodes, arranged in rows, insulated by porcelain sleeves, and terminating in platinum wires. The cylinder contained a vertical concentric axle from which projected rows of radial arms, corresponding in number and position to the electrodes in the side wall and provided with short platinum tips. The vertical axle was rapidly revolved, and a direct-current voltage of 8,000–10,000 volts applied to the electrodes. When two platinum points came opposite to one another a short arc was struck, rapidly lengthened out to 4″–6″, and broke.

In the unit used (10 K.W.) some 414,000 arcs were made and broken per minute. The results were very good—a gas with 2–3 per cent. NO, and a HNO_3 yield of 86 $\frac{\text{grams}}{\text{K.W.H.}}$ (750 kilos. per K.W. year),[2] better than any figures at present reached technically. Nevertheless, a larger unit than the above was never constructed. The reason is clear, the apparatus being far too complicated for technical use, and having a high initial cost and heavy repairs charges. (In addition to the many platinum electrodes, each separate arc was provided with a large series resistance [in oil] for regulating the discharge.) Moreover, the size of the unit was excessive for its load—10 K.W.; a commercial unit should take hundreds of kilowatts.

An early apparatus of **Moscicki and v. Kowalski**[3] also failed because of its complications, though a 75-K.W. plant was run for some time. These investigators used an alternating current arc of high voltage and high frequency. A large number of arcs discharged in parallel towards a common earthed conductor. Current of ordinary commercial frequency was primarily used, and the high frequency (6,000–10,000 periods) obtained by a suitable arrangement of condensers. The phase difference thus produced was compensated by suitably-arranged inductances. A maximum output of 412 kilos. HNO_3 per K.W. year $\left(47\ \frac{\text{grams}}{\text{K.W.H.}}\right)$ resulted. Haber and Platou[4] have shown since that on a small scale the use of high frequencies gives rather worse results,

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[1] *Electrochem. Ind.* 1, 20 (*1902*); *Zeitsch. Elektrochem.* 9, 381 (*1903*)

[2] Cf. results of Morden, Holwech, and Koenig (p. 509).

[3] *Electrochem. Ind.* 5, 491 (*1907*).

[4] *Zeitsch. Elektrochem.* 16, 797 (*1910*).

but express the opinion that in large arcs a change of frequency has no appreciable effect.

Moscicki and v. Kowalski have more recently adopted quite a different kind of apparatus, resembling that of Birkeland and Eyde (see below). A high-tension arc (either direct or alternating current) plays between two concentric cylinders or rings. Then, by means of a magnetic field parallel to the axis of the cylinder, this arc is made to rotate radially around the intervening space. In plan the appearance of the arrangement is that of a luminous ring enclosed between two ring electrodes. The air, of course, passes through this space. Using a 27-K.W. unit, 60 grams per K.W.H. (525 kilos. per K.W. year) of HNO_3 were obtained. With a larger plant still better results are anticipated. **Brion**[1] describes elaborate experiments carried out with a very similar apparatus. With a 1 per cent. NO concentration he got 55 $\frac{\text{grams}}{\text{K.W.H.}}$ HNO_3, with 1·5 per cent. 50 $\frac{\text{grams}}{\text{K.W.H.}}$, but with 2 per cent. NO only 35 $\frac{\text{grams}}{\text{K.W.H}}$. His apparatus, however, only consumed 2–4 K.W. Alternating discharges gave distinctly the better results.

The three processes actually in successful technical operation must now be discussed. The Birkeland-Eyde process is worked at Notodden, Saaheim, and Zinnfoss, and the Schönherr process at Saaheim and Christiansand, all in Norway; while the Pauling process is operated near Innsbruck, and in the Hautes-Alpes department of France.

3. Birkeland-Eyde Process

The difficulty of producing stable high-current, high-voltage arcs has already been mentioned.[2] In order to design apparatus with a high electrical energy consumption per unit, inventors have therefore attempted to break up this single heavy-current discharge into a large number of low-current, high-voltage arcs. We have seen that such attempts have generally failed, on account of the complications thereby introduced. Birkeland and Eyde succeeded for the first time in evolving a technically successful apparatus in which this is effected, an apparatus of very simple construction and giving a perfectly stable discharge.

Imagine two electrodes 1 or 2 cm. apart in air, and connected in series with a resistance and a high-voltage source of direct current. The high-tension arc first produced quickly breaks down to a low-voltage arc carrying a heavy current, a type of discharge useless for HNO_3 synthesis. Suppose now that the arc be put between the poles

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[1] *Zeitsch. Elektrochem.* **13**, 761 (*1907*).

[2] P. 187.

of a powerful electromagnet. As we have seen, an electric arc is deviated in the magnetic field, just like any other conductor carrying a current. Consequently the path of the discharge will be bent outwards from the electrodes in semicircular form. The resistance of the arc thereby increases, the current falls, and the voltage rises. When this has risen sufficiently to strike again across the electrodes, a second arc will be formed, which, before it has time to break down to the low-tension arc, will be similarly bent away from the electrodes parallel to and concentrically with the first. By suitable regulation it will be possible to produce a large number of parallel semicircular arcs travelling outwards from the electrodes.

The total current will then be *the sum of the currents in all these arcs*, whilst the voltage will be that of an ordinary high-tension arc. An unlimited number of arcs cannot be produced, as they will finally extinguish when so long and of such a resistance that the applied voltage no longer suffices to keep them playing. This is the very simple principle used by Birkeland and Eyde. Only, instead of direct, they employ alternating current. The arcs are thus extinguished at the end of every half-period, even supposing this not to occur *during* the half-period. Further, the arcs are not all bent out on one side of the electrodes, but alternately on either side, according to the direction of the current. The discharge appears then as in Fig. 130. Owing to the extreme rapidity of the making and breaking of the arcs, what is seen is apparently a disc of light. It is obvious that such an arrangement permits a great concentration of power in a limited space, and that air introduced near the electrodes and removed at the periphery of the disc will be very fully exposed to the action of the discharge.

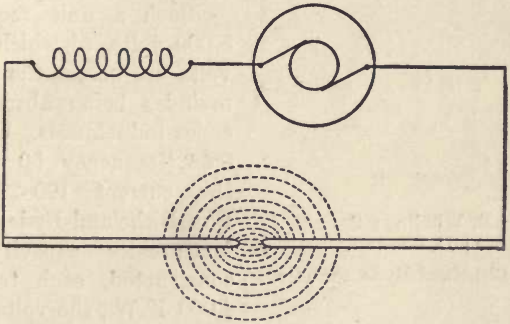

FIG. 130.—Birkeland-Eyde Arc.

In the technical unit,[1] the electrodes are copper tubes, water-cooled, and placed about 1 cm. apart. The flaming disc, its temperature estimated at about 3200° C., burns vertically in a furnace cased with

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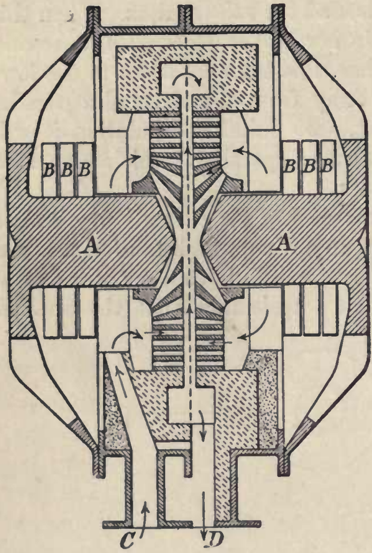
[1] *Trans. Farad. Soc.* **2**, 98 (*1906*); and private communication.

steel and lined with firebrick, perforated by holes through which the air enters. The furnace chamber in a 750-K.W. unit (often, however, loaded in practice with 850–900 K.W.) is about 5′ in length and breadth, corresponding to the dimensions of the disc, but very narrow (2″–6″) in the direction of the magnetic field. The two electromagnets themselves are connected with the external casing. They absorb 0·35–1 per cent. of the total furnace load. Fig. 131 is a sectional elevation at right angles to the disc. The passage of the air is indicated by the arrows. It enters the chamber through the channels shown in the lining.



A, Core ; B, Winding ; C, Gas entrance ; D, Gas exit.

FIG. 131.—Birkeland-Eyde Furnace.

Such a unit requires about 5,000 volts, of which 3,300–3,900 volts are across the arc, the remainder being absorbed by the series inductances. Cos θ is 0·66–0·68 (frequency 50 periods) and the current 190–200 amperes. But Birkeland-Eyde furnaces of far greater capacity are now constructed, each taking 3,200–4,000 K.W., the voltage relations being the same. Thus the Notodden factory contains four 3,500 K.W. units working with a current of 940 amps. The discharge burns very steadily, hardly needing attention. The electrodes last some 300 hours without repair, and can be rapidly changed. The furnace lining is very durable. The furnace gases contain about 1–1·2 per cent. NO. The yield of HNO_3 is about 67 $\frac{\text{grams}}{\text{K.W.H.}}$ (580–590 kilos. per K.W. year).

4. Pauling Process[1]

Fig. 132 represents diagrammatically the arrangement employed. The two electrodes *aa* resemble horn lightning conductors. They are of cast steel, water-cooled, and 30 cm. long. The air, preheated by the hot furnace gases, is blown up into the intervening space through the nozzle *e*. The electrodes are provided with vertical slits at the points nearest to one another (4 cm. apart), and through these slits pass thin strips ('ignition knives') of iron, *bb*. Their distance apart, 2–3 mm.,

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[1] *Zeitsch. Elektrochem.* **15**, 544 (*1909*); **17**, 431 (*1911*).

is regulated by mechanism at *dd*, which is insulated by *cc* from the electrodes. The strips are so thin that they do not affect the current of air from *e*. To start the arc, a suitably-connected auxiliary current, of low wattage but of the necessary high voltage, is used. The alternating current arc strikes between *bb*. The rapid stream of air deforms it, and carries it up and along the electrodes *aa* in the form of a flame, about 3′ high in actual practice. At every reversal of current a fresh arc strikes, and the whole appearance is that of a large flaming arc, such as was used by Brode and others. The temperature is high and the flame intensely white, owing to the presence of iron vapours.

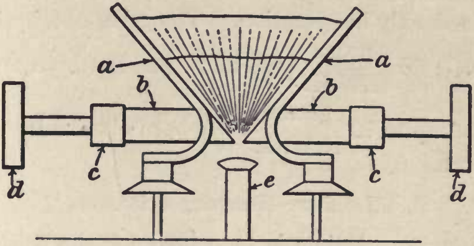

Fig. 132.—Pauling Arc and Electrodes.

The life of the electrodes is short—200 working hours for the cooled main electrodes, and 20 hours for the 'ignition knives,' which must constantly be pushed up towards one another. They can be readily replaced. Two such arcs in series are contained in each furnace (front and side elevation, Fig. 133). Each is in a separate chamber, these being connected with a common flue. The hot reaction products

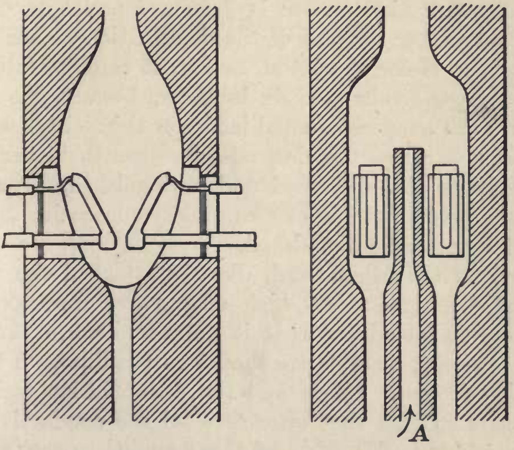

Fig. 133.—Pauling Nitric Oxide Furnace.

are cooled by introducing through A cold gases which have already been through the discharge. The whole leaves the furnace at about 1000°. Such a furnace consumes 400 K.W., 200 K.W. per arc, and takes 4,000 volts. Assuming $\cos\theta = 0{\cdot}7$, the current passing will be about 140 amperes. Several furnaces are worked in parallel. Lately their load has been increased to 600 K.W., and 1,000 K.W. units are expected to be shortly in operation. The gases obtained contain 1·1–1·5 per cent. NO; 60 $\frac{\text{grams}}{\text{K.W.H.}}$ (525 kilos. per K.W. year) of HNO_3 are guaranteed, and up to 70 $\frac{\text{grams}}{\text{K.W.H.}}$ have been obtained.

5. Schönherr-Hessberger Process [1]

Quite a different principle is here used for the construction of a commercial unit carrying a heavy load. As has been emphasised, a long, heavy-current, high-tension arc is a very unstable thing. It is easily extinguished, particularly if cold air, impinging on it, deforms or cools it. In the two processes above discussed this fact is accepted, and no attempt made to circumvent it. The electrodes are placed very close together, and the air supplied is caused to enter at right angles to the path of the arc—in the direction, in fact, in which it is most capable of extinguishing the arc. By suitable means (magnetic field or strong current of air) the arc is deformed or lengthened until it finally goes out, either because of the deformation or because of the current reversal. If for the latter reason, it cannot restrike at the same point when the voltage again increases, because the air passing through lowers the temperature and increases the resistance too much. A fresh arc strikes across the electrodes between their nearest points, and is in its turn also deformed and extinguished. The discharge therefore consists of a number of arcs rapidly succeeding one another, striking, and becoming extinguished.

Schönherr, on the other hand, directly attacked the problem of producing a stable, high-current, high-voltage arc. He recognised that, if the air were so introduced that it did not deform the discharge or cool it excessively, a stable arc should be possible with both direct and alternating current. Using the latter, it should be possible to keep the temperature so high that after reversal the conductivity suffices for the arc to re-form. He achieved these conditions very simply. As in the Pauling furnace, it is the air current which draws the arc out from a short to a great length; yet it is introduced, not at right angles to the discharge, but so that it surrounds the latter and travels along in a parallel direction. It is not forced into the discharge, but enters it by diffusion and through eddy currents, and from all sides

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[1] *Trans. Amer. Electrochem. Soc.* **16**, 131 (*1909*); also private communication.

simultaneously. The arc is neither deformed nor unduly cooled, and burns quietly and stably.

Fig. 134 shows the cross-section of a furnace.[1] The discharge chamber (4) consists essentially of a vertical iron pipe, connected to earth and serving as one electrode. It is 20′–25′ in length, a few inches in diameter, and water-jacketed at its top end. Its base is slightly widened out, and contains the other electrode, also vertically placed and carefully insulated. This consists (E) of a rod of iron, passing through a water-cooled copper block. The iron, which takes the total current, is slowly consumed, and must be occasionally pushed up through the copper block. The central discharge chamber is surrounded by other concentric vertical iron pipes, and finally cased with iron lined with firebrick. The air enters at C, traverses the annular spaces (2) and (3) between the vertical pipes, where it becomes preheated, enters (4) near the bottom electrode, passes out of the same at the top, and finally leaves the furnace at D. Its course throughout is indicated by the arrows. GGG are peep-holes. One pole of the source of current, in series with a regulating inductance, is connected with E. The other pole is earthed.

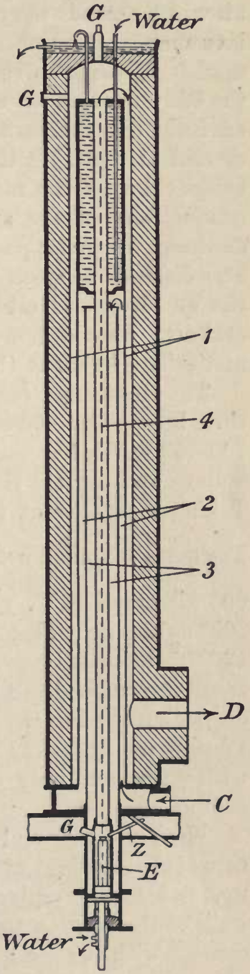

FIG. 134.—Hessberger Furnace.

To start the arc, the iron bar Z, actuated by the lever shown, is moved down until it makes contact with E. The discharge commences, Z is withdrawn, and a short arc plays between E and the adjoining wall of the furnace. The air is now introduced through holes regularly placed in the wall of the furnace round E. These air entrances are directed tangentially to the furnace wall, and the incoming air consequently ascends the latter with a *helical* motion, carrying up the end of the arc with it. The number of entrances thus opened can be regulated. The length of the arc is determined by the applied voltage and by the conductivity, hence by the temperature, hence by the velocity of the surrounding air layer. By adjusting the air supply, therefore, the point at which the arc strikes across to

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[1] Designed by Hessberger.

the furnace wall can be regulated, and it is arranged that this occurs somewhere in the water-cooled part of the latter.

The result of this regular directed introduction of air is a perfectly stable arc some 20′ long, which plays between E and some point in the water-jacketed furnace top. This arc is surrounded by a cushion of air which ascends the pipe in a more or less spiral-like path. Constant interchange of gases necessarily takes place between air layer and discharge, owing to the temperature difference between them, and to the eddy motions set up by the continual temperature changes in the arc itself, due to the alternating current variations. But as the amount of cool air entering the discharge in a short space of time is small compared with the mass of heated air present, the temperature and conductivity of the arc gases are not materially lowered, and the discharge continues passing despite the half-period reversals of voltage. The distance between E and the furnace wall is sufficient to prevent the arc ever preferably striking at that point across the incoming cold air. Should, however, the arc go out, the voltage rises, it automatically relights at the bottom, and is again carried up.

The Hessberger furnaces are usually fed with three-phase current, three being combined together in star. The largest built take nominally 700–750 K.W., but can be loaded up to 1,000 K.W. Such a unit has voltage and current respectively about 3,500 volts and 290 amperes. Taking into account the series inductance necessary, cos θ is 0·66. The gases contain 1·5–2 per cent. NO, and the yield is 68 $\frac{\text{grams}}{\text{K.W.H.}}$ (590–600 kilos. per K.W. year) of HNO_3. The entering air is warmed to 500° during its passage into the arc chamber, leaves the same at about 1200°, and cools to 850° before leaving the furnace. Its residual heat is suitably utilised. Schönherr calculates that about 40 per cent. of the energy supplied to the arc appears as hot water, 30 per cent. as steam, 17 per cent. is lost as radiation, 10 per cent. lost by the final cooling with water, and only 3 per cent. used in the formation of nitrogen compounds.

Wear and tear and first cost of the plant are both low. The iron core of the middle electrode (E) gradually oxidises away, must be pushed up, and finally replaced. This can be rapidly effected. The iron walls of the furnace are protected by an air layer, and only come into contact with the arc at the outset. The upper part, where the arc plays, is water-jacketed and only very slowly oxidised. It is made in a separate piece to facilitate renewal.

A comparison of these three processes is interesting. The Schönherr and Birkeland-Eyde processes furnish almost identical yields, but the former gives a richer gas. The furnace is, further, of very simple construction and durable. The Birkeland-Eyde furnaces are less simple and cost more initially, but far larger units can be built, which is a great advantage. The Pauling apparatus is exceedingly simple, but gives yields about 10 per cent. lower. The units are about the size of the Hessberger furnaces. All three furnaces appear to require very little attention whilst working, and this fact, of course, lessens the undoubted advantages of the large Birkeland-Eyde units. Nevertheless, the recent Norwegian large-scale tests appear to have indicated that the Birkeland-Eyde furnace (3,500 K.W.) is at least as satisfactory technically as the Hessberger furnace (750 K.W.), if not more so.

From the point of view of the theory of NO formation, the comparative results obtained certainly do not support the correctness of the thermal hypothesis. The NO concentration is lower in the Pauling process, in which cooling gases are used, than in the Schönherr process, in which the air passes slowly along and through the arc. We should expect the opposite result. There seems no doubt that the electrical theory is primarily the correct one. That powerful thermal effects are superposed is clear, but the more prominent they are, the lower the NO concentration and the yield.

6. Working up of Furnace Gases

Having discussed the formation of NO in the furnace, we must now consider the working up of the gas to HNO_3 and other products. The gases leave the furnaces at temperatures between 600°–1000°. Below 600° the combination of NO and oxygen commences. Below 140° it is complete. It is a reaction which takes place with a low velocity[1] that appears, according to Bodenstein and to Foerster, to have a slight negative temperature coefficient, the only known case. The next stage is the absorption of the resulting $N_2O_4-NO_2-NO$ mixture in water or a suitable alkaline solution. We owe to Foerster and Koch[2] a detailed study of the action of water on NO_2 gas. The gas at the outset behaves as a mixture of N_2O_3 and N_2O_5, and gives a solution containing HNO_2 and HNO_3.

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3.$$

But this solution is only stable when exceedingly dilute. Otherwise the HNO_2 decomposes as follows:

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

Summing these two equations, we have

$$3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO,$$

expressing the total result of the action of NO_2 gas on water. This reaction is reversible. NO gas, passed into strong HNO_3, evolves NO_2.

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[1] Holwech, *Zeitsch. Angew. Chem.* 21, 2131 (*1908*).

[2] *Zeitsch. Angew. Chem.* 21, 2161, 2209 (*1908*).

Consider now the absorption of the dilute technical gases by water in the light of this equation and of the mass-action law. There is always a certain tendency for the reaction to take place from right to left, as the gases invariably contain some unoxidised NO. Further, in a fairly strong HNO_3 solution, much of the water present is combined with the anhydrous acid as hydrate, and is unable to react according to the above equation. Lastly, the NO_2 partial pressure in the gases treated is very low, and the vapour pressure of the HNO_3 continually increases. These facts show that an equilibrium concentration of HNO_3 must be reached which cannot be exceeded by further bubbling the gases through, and this concentration will be greater the greater the NO_2 partial pressure in the gases. It was found to be (at room temperature) 68–69 per cent. HNO_3 with [1NO : $2O_2$], $>$ 55 per cent. HNO_3 with 5 per cent. NO_2, 52 per cent. HNO_3 with 2 per cent. NO_2, 46 per cent. HNO_3 with 1 per cent. NO_2. With technical furnace gases it should be possible, then, to produce a 46–52 per cent. acid.

The behaviour of the gases towards an alkaline solution is equally interesting. As long as they contain some NO, a nitrite is quantitatively and rapidly formed; *i.e.* they behave as if the NO were present combined with NO_2 as N_2O_3. Le Blanc suggested this actually to be so, and Foerster and Blich[1] subsequently proved experimentally the supposition to be correct. An excess of NO_2 acts more slowly, giving a mixture of nitrite and nitrate.

On the large scale, HNO_3 is made by the Pauling plants. The formation of NO_2 is given time to take place by passing the gases slowly through a large reaction chamber, much of their heat being first suitably utilised. The absorption takes place in towers of granite, sandstone, earthenware, etc., packed with a substance like quartz. The counter-current principle is used and a 35–40 per cent. acid results.[2] This is further concentrated by waste heat to 60 per cent. acid. Finally, by distilling this 60 per cent. acid with twice its weight of 92 per cent. H_2SO_4 (done by spraying the mixture into a tower filled with lava and heated from without) a 98 per cent. acid results. The H_2SO_4 is concentrated and used again. At Notodden a 40 per cent. acid is got in the first tower. Succeeding towers give about 25 per cent. and 10 per cent. acid. In all cases the gases, after leaving the last acid absorption tower, pass through iron absorption towers, where they react with NaOH or Na_2CO_3 liquors. They usually contain enough NO to give a product[3] containing 95 per cent. of its nitrogen as nitrite and only 5 per cent. as nitrate. Small quantities of nitrogen compounds

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[1] *Zeitsch. Angew. Chem.* **23**, 2017 (*1910*).

[2] It is obvious that here, as in the other cases, insufficient time is given to reach the equilibrium state observed by Foerster and Koch.

[3] Used for the nitre-pots of the sulphuric acid chamber process.

escape, up to 4 per cent. of the whole. Of the amount absorbed, four-fifths is held by the acid, one-fifth by the alkaline towers.

In the Norwegian plants, the acid produced chiefly serves to dissolve limestone to $Ca(NO_3)_2$. The solution obtained is concentrated, and finally allowed to solidify. The product contains 12·75–13·1 per cent. nitrogen. Much NH_4NO_3 is produced by direct neutralisation of gas-works' ammonia liquors. At Christiansand (Hessberger furnaces) the gases are absorbed hot (200° C.) by NaOH liquors. About 98 per cent. is so retained, the sole product being $NaNO_2$ (96·4 per cent. pure).

Many other methods have been suggested for working up the furnace gases. Some of these are of considerable interest. In Schloesing's patent, the nitrous gases are absorbed at 300°–350° by quicklime. Anhydrous $Ca(NO_2)_2$ and finally $Ca(NO_3)_2$ result. Guye proposes to compress the moist gases to five atmospheres, and then suddenly to expand, when a cloud of 95 per cent. HNO_3 is claimed to result. Another suggestion is treatment with ozone.[1] In presence of water, concentrated HNO_3 results at once. But cheap ozone is needed.

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[1] *Zeitsch. Elektrochem.* **12,** 549 (*1906*); also see Foerster and Koch, *loc. cit.*

CHAPTER XXVIII

OZONE

1. Theoretical[1]

OZONE, a polymerised form of oxygen, of molecular formula O_3, is, at ordinary temperatures, a strongly smelling gas. It has powerful oxidising and bactericidal properties, and is extensively used for water purification. Its formation from oxygen is an endothermic reaction. At room temperature

$$3O_2 \longrightarrow 2O_3 - 68200 \text{ Cals.}$$

The proportion of ozone in the equilibrium mixture with oxygen is very low, but increases as the temperature rises. At 1300° it is 0·1 per cent., 1 per cent. at 2000°, and at 4500° about 10 per cent. By heating oxygen to a very high temperature and rapidly cooling, it is thus possible to produce ozone,[2] but only in low concentrations owing to its very rapid decomposition. But the use of a silent electric discharge at room temperature avoids this difficulty. Ozone is produced until a definite electrical equilibrium has been reached. This equilibrium corresponds to a thermal equilibrium at a higher temperature,[3] and hence the ozone concentrations resulting can be quite considerable.

When the electrical equilibrium has been reached, we must assume equal rates of formation and decomposition of the ozone molecules, and the yield of ozone per ampere-hour or K.W.H. drops to zero. Further, the smaller the ozone concentrations, the greater the yield, a limiting value being obtained at zero concentration. The yield must always, therefore, be defined in reference to the concentration. To characterise the behaviour of an apparatus under given electrical conditions, we require to know the yield per ampere-hour at zero concentration (*limiting yield*), the limiting concentration of ozone attainable, and the rate of variation of yield with concentration.

In Chap. XIV. the simplest forms of silent discharge—positive and

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[1] Warburg, *Jahrb. der Radio.* **6**, 184 (*1909*).

[2] Fischer and pupils, *Ber.* **39**, 940, 2557, 3631 (*1906*); **40**, 443, 1111 (*1907*).

[3] P. 191.

negative point discharge—their appearance and their characteristics, were briefly discussed. In technical apparatus we usually encounter a rather more complex form of discharge, viz. alternating current discharge between electrodes of small curvature, of which at least one is an insulator or bad conductor. Such is the discharge in an ordinary ozone tube. In the older all-glass apparatus (diagrammatically shown in Fig. 135) we have two coaxial glass tubes, the outer surface of the outer and the inner surface of the inner being covered with tinfoil connected with the poles of a source of high voltage. The discharge passes from one glass surface to another across the annular space between the two tubes. In later forms the inner tube is of metal—aluminium, gilded brass, etc. In such ozonisers, with their large discharge surface, the current density is at first much lower than with a point discharge and the glowing much weaker. But as voltage and current rise the glowing becomes more pronounced, and brush discharges begin to pass between isolated points on the two surfaces. Ultimately the whole space becomes uniformly luminous.

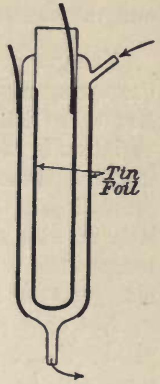

FIG. 135.
Glass Ozoniser.

In all forms of discharge there is a close connection between the luminous phenomena observed and the ozone produced, as measured by the limiting yield. Ozone is only appreciably formed in those regions which are luminous. This is plainly seen on comparing the yields given by the different forms of point discharge at different voltages with the corresponding luminous phenomena. If, moreover, the distance between a negatively-charged point and an earthed electrode be increased, keeping the current and the size of the 'positive column' constant, no increase is observed in the ozone formed, showing that it arises solely in the luminous positive column. In ozone tubes the *limiting yield* is increased by increasing the width of the inter-electrode space, but the *rate* at which the ozone yield diminishes with increase of concentration increases still more rapidly, and consequently *smaller limiting ozone concentrations* are possible in such tubes than in tubes with a narrow annular space.

The relation between A_C—the yield of ozone per amp.-hour at an ozone concentration C—and the limiting yield A_o is, if C is not too high,

$$A_C = A_o - \beta C.$$

β is therefore a measure of the rate of de-ozonisation. The highest possible concentration C_o is given by[1]

$$C_o = \frac{A_o}{2\beta}.$$

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[1] This and other results must be taken for granted here.

In a certain case, using oxygen, A_0 was 548, β 2·19, C_0 125, which gives some idea of the size of these magnitudes. The yields are in grams and the concentrations in $\frac{\text{grams}}{\text{metre}^3}$.

The gas pressure affects the limiting yield considerably, the latter decreasing rapidly as the pressure falls. In air the limiting yield is less than half that possible in oxygen. The effect of temperature variation is rather complex. In all cases a rise in temperature rapidly increases the rate of de-ozonisation—*i.e.* β increases. The limiting concentration is therefore greatest at low temperatures. This is particularly so with air, for not only does β increase but A_0 decreases as the temperature is raised. The reason is probably the formation of oxides of nitrogen, as A_0 for pure oxygen is practically independent of temperature.

Not only nitrogen oxides, but other gases present, can lower the yield of ozone. Chlorine acts very strongly, and aqueous vapour must also be avoided. Thus in moist air, with an aqueous vapour pressure of 7 mm., the limiting yield can easily fall to 60–70 per cent. of that given by the dried gases. The reason is probably that the gaseous ions condense the moisture around them—a well-known phenomenon. Their velocity and their power of ionising by impact are thereby lowered.

Technically the yield per K.W.H., not that per ampere-hour, is all-important; and in that connection the low power factor of most ozonisers (they use alternating current) must be noted. An ozone tube or apparatus can be regarded electrically as a number of condensers or capacities in series, with an ordinary ohmic resistance in parallel with one of them. This ohmic resistance is due to the air space, which acts both as a conductor and as a dielectric. In such an apparatus cos θ will be very low. (Cf. footnote on p. 180.) If the air were a perfect non-conductor the system would consist entirely of capacities, and cos θ would be zero. If, again, the air were a perfect conductor the same would hold good. Cos θ reaches a maximum value for a certain intermediate conductivity of the air gap. The dimensions of the same and the current density used must therefore be carefully planned in order to secure the best results. A low current density is used in practice. The frequency of the discharge should be high, as this favourably affects cos θ. Finally, it is better to use an apparatus with one metal electrode than one with both electrodes insulators. A small metal apparatus working with a high frequency takes as much power and can give as much ozone as a large all-glass apparatus using a low frequency discharge at the same voltage.

Table LXX[1] contains some data bearing on these and other points. A is the yield per K.W.H. and C the concentration in $\frac{\text{grams}}{\text{metre}^3}$.

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[1] Warburg and Leithäuser, *Drud. Ann.* **28**, **1** (*1909*).

TABLE LXX

A for C = 10	A for C = 4	A_0	C_0	Distance between electrodes in cm.	Periods per second	Voltage	Current in amps.	Cos θ.
38·3	41·9	45·5	36·5	0·51	50	8,050	0·182	0·185
—	—	—	—	1·40	50	10,080	0·102	0·314
52·3	55·1	56·8	59·2	1·40	50	16,900	0·193	0·243
51·1	56·1	60·1	31·2	3·72	50	17,500	0·160	0·415
72·2	78·4	82·6	40·5	2·26	50	10,800	0·182	0·431
53·3	62·4	68·4	20·2	4·66	50	13,900	0·169	0·450
75·7	81·4	85·2	51·6	2·26	100	9,480	0·308	0·451
54·0	63·0	69·0	16·8	4·66	100	12,300	0·280	0·447
57·1	66·0	71·9	18·3	2·26	510	9,340	1·58	0·537
33·0	58·0	74·7	11·4	4·66	510	12,100	1·19	0·704

(Lines 1–4 for glass, 5–10 for metal ozonisers.)

These figures make it clear that the best design for an ozone apparatus will vary considerably according to the relative importance attached to a good power factor, a high absolute yield, or a high concentration. Each single case must be decided on separately.

2. Technical

The number of proposed technical ozonisers is enormous, and we must simply briefly describe a few of those actually used in water-purification plants. The **Siemens and Halske** apparatus is very important. In principle it resembles the ordinary ozone tube. A commercial unit (Fig. 136) consists of an iron box provided with glass windows. Through the bottom of this pass upwards a number of

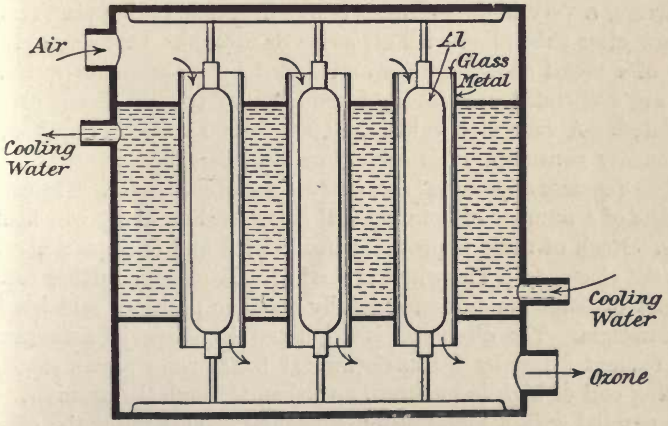

Fig. 136.—Siemens and Halske Ozoniser.

vertical glass cylinders, coated outside with metal, which serve as one set of electrodes. Concentrically inside these tubes are placed the other electrodes, consisting of cylinders of aluminium foil. The air, after drying by $CaCl_2$, passes along the annular spaces between the electrodes. Water is run through the iron box to cool the apparatus, and is sometimes also run through the inner electrodes. These are carefully insulated, and connected with a source of high-voltage alternating current, which passes from them across the air gaps, through the glass cylinders and cooling water to the iron box. This is earthed, and there is thus no risk to the operator. The ozonisers are kept in a darkened room, it thus being possible to tell from the luminous appearance whether or not they are running smoothly.

The ozonised air is compressed and forced up towers, down which the water passes. The latter must be first freed from organic matter, and any iron should be removed or oxidised to the ferric condition; otherwise losses in ozone occur. A plant at Paris[1] uses 110 volts, transformed up to 4,000 volts. The energy consumed in the ozoniser is 57 K.W.H. per million gallons of sterilised water. The energy expended in compressing the gases exceeds this, the grand total amounting to 133 K.W.H. per million gallons. In St. Petersburg[2] the ozonisers are fed with current at 7,000 volts (500 periods). An ozone of concentration $2{\cdot}5\ \frac{\text{grams}}{\text{metre}^3}$ is produced. Some 50,000 metre^3 of water are thus purified daily.

In the **Tyndall** apparatus, as modified by de Vries, the current passes between metal electrodes. To avoid sparking and an unstable discharge, a very high resistance is put in series, taking the form of a narrow glass tube filled with glycerine or alcohol. One electrode consists of a metal chest, earthed and cooled by a current of water. In this are suspended a number of semicircular copper plates, carefully insulated. A very high voltage, 40,000–50,000 volts, is required, and the energy consumption is correspondingly large.

The **Vosmaer** apparatus[3] also uses all-metal electrodes. The ozoniser consists of a number of long vertical copper tubes, along which the air flows. Each of these is provided inside with and is connected with a long flat electrode. The whole is earthed. Each tube further contains a series of point electrodes, carefully fixed in position, and insulated by porcelain. The discharge is regulated by a special arrangement. The current given by a transformer at 5,000 volts passes through a choking coil of high inductance, and then through the ozoniser, which is in parallel with a high-tension condenser. This raises the effective voltage on the ozoniser to 10,000 volts. The apparatus appears to

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[1] *Electrochem. Ind.* **7,** 411 (*1909*).

[2] *Zeitsch. Elektrochem.* **17,** 764 (*1911*).

[3] *Electrochem. Ind.* **2,** 511 (*1904*).

work very efficiently. The last type of ozoniser we will refer to is that of **Otto,** used extensively in France. Both electrodes are of metal, discharge taking place between the inside of a metal chest and a number of aluminium discs attached to an insulated axle which revolves inside the chest.

All the above ozonisers are big technical units, intended for large-scale water treatment. But smaller units are also designed, suitable for household or portable use. They are mostly of the Siemens-Halske type.

APPENDICES

I. Transport Number of Anion (N_A) for different Aqueous Salt Solutions at 18°

$[C]$ Equiv. =	0·01	0·02	0·05	0·1	0·2	0·5	1	1·5	2	3	5	7	10
KCl KBr KI NH_4Cl	0·506	0·507	0·507	0·508	0·509	0·513	0·514	0·515	0·515	0·516	—	—	—
NaCl	—	—	0·614	0·617	0·620	0·626	0·637	0·640	0·642	0·646	0·650	—	—
LiCl	0·63	0·65	0·67	0·69	0·71	0·73	0·739	0·741	0·745	0·752	0·763	0·774	—
KNO_3	—	—	—	0·497	0·496	0·492	0·487	0·482	0·479	—	—	—	—
$NaNO_3$	—	—	—	0·615	0·614	0·612	0·611	0·610	0·608	0·603	0·585	—	—
$AgNO_3$	0·528	0·528	0·528	0·528	0·527	0·519	0·501	0·487	0·476	—	—	—	—
$KC_2H_3O_2$	—	—	—	0·33	0·33	0·33	0·331	0·332	0·332	0·333	0·335	—	—
$NaC_2H_3O_2$	—	—	—	0·44	0·43	0·43	0·425	0·422	0·421	0·417	—	—	—
KOH	—	—	—	0·735	0·736	0·738	0·740	—	—	—	—	—	—
NaOH	—	—	0·81	0·82	0·82	0·82	0·825	—	—	—	—	—	—
LiOH	—	—	—	0·85	0·85	0·861	0·873	0·890	—	—	—	—	—
HCl	—	—	0·172	0·172	0·172	0·173	0·176	0·180	0·18	0·200	0·238	0·292	—
½ $BaCl_2$	0·56	0·565	0·575	0·585	0·595	0·615	0·640	0·650	0·657	—	—	—	—
½ $CaCl_2$	0·58	0·59	0·61	0·64	0·66	0·675	0·686	0·695	0·700	0·710	0·737	0·764	0·79
½ $MgCl_2$	—	—	0·63	0·66	0·68	0·69	0·709	0·718	0·729	0·747	0·766	0·799	—
½ $CdCl_2$	0·57	0·58	0·59	0·62	0·65	0·69	0·72	0·73	0·745	0·767	0·865	0·995	—
½ CdI_2	0·56	0·59	0·64	0·71	0·83	1·00	1·12	1·18	1·22	1·25	to	2·5	—
½ K_2CO_3	—	—	0·39	0·40	0·41	0·435	0·434	0·421	0·413	0·404	0·380	0·355	—
½ Na_2CO_3	—	—	0·52	0·53	0·53	0·54	0·548	0·546	0·542	0·530	—	—	—
½ $MgSO_4$	—	—	0·60	0·64	0·66	0·70	0·74	0·75	0·76	0·760	—	—	—
½ $CuSO_4$	—	0·62	0·626	0·632	0·643	0·668	0·696	0·714	0·720	—	—	—	—
½ H_2SO_4	—	—	0·193	0·191	0·188	0·182	0·174	0·169	0·168	0·170	0·190	0·216	0·268

II. Current Densities used in Technical Practice, given in amps./dm.².

Copper refining (multiple)	1–4	
Do. (Hayden)	1·6–2	
Copper extraction (Laszczynski)	0·5–1	(cathode)
Do. (Siemens-Halske)	0·16	(cathode)
Do. (Hoepfner)	2	(cathode)
Silver refining (Moebius)	2·5–3·5	
Do. (Moebius—for anodes rich in gold)	0·75	
Do. (Balbach)	2–2·6 4–5	(cathode) (anode)
Do. (Balbach—for anodes rich in gold, the electrolyte containing gelatine)	5–5·5	(anode)
Do. (Dietzel)	1·5	

Gold refining (Wohlwill)	10–15
Do. (Wohlwill—for anodes rich in silver)	5–7
Do. (Wohlwill — modified process for anodes rich in silver)	12
Gold extraction (Siemens-Halske)	0·004
Zinc extraction (Siemens-Halske)	1·5–3 (cathode)
Do. do.	30–75 (anode)
Do. (Laszczynski)	1·0
Do. (Hoepfner)	1·0
Detinning (Goldschmidt)	0·8–1·0 (cathode)
Nickel extraction (Savelsberg-Wannschaff)	1–1·2 (cathode)
Iron refining (Merck)	3–4
Do. (Fischer-Pfanhauser)	10–20
Lead refining (Betts)	17–20
Electroplating	0·1–2·0
Electrotyping	2–8

Kellner's hypochlorite electrolyser	50–75
Haas-Oettel's do.	10
Chlorate cells	10–20 (anode)
Castner 'rocking' cell	7 (cathodic mercury)
Solvay cells	10–20 (mercury)
Whiting cell	11 (mercury)
Wildermann cell	Up to 60 (mercury)
Do.	10 (anodes)
Griesheim cell	1–2 (diaphragm)
Bell-jar cell	2 (bell-jar)
Billiter-Leykam cell	4·3 (bell-jar)
Billiter-Siemens cell	4–6 (diaphragm)
Hargreaves-Bird cell	2 (diaphragm)
Townsend cell	15 (diaphragm)
Finlay cell	2 (diaphragm)
White lead production	0·24 (anode)
Bromine (Wünsche)	1·15
Bromate production	10–15 (anode)
Iodoform do.	1–2 (anode)
Anthraquinone (Moest)	5 (anode)
Chromic acid regeneration	3 (anode)
Perchlorate production	8 (anode)
Permanganate do.	8·5 (?) (anode)

Sodium (Castner)	200–250 (cathode)
Magnesium production	30 (cathode)
Calcium do.	10,000 (cathode)
Zinc (Swinburne-Ashcroft)	43 (cathode)
Do. (Vogel)	16 (cathode)
Aluminium	80–100 (anode)
Acker process	300 (anode)

Carbon electrodes in electrothermics	300–400	(Can be taken much higher, but rapidly burn away.)
Graphite do. do.	2,000	
Stassano steel furnace (carbon)	2,000	
Héroult steel furnace (carbon)	400–500	
Do. do. (graphite)	1,500–1,600	
Girod steel furnace (carbon)	500	
Limit for pinch effect about	50,000	
Ferro-silicon furnaces (carbon)	300–700	
Carbide furnaces (carbon)	350–600	
Carborundum furnace	300 (in core)	

III. Yields and Energy Expenditure in Technical Practice

Product	K.W.H. per kilo.	Tons per H.P. year.
Refined copper (multiple)	0·3	21·8
Do. (Hayden)	0·15	43·7
Extracted copper (Laszczynski)	2·1	3·1
Do. (Hoepfner)	0·37	17·5
Refined silver (Moebius)	0·42	15·6
Do. (Balbach)	0·84	7·8
Refined gold	0·32	20·5
Extracted zinc (Siemens-Halske)	3·3–3·9	1·7–2·0
Do. (Hoepfner)	3·1	2·1
Recovered tin (Goldschmidt)	1·9	3·4
Extracted nickel (Savelsberg-Wannschaff)	4·2	1·56
Do. (Browne)	3·6	1·85
Refined lead	0·098	66·9
Extracted lead	1·0	6·55
$KClO_3$	7·3	0·9
NaOH (see p. 383)	2·0–3·8	1·6–3·3
White lead	0·25–0·3	22–26
Bromine (Wünsche)	1·6	4·1
Do. (Kossuth)	2·7–3·0	2·2–2·4
Iodoform	1·5–1·9	3·4–4·4
Anthraquinone (Moest)	2·5	2·6
$NaClO_4$ (from $NaClO_3$)	3·5	1·9
$KMnO_4$	0·7 ?	9·4
Sodium (Castner)	11·7	0·56
Magnesium	17·7	0·37
Calcium	42	0·1
Zinc (Swinburne-Ashcroft)	3·75	1·75
Aluminium	23	0·29
NaOH (Acker process)	4·7	1·39
Pig-iron (see p. 441)	1·7–3·2	2·1–3·8
Steel (from hot charges)	0·12–0·4	16·4–55
Do. (from cold charges)	0·6–1·3	5·0–10·9

Product	K.W.H. per kilo.	Tons per H.P. year.
50 per cent. ferro-silicon	5·3–16	0·41–1·2
70 per cent. ferro-chrome	8	0·82
85 per cent. carbide	3·8–7	0·93–1·6
Cyanamide (from carbide)	0·1	65·5
Carborundum	8·5	0·77
Graphite	3·3	2·0
Alundum	2·1	3·1
Zinc (de Laval)	4·8	1·37
Phosphorus	11·6 (?)	0·56
Carbon bisulphide	1·15	5·7
Nitric acid	14·7–16·7	0·39–0·45

IV. Theoretical Quantities of Electrolytic Products resulting from the Passage of 1 ampère-hour of Electricity

Copper (from cupric salts)	1·186 grams
Do. (from cuprous salts)	2·372
Silver	4·023
Gold (from auric salts)	2·451
Do. (from aurous salts)	7·354
Zinc	1·219
Iron	1·042
Nickel	1·094
Lead	3·857
Tin (from stannic salts)	1·109
Sodium	0·859
Magnesium	0·454
Calcium	0·747
Aluminium	0·337
Hydrogen	0·0376
Oxygen (free or bound ‘ active ’ oxygen)	0·298
Chlorine (free or bound ‘ active ’ chlorine)	1·322
Bleaching powder with 34 per cent. ‘ active ’ chlorine	3·89
Bromine	2·981
Potassium chlorate	0·762
Sodium chlorate	0·662
Potassium perchlorate (from potassium chloride)	0·646
Potassium hydroxide	2·094
Sodium hydroxide	1·494

INDEX OF AUTHORS AND FIRMS

The references are to pages

Abbott, 395
Abegg, 34, 76
Abel, 335, 341
Abel (book), 341
Acheson, 488,492,493
—— Company, 495
Adolph, 372, 404
A.F.A.G. Berlin-Hagen, 224
Allmand, 84, 205
Aluminium Corporation, 427
—— und Magnesium Gesellschaft, 417
Amberg, 443, 490
Amberg (article), 504
Andreoli, 278
Angeli, 402
Appelberg, 162
Arndt, 159, 164, 416 ,419, 421
Arrhenius, 68, 70, 71, 75
Ashcroft, 414, 415
Askenasy, 225, 384, 385, 399, 400
Askenasy (book), 443, 464, 468, 472, 485, 504

Badger, 164
Badische Anilin und Soda Fabrik, 385, 479
Baekeland, 380
Bahntje, 126
Balbach Smelting and Refining Co., 295
Barker, 383
Barnes, 217
Baum, 247, 256
Bechterew, 214
Becker, 412
Bein, 55
Bein (book), 219, 244
Bemmelen, van, 239
Bernfeld, 260, 306
—— (firm, Leipzig), 155
Berthelot, 14, 402, 507
Betts, 155, 302, 307
Betts (book), 307
Beutner, 214, 472, 481
Bicknell, 420
Billiter, 153, 297, 362, 370, 373, 375
Billiter (book), 385
Biltz, 147
Binschnedler, 389
Birkeland, 512, 513
Blich, 520
Block, 63
Bodenstein, 15, 519
Bodländer, 277
Boericke, 132, 390
Bölling, 492
Borchers, 212, 214, 261, 416, 417, 418, 419, 493
Borchers (book), 182
Bose, 273, 391
Bottomley, 496
Bradley, 469, 511
Bran, 151
Brand, 399, 400, 401
Bredig, 482, 483
Breuer, 363
Briner, 359, 509
Brion, 185, 188, 512
Brislee, 134
British Aluminium Co., 428
Brochet, 359, 365, 368
Brochet (book), 385
Brode, 409, 410, 411, 507, 515
Brown, 293, 311, 501, 502
Browne, 298
Bruner, 214
Brunner, 314
—— Mond & Co., 281, 286
Bucherer, 212, 214
Buchner, 155
Bugarszky, 84
Bullier, 469
Bunsen, 201, 412, 416, 418
Burgess, 299, 301, 310, 316, 389

Canadian Copper Co., 298
Cantoni, 351
Carborundum Co., 488
Carlson, 482
Caro, 402, 479, 481, 485
Caron, 417
Carrier, 412, 414, 415
Caspari, 118

Castner, 350, 351, 408
Castner-Kellner Co., 352, 385
Catani, 435
Chattaway, 200
Chloride Co. (accumulators), 225
Clacher, 428
Clancy, 279
Clausius, 68
Coehn, 36, 118, 131, 265, 271, 272, 314
Coffetti, 120
Cohen, 200, 260
Collins, 172, 490
Conrad, 182, 464, 472
Consortium für electroch. Industrie, 404
Corbin, 340
Côte, 501, 502
Couleru, 401
Cowper-Coles, 317
Cramp, 185
Crookes, 505
Cumming, 233
Czepinski, 163, 164

Daniell, 57
Danneel, 125, 415
Dannenberg, 118
Darling, 408
Darmstädter, 396
Davies, 192
Denham, 57, 76
Denison, 55
Denso, 151
Deutsche Quarz-Gesellschaft, 496
Deville, 417
Dietzel, 284
Dolch, 289
Dolezalek, 227, 229, 231, 233
Dolezalek (book), 244
Donnan, 84, 383
Durand, 509

Eckardt, 289
Edison, 203, 234
Egli, 260
Elbs, 127, 147, 303, 394, 403
Electrolytic Alkali Co., 153, 376, 378
Engelhardt, 285, 329, 450
Engelhardt (book), 341, 406
Engemann, 294, 300
Erlwein, 472, 479, 481
Eschmann, 481
Ewan, 410
Eyde, 512, 513

Fabian, 294
Faraday, 29, 50, 141
Farbwerke Höchst, 396
— — vorm. Meister, Lucius und Bruning, 396
Faure, 223
Faust, 239
Ferchland, 154, 285
Ferranti, 454
Field, 313
Finckh, 506
Findlay (book), 17
Finlay, 380
Fischer, 224, 299, 522
Fitzgerald, 489
Fleischmann, 213
Foerster, 105, 120, 121, 132, 133, 134, 142, 153, 237, 239, 240, 241, 242, 243, 247, 252, 256, 282, 283, 289, 294, 295, 299, 306, 314, 319, 320, 323, 325, 326, 336, 337, 338, 344, 356, 369, 372, 390, 395, 401, 482, 483, 484, 519, 520, 521
Foerster (book), 116, 147
Fontana, 396
Foster, 213
Fraenkel, 482
Frank, 479
Franke, 261
Frary, 164, 420
Frauenberger, 141
Frazer, 41
Fredenhagen, 141
Friedberger, 146, 403
Friedrich, 206
Fromm, 125, 282, 283

Gahl, 119
Gall, 338
Gay Lussac, 40, 321
Geibel, 339
Geilenkirchen, 443
Geipert, 429, 430, 431
Gessler, 159, 421
Gillett, 389, 487
Gin, 442, 444
Girod, 449, 468
Gladstone, 222, 226
Glaser, 302
Goldschmidt, H., 289
Goldschmidt, K., 291
Goodwin, 420, 421
Gordon, 163
Grabau, 413
Gräfenberg, 236
Grau, 192, 507
Grave, 142
Greene, 442
Greenwood, 463, 486
Griesheim Elektron Co., 412
Grinberg, 151, 344
Grönwall, 439
Grotthuss, 49
Grove, 201, 211
Grube, 131, 133
Grünauer, 422, 423
Guertler, 463
Günther, E., 261, 296, 298
Günther, E. (book), 307

Günther, O., 282
Guye, 156, 358, 359, 361, 478, 509, 510, 521
Gyr, 320

Haagn, 63
Haanel, 437, 439, 440
Haber, 105, 122, 125, 127, 133, 141, 146, 151, 192, 201, 209, 213, 214, 218, 309, 344, 425, 426, 427, 428, 429, 430, 431, 467, 472, 476, 478, 479, 499, 507, 508, 509, 510, 511
Haber (book), 147, 406
Hambuechen, 299, 301, 316, 389
Hansen, 176, 504
Hantzsch, 283
Härdén, 435, 450, 453, 455, 504
Hatfield, 34, 35
Häussermann, 362
Hayek, v., 398
Helfenstein, 159, 174, 474
Helfenstein (article), 464, 468, 472, 485
Helmholtz, 63
Hempel, 500
Heraeus (firm), 496
Hering, 173, 176, 178, 453
Herold, 239, 242, 243
Héroult, 438, 439
Herrmann, 500
Herschkowitsch, 138
Herz, 394
Hessberger, 517
Hevesy, v., 161, 411
Higgins, 496
Hill, 383
Hirsch, 122
Hittorf, 52, 54, 55, 56, 57, 140
Hoepfner, 264, 286, 296
Hofer, 164, 431, 506
Hoff, van't, 39, 40, 45
Hohler, 418
Holland, 234, 238
Holland (book), 244
Holwech, 509, 511, 519
Hooker Electroch. Co., 378
Hopfgartner, 53
Howles, 505, 506
Hoyle, 185
Hulin, 164, 413
Hurter, 338
Huth, 285
Hutton, 450, 496

Ihle, 202
Imhoff, 322
Inglis, 143
Isambert, 19
Isenburg, 389

Jacobsen, 271, 272, 314
Jacoby, 482, 484
Jacques, 214
Jahn, H., 53, 55, 84
Jahn, S., 36
Jakowkin, 319
Janeczek, 409
Jellinek, 405, 406, 506, 508
Johnson, 204, 205, 221, 501, 503, 504
Joost, 134, 152, 153
Jordis, 315
Jorre, 320, 356
Jungner, 214, 216, 234
Just, 225

Kailan, 164, 165
Kalmus, 159
Keller, 438, 439, 450
Kellner, 332, 333, 351
Kemmerer, 166
Kern, 126, 294
Kiliani, 250, 282
King, 474
Klonowski, 399, 400
Koch, 519, 520, 521
Koenig, 192, 507, 508, 509, 510, 511
Kohlrausch, 56, 63, 65, 66, 67
Kossuth, 392
Kowalski, v., 511, 512
Kretzschmar, 320, 390
Kügelgen, v., 413

Lalande, 203
Lampen, 470, 487
Landis, 501
Langbein, 310, 312, 315
—— und Pfanhauser, 299
Langer, 213, 214
Laszczynski, 285
Le Blanc, 75, 141, 142, 155, 157, 192, 232, 320, 351, 389, 396, 397, 409, 410, 411, 412, 481, 520
Le Blanc (book), 37, 48, 57, 76, 105
Le Rossignol, 479
Lee, 299, 300
Leithäuser, 507, 524
Lenz, 265
Lepsius, 152, 362
Lindblad, 439
Loeb, 53
Loebe, 394
Lombard, 481
Lorenz, 158, 159, 161, 162, 164, 165, 166, 204, 206, 388, 418, 421, 422, 423
Lorenz (book), 37, 76, 116, 166, 433
Louis, 175
Lovejoy, 511
Lucion (book), 385
Luckow, 388, 389
Luther, 134, 335, 341
Lyon, 439

McCaughey, 315
McDougall, 505, 506
Macgregor, 442

Magnus, 256
Marshall, 402
Mathers, 302
Matignon, 481
Matthes, 363
Matthiessen, 418
Mellor (book), 25
Merck (firm), 301
Meves, 395
Miller, 389
Mitrofanoff, 225
Moebius, 268
Moest, 396
Mögenburg, 493
Mohn, 306
Moissan, 469, 482
Möller, 133
Mond, L., 213, 214
Mond, R., 217
Montlaur, 338
Morden, 509, 511
Morse, 41
Moscicki, 511, 512
Moser, 213
Moser (book), 146, 147, 406
Mott, 119
Mugdan, 385
Mühlhaus, 376
Müller, E., 105, 126, 129, 132, 146, 147, 154, 322, 323, 325, 326, 336, 337, 338, 394, 397, 403
Müller, R., 500
Mustad, 121, 299
Muthmann, 141, 164, 431, 506
Mylius, 125, 282, 283

Naville, 510
Nernst, 53, 63, 92, 93, 133, 506
Nernst (book), 25
Neumann, 251, 278, 296, 427, 429, 430, 435, 443
Nobis, 119, 131, 134, 215, 219
Norton Emery Wheel Co., 495
Noyes, 54, 55, 64, 74, 76
Nübling, 303
Nüranen, 192

Oechsli, 401
Oesterle, 501, 502
Oettel, A., 164, 416, 417, 418
Oettel, F., 32, 33, 330, 417
Olsen, 429, 430
Orford Copper Co., 298
Osaka, 131
Osann, 443
Ostwald, 73, 209

Parker, 500
Patten, 315
Pauli, 390
Perkin, 396
Pfaff, 299, 301
Pfanhauser, 309
Pfeffer, 40, 41
Pfleiderer, 134
Pick, 465
Pierron, 501, 502
Pietzsch, 404
Piguet, 132, 401
Planck, 68, 73
Planté, 223
Plato, 419, 420
Platou, 507, 511
Pohl, 15
Poincaré, 416, 421
Polzenius, 482
Potter, 487
Preuner, 20
Pring (book), 11
Puschin, 137, 138
Pyne, 426

Ramsbottom, 399, 400, 401
Raoult, 45, 71
Rathenau, 419
Rayleigh, 505
Readman, 500
Reason Mfg. Co., 34
Regelsberger, 396
Reinartz, 262
Richards, J. W., 8, 170, 409, 425, 426, 427, 429, 435, 476, 501
Richards, T. W., 32, 159, 163
Richardson, 237, 429, 431
Rodenhauser, 458
Rodenhauser (book), 182, 468
Rothmund, 18, 470
Roush, 395
Ruckstuhl, 166
Rudolphi, 470, 471, 482, 483
Ruff, 419, 420
Rumpf, 231
Russ, F., 192, 507
Russ, R., 127, 133

Sacerdoti, 119, 120, 133, 153, 343
Sacher, 411
Sack, 122
Sackur, 141, 142, 213
St. Gilles, 14
Savelsberg, 297
Schleicher, 225
Schloesing, 521
Schlötter (book), 317, 406
Schmiedt, 146, 154, 398
Schoch, 122, 292, 293
Schoenawa (book), 182, 468
Schönherr, 147, 403, 516, 518
Schoop, 222, 239, 240
Schultze, G., 143
Schultze, H., 422
Schwab, 247, 256
Schwabe, 306
Schweitzer, 121, 292, 293

Seidel, 247, 256
Senn, 302
Seward, 413
Siemens und Halske, 285, 307
Sjöstedt, 438
Snyder, 170, 502
Soller, 146, 154, 397
Solvay Co., 352
Sonneborn, 344
Speketer, 363
Spitzer, 120, 312
Sprösser, 153, 346
Stålhane, 439
Stansfield (book), 182
Stassano, 437
Steele, 55
Steiner, 372
Stockem, 414, 415, 419
Strasser, 119
Streintz, 230, 231, 232
Strutt, 509, 510
Stull, 159
Suchy, 422
Swinburne, 423, 424

Tafel, 30, 119, 130
Taitelbaum, 215, 216
Tammann, 463
Tardy, 156, 361
Taussig, 174, 348, 353, 354
Taylor, E., 498
Taylor, W., 143
Teeple, 395
Thermal Syndicate, 496
Thiele, 323
Thompson, 24, 237, 261, 262, 264, 429, 430, 470, 471, 481
Thomson, 183
Toepler, 184
Tombrock, 200
Tone, 488, 489
Tower, 55
Traube, M., 40
Traube, W., 147
Tribe, 222, 226
Tronson, 420
Tscheltzow, 231
Tucker, 420, 487
Tudor, 224

Ulke (book), 280
Umbreit und Matthes, 203
Union Carbide Co., 475
United States Steel Corporation, 174, 442
Uslar, v. (book), 280

Veesenmayer, 217
Villeroy und Bock, 155
Vogel, 424
Vries, de, 40

Wannschaff, 297
Warburg, 192, 507, 522, 524
Warth, 472, 481
Weber, 363
Weckbecker, 493
Wedekind, 203
Weiss, 164, 431
Welsbach, v., 221
Weston Chemical Co., 385
Whitney, 420
Wilke, 482
Willner, 164, 419
Willson, 469
Wilsmore, 95
Winteler, 356, 401
Wöhler, 164, 419, 420, 421
Wohlwill, 248, 272, 274, 275
Wolff, 161
Wologdine, 173

Yamasaki, 132, 289, 390
Yngström, 435

Zedner, 239

SUBJECT INDEX

The references are to pages

'Absolute' scale of potential, 95
Accumulators, 220 ff
—— plates, 223, 234
Acetic acid, 224
Acetone, 393 ff
Acetylene chlorides, 385
Acid, formation in brine electrolysis, 344, 361, 366
Acker process, 431 ff
Active mass, 18
Addition agents; for metal deposition, 126; for rapid forming, 224
A.F.A.G. plates, 224
Affinity, 86
Air, electric discharges through, 183 ff, 479, 505 ff; electrode, 215, 216; for fuel combustion, 168 ff; in blast furnace, 435; ozonisation, 524 ff
Alby furnace, **477**, 478
Alcohol, 393 ff
Alizarin, 395
Alkali, electrolytic production, 342 ff
Alkali-chlorine cells, 318, 342 ff
—— classification, 347; comparative, 355, 383; counter-current, 366 ff; diaphragm, 355 ff, 375 ff; mercury, 347 ff; theory, 342 ff, 355 ff, 366 ff
Alkaline bromide electrolysis, 390 ff; chloride electrolysis, 318 ff, 342 ff
Alkaloids, 130
Alloys; anodic solution of, 136 ff; cathodic deposition, 121
Alternating current; arcs, 187, 508; discharge in gases, 185; for conductivity measurements, 60, electric heating, 179 ff, induction furnaces, 167, **451**, ozonisers, 524; in gold refining, 275; rectifier, 142
Alumina, 410, 464, 473, 478, 493; for aluminium, 425 ff, alundum, 496; from bauxite, 426; solution in cryolite, 426 ff
Aluminium; electrolytic production of, 425 ff; electroplating on, 309; fusion, 454; passivity, 142; rectifier, 142
Alundum, 172, **495**
Amalgams; as anode, 350; cathodic production, 122, 342, 347 ff
Ammeter calibration, 35
Ammonia; in electric discharge, 190 ff; equilibrium, 23; from cyanamide, 480; synthesis, 24, 385, 479
Ammonium chloride, 199, 206, 208, 301, 315, 402
Ammonium salts, 104, 315, 401 ff, 521
Ammonium sulphate, 255, 301, 311, 403, 404, 478, 479
Amorphous carbon, 492, 493, carborundum, 492
Ampère, 6
Amphoteric electrolyte, 320
Aniline, 126, 127, 385
Anion, 29; cathodic formation, 126; discharge, 130 ff
Anode, 27; effect, 160, **164**, 420, 429 ff; fall, 188
Anode slimes, 136, 248, 250, 252, 258, 268, 270, 274, 276, 284, 287, 293, 295, 304; resistance, 268, 304, 305
Anodes (insoluble), catalytic action, 146, 397, technical, 151 ff, 166
Anodes (soluble), for primary cells, 199
Anodic current efficiency, 31, polarisation, 108, processes, 130 ff
Anodic impurities in refining copper, 249 ff, gold, 273 ff, lead, 303 ff, nickel, 295, silver, 265 ff, zinc, 284
Anodic solution of metals, 135 ff; effect of physical condition, 135, 292; of alloys, 136; with more than one cation, 136, 248, 271, 289
Anolyte, 27
Anthracene, 395, 396
Anthracite for carbide, 473, 478, carborundum, 488, ferro-silicon, 464, graphite, 493
Anthraquinone, 395
Antimony, in refining copper, 250 ff, 258, lead, 303, 305; refining, 307
Arc, direct current, 509, 510, 511; furnaces, 167, 174, 437 ff, 444 ff,

459 ff, 464 ff, 473 ff, 488, 496, 500, 503, 512 ff; heating, 167, 169, 171; in gases, 185 ff
Arsem furnace, 470
Arsenic in copper refining, 250 ff, 255, 258
Asbestos diaphragms, 155, 356, 374 ff, 387
Ashcroft process, 414
Avogadro's law, 41
Azobenzene, 127
Azoxybenzene, 127

Back electromotive force, 113
Baker process, 421
Balbach-Thum process, 268, 269
Barium salts, 162, 375, 376, 480, 482
Bauxite, 174, 426, 496
Bayer process, 426
Becker process, 412
Becquerel cell, 210
Bell-jar cell, 347, 369, **371**, 374, 383, 397; for chromic acid, 397
Benzal chloride, 385
Benzyl chloride, 385
Bergsoe process, 288
Bernfeld diaphragms, 155, 383
Betts process, **302**, 307
Bichromate cell, 202
Billiter-Leykam cell, **373**, 383, 384
Billiter-Siemens cell, 155, **375**, 383, 384
Bi-polar electrodes, 149, 253, 258, 327 ff, 340, 387, 388, 392, 410
Birkeland-Eyde process, **512**, 518, 519
Bismuth; in refining copper, 250 ff, 258, lead, 302 ff; passivity, 143; refining, 306
Blast furnace process, 435, 437
Bleaching liquors (electrolytic), 319, 384. See *Hypochlorites*
'Block' furnaces, 473 ff
Board of Trade unit, 6
Bone ash, 500
Borchers cell, 216
Boric oxide, 493, 495
Boyle's law, 40
Bradley-Lovejoy furnace, 511
Brass; electrodes, 313, 316, 339; electrolytic, 309; fusion, 454; hydrogen overvoltage, 119; plating, 312
Brine, 375 (see also *alkaline chloride* and *sodium chloride*)
Bromates; electrolytic production, 390 ff, 393; from hypobromites, 320, 391, 393, 394; in bromine cells, 392
Bromic acid, 199
Bromine; anodic production, 390 ff; cathodic reduction, 392; for electricity meter, 35; hydrolysis, 319, 390; overvoltage, 132
Bromion, 132, 134, 140
Bromoform, 393, 394
Browne process, 298
Browne-Neil process, 288
Brush discharge, 185, 186, 523
Buckling of plates, 222
Bullier furnace, 477
Bullion parting, 269, 273
Bunsen cell, 115, **201**, 203

Cadmium, 138, 199, 221, 285; cell, 91
Calcium, electrolytic production, 418 ff; salts, 160, 401, 402, 418 ff, 424, 444, 472, 473, 480, 481, 483, 500, 502, 521
Calcium carbide; action of nitrogen, 479 ff; commercial, 471, 474, 477; decomposition by heat, 472, 481; dissociation, 470, 471; technical production, 472 ff; theory of formation, 469 ff; produced in steel furnaces, 444, 447
Calcium chloride, 158, 159, 206, 208, 301, 402, 421, 482 ff, 526; dehydration, 418; electrolysis, 418 ff; for ore extraction, 264, 286, 296, 297
Calcium cyanamide, action of steam, 480, for gold extraction, 279, from carbide, 479 ff, technical production, 484
Calcium fluoride (see also *fluorspar*) as catalyst, 472, 482 ff; in fused salt electrolysis, 417, 418, 419, 420, 425, 427
Calcium salts in crude salt, 433; in brine for alkali-chlorine cells, 349, for bleaching liquors, 323, 327, 333, for chlorates, 340
Calomel electrodes, 104
Calorie, 7
Capacity of alternating current circuits, 180, 457, 524, cells, **201**, 204, 209, 220, 222, 225, 226, **230**, 231, 235, 236, **238**, 243, induction furnaces, 452, 454, 457, 458
Carbon; allotropic forms, 492; bisulphide, 497, **498**, 502; electrodes for furnaces, 175 (see also *furnace electrodes*); for furnace charges, 464, 473, 488; hydrogen overvoltage at 119, 348; ionisation of 210; furnace linings etc., 173, 425, 465, 467, 477, 478; resistors, 484, 496, 497, 499; tetrachloride, 385
Carbon anodes, 151, **152**; acid produced at, 361, 367; anode effect, 164, 430, 431; attacked by oxygen, 345; disintegration, 345; in primary cells, 210, 214; manufacture, 152, 428; porosity, 345, 346; testing, 346
Carbon dioxide, electric discharges through, 190; for white lead, 389;

in anodic chlorine, 345, 346, 349, 362, 376, 383; in Hargreaves-Bird cell, 377, 378
Carbon monoxide, equilibrium pressures (carbide reactions), 470, 471; from blast furnace, 435 ff, electric furnaces, 435 ff, 438, 443, 489, 490, 500, 502, 503; in aluminium bath, 428, 429
Carborundum, 486, 487, **488 ff**, 493, 497; anodes, 151, 153; bricks, 174, 489; furnace, 167, **489**, 495; refractory, 172
Carmichael process, 261, 262
Carnallite, 416, 417
Caro's acid, 402, 403
Cast anodes, 135
Cast iron (electrothermal), 437, 438
Castner mercury cell, **349**, 383; sodium process, **408**, 413
Castner-Kellner cell, 352
Catalyst, 13
Cathode, 27; catalytic action of, 129; contact, 413, 419, 420; fall, 188; heated, 509; primary cells, 199; rotating, 270, 286, 287, 316, 317
Cathodic current efficiency, 31, 159, depolarisers, 197, polarisation, 108, processes, 117
Cathodic metal deposition, 120 ff; alloys, 121, 312; amalgams, 122; metals with more than one cation, 122, 245, 272
Catholyte, 27
Cation, 29
Caustic alkali, potash, soda (see *alkali*, *potassium hydroxide*, *sodium hydroxide*)
Cell constant, 61
Cement diaphragms, 155, 356, **363**, 377, 399
Ceric sulphate, 146, 199, 221, 395, 396
Characteristic curve, 184, negative, 185, 187, 189
Charcoal for carbide, 473, 478, carbon bisulphide, 499, iron, 438 ff, ferro-silicon, 464 ff, phosphorus, 500, zinc furnaces, 503
Charge (of accumulators), **228**, **237**, 241, 243, 244
Chile deposits, 478, 479
Chloral, 385
Chlorates; electrolytic reduction, 126, 193; in alkali-chlorine cells, 344, 345, 361, 362, 364, 372, 376; from hypochlorite (chemical), 320, 321, 338, (electrochemical), 323, 336; technical production, 338 ff; theory of formation, 318 ff, 335 ff
Chlorbenzene, 385
Chloric acid, 199, 224, 225, 401
Chlorine, action on alkali, 321 ff; anodic, 286, 297, 298, 346, 349, 353, 362, 364, 365, 376, 379, 383, 384, 431, 433; cathodic solution, 219, 286, 349, 385; hydrolysis, 319; liquefaction, 385; for nickel ores, 297, 298; overvoltage, **132**, 134, **153**, 318; uses, 384
Chlorion, 132, 140, 146, 271, 290, 292, 299, 318, 377, 388
Chloroform, 385
Choking coil, 188, 526
Chromate for brine electrolysis, 322
Chrome yellow, 302, **388**
Chromic acid, 202, 389, 395, 397; electrolytic regeneration, 146, **396 ff**, 401, 404; in primary cells, 199, 202
Chromium, 139, 140, 199; chromate, 322; sulphate, 395
Circulation; of electrolyte, 254, 259, 264, 270, 275, 287, 303, 329, 330, 338, 339, 392, 402; in induction furnaces, **452**, 458, 460; of mercury, 350, 352, 353, 354
Clancy process, 279
Clark cell, 82, 83, 91
Cobalt, 131, 221, 250, 320
Coefficient of self-induction, 181
Coke for carbide, 473, carbon bisulphide, 499, carborundum, 488, 489, iron, 435 ff, ferro-silicon, 464 ff, graphite furnaces, 493 ff
Colby furnace, 455
Cold galvanising, 310
Colloids, 125
Complex ions, 57, 120, 123, 125, 136, 161, 166, 248, 264, 272, 302, 416, salts, 125, 309
'Concentrates,' 277
Concentration; cell, 89, **103**, 163; changes during electrolysis, 27, 51, 57, 198, 206, 218, 222, 229, 240, 397; effect on cathodic deposit, 124, electrolytic dissociation, 68, electrolytic oxidation, 145, electrolytic reduction, 129, equivalent conductivity, 65, specific conductivity, 64; polarisation, 114, **115**, 119, 135, 165, 198, 229
Condenser, 63, 511, 526
Conduction losses (thermal) from furnaces, 173
Conductivity (electrical); of electrolytes, 58, of gases, 183, of hot oxides, 457, measurement, 59 ff, 159, of molten electrolytes, 158, of working cell, 62, vessels 62
Conductivity (thermal) of refractories, 174
Conductors, 26
Contact electrode, 413, 420, 421, process, 408, 412, 418, 419
Continuous block furnace, 475

Convection disturbances, 347, 355, 366, 369, 371, 373, 374, 410

Copper, 137, 138, 266, 273, 285, 303, 309, 457; anodes, 217, 249, 258, 315, 316, 388; anodic solution, 248; cathodes, 129, 151, 217, 254, 262, 263, 264, 339, 377, 385; cathodic, 124, 126, 252, 298; coulometer, **32**, 36; electro-deposition, 120, 121, 125, 245 ff, 312; extraction, 260 ff; fusion, 454, 504; hydrogen over-voltage, 118, 119, 201, 227, 312, 343; matte anodes, 260, 261; plating, 312; refining, 245 ff; sub-oxide, 205; salts, 123, 327, 339

Coulomb, 6

Coulometers, 31 ff

Counter-current cells, 366 ff

Counter-current principle, 305, 520

Cryolite, 425 ff

Cupric compounds, 57, 147, 264, 296, oxide, 199, 203 ff, 214, 221, 388, sulphate, 57, 199, 200, 245 ff, 255, 315, 316

Cupro-ions, complex forming, 123, 136, 248, 264, 265

Cupron cell, 203

Cuprous oxide, 205, 250, 388, 389, salts 216, 250, 264, 277, 297, 312

Current, 5, concentration, 30, 406, electrode-potential curve, 113, measurement, 31

Current density, 5; effect on anode effect, 164, anodic solution of alloys, 139, bath voltage, 150, cathodic deposits, 120, 123, 124, 247, 256, 262, 266, 278, 283, cell capacity, 230, 243, cell polarisation, 230, chemical losses in mercury cells, 349, current efficiency in diaphragm cells, 361, current efficiency in fused melt electrolysis, 160, 422, diffusion losses, 361, electrolytic oxidation, 145, electrolytic reduction, 128, hypochlorite concentration, 325 ff, 337, Luckow reactions, 389, over-voltage, 119, 131, passivity, 140, 271, pinch effect, 453, quality of anodic chlorine, 346, working of counter-current cells, 371, 376 (see also Appendix II.)

Current efficiency, 30, 31, anodic, 31, calculation of 36, cathodic, 31, influence of iron, 162

Cyanides, 479, 480

Cyanide bath, for electroplating, 312 ff, deterioration, 277, 314

Cyanogen chloride, 277, bromide, 277, iodide, 279

Daniell cell, 3, 77, 82, 84, 94, 99, 106 ff, **200**

Decinormal calomel electrode, 105

Decomposition voltage, 108, 112

Decrease of free energy, 78, 81, 85, total energy, 78, 81, 85

Degree of dissociation, 70

Dehydration of fused salts, 409, 416, 418, 421 ff

Deozonisation, 523, 524

Dephosphorisation of steel, 443

Depolarisation, 115, 121, 128, 134, 197, 206, 208, 262, 308

Depolarisers, 115, 197, 199; in primary cells, 199, secondary cells, 221

Design of electrodes, 176, furnaces, 171

Desulphurisation of steel, 443, 444, 461

Deterioration of electrolyte, 253, 257, 261, 277, 288, 290, 304, 314, 318, primary cells, 198

Detinning, 288 ff, 385

Diamantin, 496

Diaphragm cells, 347, 355 ff, 375 ff

Diaphragms, 154 ff, 369 ff

Dietzel process, **269**, 284

Diffusion coefficient of diaphragms, 156

Diffusion effects, 114; in alkali-chlorine cells, 355, 360 ff, 371, lead accumulator, 229, 230, primary cells, 197, 198, 203, sodium cell, 410, 411, 415

Dilution law, 72

Direct current arc, 509, 510, 511

Discharge of accumulators, **228**, **237**, 240 ff

Discontinuous block furnace, 473

Disintegration of carbon anodes, 152, 345, graphite anodes, 152, 345, 349, ferro-silicon, 464

Dissociation constant of water, 117, pressure 17, of electrolytes, 47

Dolomite (calcined), 172, 446, 447, 457, 458

Domnarfvet experiments, 439

Dow cell, 393

Dry cells, 208

Dujardin-Planté plates, 224

Eddy current losses, 182, 452

Edison cell, 221, **234**

Edser-Wildermann cell, 354

Efficiency of electrolytic processes, 30, 110, furnaces, 8, **170**

Electric furnaces, 167 ff, heating, 167 ff, losses in induction furnaces, 452, 455, shaft furnace, 439

Electrical discharge in gases, 183 ff, double layer, 93, energy, 4, equilibrium in gases, 191, 509, 522, units, 4

Electricity meter, 34

Electrochemical processes, 3, 4, combustion of fuels, 209 ff

Electrode, 27; bipolar, 149, constant,

179, design, 176, for furnaces, 175 ff, gas, 99, heat losses in, 175 ff, in parallel, 148, in series, 149, ionising, 92, loss (heat), **172**, 446, 460, 462, 500, manufacture, 152, 175, 428, oxidation-reduction, 100, potential, 95, 97, 104, standard, 104
Electrodeposited anodes, 135
Electrogalvanising, 310
Electrolysis, 26; bath, 148, ff, causes of loss during, 30, concentration changes during, 27, 51, 57, of molten electrolytes, 159 ff, 407 ff
Electrolytes, 26; conductivity, 58 ff; deviations from solution laws, 46; molten, 158 ff; technical, purity desirable, 4, 260, 263
Electrolytic cell, 27, cleaning of metal surfaces, 309, conductor, 26, dissociation, 67 ff, oxidation, 34, **144**, potential, **95 ff**, 135, processes, 87 ff, rectifier, 142, reduction, 34, **126**, solution pressure, **92**, 121
Electromotive force, 6; induced, 451, measurement, 90, of accumulators, 227, 237, fuel cells, 210, 212, primary cells, 195 ff, temperature coefficient, 83
Electron, 183, 187, 189
Electronic conductor, 26, 415
Electroplating, 308 ff
Electrothermics, 167 ff
Electrotyping, 308, **315**
Elmore process, 316
Endosmose, 360
Endothermic reaction, 23
Energy efficiency, 110
Equilibrium, 12 ff, constant, 14
Equivalent conductivity, 65, at infinite dilution, 66
Equivalent ionic conductivity, **66**, 71
Ethylene chloride, 385
Exothermic reaction, 23

Faraday, 29, dark space, 182
Faraday's laws, 28 ff, 159
Faure plates, **225**, 234
Ferric oxide, 208, 364, 380, 435, 436, 443, 493, 494, compounds, 284, 288, 380, 417, 426, 489
Ferro-alloys, 434, 444, **462**
Ferro-chrome, 462, 467, furnace, 438, 467, 468
Ferro-manganese, 454, 462
Ferro-molybdenum, 462, 468
Ferro-nickel, 438, 439
Ferro-silicon, 444, 462, 463, **464 ff**, 469, 487, anodes, 151, furnaces, 167, 172, 173, 438, **464 ff**, 473, 477, 488
Ferro-tungsten, 462, 468
Ferro-vanadium, 462, 468
Ferrous compounds, 239, 260, 288, 300, 301, 307, 364, 443, 444
Finlay cell, 368, 375, **380**, 383, 384, 387
Flaking of electrodeposits, 294, 300, 308
Flaming arc, 505 ff, 515
Fluorion, 146, 404, 430
Fluorspar, 303
Forming of plates, 223 ff
Free charged ions, 68, 75
Free energy decrease, 78, of fuel combustion, 210 ff
Frequency, **181**, 454, in technical furnaces etc., 440, 455, 457, 458, 514, 524, 526
Frick furnace, 455, 456
Fuel cells, 209 ff, heating, 168 ff, 209
Furnace efficiency, 8, 170, 475, 478, 494, 500, gases, 172, 174, 437, 439, 440
Furnace electrodes, consumption, 438, 439, 441, 446, 448, 450, 460, 461, 466, 467, 514, 515, 517, 518; cooling, 175, 440, 446, 447, 449, 450, 478, 490, 499, 513, 514, 517; regulation, 438, 440, 446, 447, 449, 465, 466, 467, 474, 476, 496, 515
Fused quartz, 496

Galena, 306
Gall-Montlaur process, 338
Galvanic deposits, 308 ff
Garuti electrolyser, 387
Gas cells, 212 ff, constant, 41, electrodes, 99, ions, 183, 189, 524, power, 10, 385, 435
Gases, electrical discharges in, 183, in steel, 444, 459
Gay Lussac's law, 42
Gelatine, added during forming, 226, effect on cathodic deposits, 126, 269, 302 ff
Generator-gas cells, 211
Gibbs-Helmholtz equation, 83, 85, 231
Girard-Street furnace, 468
Girod ferro-alloy furnace, 468, steel furnace, 444, 445, **449**, 450, 457, 461, 462, 465, 466
Glow discharge, 185, 186
Glue, 303, 304
Glycerine, 206, 208, 226
Gold; anodes, 273, 274, 314, anodic behaviour, 139, 140, 271, 276, 314, 315, cathodes, 274, cathodic, 273, 278, cathodic deposition, 273, 314, chemical solution, 276, compounds, 271 ff, 277, 279, 314, extraction, 154, **276 ff**, ores, 277 ff, plating, 314, refining, 271 ff
Goldschmidt detinning processes, 288, 291, 385, thermite process, 1, 462
Graphite anodes, 151, **152**; anode effect, 164; chlorine overvoltage, **153**, 345, 378; cathodes, 151, 166;

electrodes for furnaces, 175, 448; electrodes, manufacture, 495; electrode furnace, 495; found in carborundum furnace, 490; furnaces, 493, 495; hydrogen overvoltage at, 119; in solid depolarisers, 198, 207, 208, 236; manufacture, 492 ff; resistor, 489; thermal conductivity, 174
Gravity cell, 347, **371**
Griesheim-Elektron cell, 152, 153, 347, 355, 356, **362 ff**, 383, 385
Grove cell, 115, **201**

Haanel reports, 437
Haas-Oettel cell, **330**, 334, 335
Hall cell, 425
Hargreaves-Bird cell, 151, **376**, 379, 383
Hasse process, 284
Hayden process, 253, 257, **258**, 327 (also *Series system*)
Hearth electrodes, 438, 445, 449, 450, 457, 465 ff, 473 ff
Heat losses from furnaces, 172, 173, 175 ff
Heating of alkali-chlorine cells, 364, 374, 375, 377
Helfenstein furnaces, **174**, 467, 478
Helmholtz-Thomson rule, 78, 85, 335, 383, 411, 429
Henry's law, 21
Héroult ferro-alloy furnace, 466, 467, steel furnace, 174, 442, 444, **447**, 449, 450, 459 ff, aluminium process, 425, 427, 430
Hessberger furnace, 517, 519, 521
Heterogeneous equilibrium, 16, system, 13
Higgins furnace, 496
High tension arc, 185, **186** ff, 505
Hiorth furnace, 455
Hoepfner processes for extraction of copper, 264, nickel, 296, zinc, 286
Hoff, van't, factor, 47, 48, 70
Homogeneous equilibria, 14, system, 13
Horizontal diaphragms, 370, 375
Horry furnace, 475
Horse power, 6, hour, 7, year, 9
Hot galvanising, 310
Hydrazobenzene, 127
Hydrochloric acid, 190, 202, 219, 226, 250, 255, 271, 274, 287, 309, 338, 340, 345, 362, 365, 385, 404, 418, 422, 425, 433
Hydrofluoric acid, 304, 338, 404
Hydrofluosilicic acid, 302 ff
Hydrogen; action on nitrogen, 385, 479; anodic solution, **219**, 385; chlorine cell, 82, 83, **219**, 385; electrode, 95, 105; electrolytic production, 386 ff; in cathodic iron, 300; in anodic chlorine, 349, 353; oxygen cells, 213 ff; peroxide, 277, 283, 402, 403, **404**; scale of potential, 95; utilisation, 385
Hydrogen evolution, 117 ff; in accumulators, 228, 238, electrolytic reduction, 128, metal deposition, 125, 278, 311 ff, Castner sodium cell, 409 ff, mercury cells, 348 ff
Hydrogen ion; discharge from brine solution, 318, effect on passivity, 140, 292, 299
Hydrogen overvoltage, 118 ff, 129, 198, 201
Hydrolysis of halogens, 319
Hydrosulphites (see *Hyposulphites*)
Hydroxyl ion; discharge from brine, 318, 343 ff, 361; migration, 347, 355, 356, 399; velocity, 367 ff
Hypochlorites; cathodic reduction, 322; chemical decomposition, 320, 321, 327, 331; in alkali chlorine cells, 343 ff, 372, 380; ions, anodic discharge, 323 ff, 336 ff, 343; technical production, 327 ff; theory of formation, 318 ff, 321 ff
Hyposulphites, 404 ff

Impedance, 182, 187, 188
Induced current, 451, electromotive force, 451
Inductance, 180, 181, 187, 188, 451, 457, 511, 517, 526
Induction furnace, 7, 167, 444, **450 ff**, 460, 461, heating, 167, **451**
International electrical units, 5
Iodate from hypoiodite, 320, 394, 395
Iodic acid, 146, 397
Iodine, 319 ff, 393
Iodion discharge, 132, 134
Iodoform, 393 ff
Ion, **29**, 166, 183
Ionic conductivity, 66, 67, migration, 49 ff, mobility, 71, transport, 49 ff, velocity, 50
Ionisation, 69, by impact, 184, 191, 524
Iron; accumulator, 221, **234**; affects zinc deposition, 282; effect on fused zinc chloride electrolysis, 425, on nickel deposition, 294; electrolytic, 124, **299 ff**, 316; electrolytic deposition, 121, 299; electrothermal, 437, 438, 441; electrothermal production, 437 ff; for ferro-alloys, 463 ff; furnaces, 172, 435, **437 ff**; impurity in zinc extraction, 285, 286; oxides, 243, 435, 443, 444, 463, 464, 468 (see also *ferrous* and *ferric oxides*, *magnetite*); refining, 299; salts, 122, 162, 216, 227, 260 ff, 375, 417 (see also *ferrous* and *ferric salts*)
Iron anodes; oxygen overvoltage, **131**,

132, 145, 386, 401 ; passivity, 139, 140, 199, 243, 289, 290, 299, 406 ; technical, 151, 154
Iron cathodes ; hydrogen overvoltage, **118**, **119**, 282, 290, 299, 343, 351, 386 ; technical, 151, 166
Irreversible cell, 80
'Irreversible' reactions, 12
Isothermal process, 79

Jablochkoff cell, 210
Jacques cell, **214**, 216
Jaice cell, 353
Joule, 6
Jullien and Dessolle process, 316
Jungner cell, 211, **215**

Keith processes for copper, 261, lead, 302
Keller ferro-alloy furnace, 438, **466**, steel furnaces, 449, 450
Kellner cells for alkali and chlorine, **351 ff**, 383, hypochlorites (horizontal), **332**, 334, 387, hypochlorites (vertical), **328**, 334, 387
Kieselguhr, 174
Kilogram-calorie, 7
Kilowatt, 6, hour, 6
Kjellin furnace, 168, 442, **454**, 456 ff
Kossuth process, 392

Lalande cell, **203**, 221
Laszczynski processes for copper, 261, zinc, 285
Laval, de, furnace, 167, **503**
Lead ; accumulator, 82, 83, 221, **222 ff** ; cathodic deposition, 302, 303 ; compounds, 166 ff, 222 ff, 260, 302 ff, 388, 389 ; electrolytic, 124, 302, 304 ; electrometallurgy, 301 ff ; electroplating on, 309 ; extraction, 305 ; hydrogen overvoltage, 97, 118, 119, 130, 227, 230, 342, 343, 386 ; oxygen overvoltage, 386 ; -sodium alloys, 342, 414 ff, 432 ; (see also *chrome yellow*, *galena*, *red lead*, *white lead*)
Lead peroxide ; anodes, 131, 154 ; as depolariser, 199, 221, 222 ff ; electrolytic preparation, 388, 389
Leblanc process, 384
Leclanché cell, 206
Lime, 189, 208, 262, 285, 444, 483 ; for carbide furnaces, 472 ff
Limestone, 521
Limiting yield in ozonisers, 522 ff
Liquid depolariser, 197 ff, potential difference, 90, 104
Lithium salts, 236, 483
Lixiviation of ores, difficulties, 263, 265, 281, 285, 287, 297
Load factor, 8
Local action, 198, 200, 204, 209, 222, 226
Low tension arc, 185, 187, **189**, 512
Lowering of vapour pressure, 23
Luckow reactions, 388
Luminous phenomena in gaseous discharges, 184, 186, 523
Lyon furnace, 439

MacArthur-Forrest process, 276, 279
Macdonald cell, 380, 384
Magnesia, 172, 174, 208, 285, 392, furnace lining, 450, 503 (see also *magnesite*)
Magnesite (calcined), 172, 431, 440, 446, 447, 454, 455
Magnesium, 407, 416 ff
Magnesium salts, 199, 201, 226, 334, 390 ff, 416 ff, 433 ; in brine for alkali-chlorine cells, 375, 376, for bleaching liquors, 327, 334, for chlorates, 340
Magnetic field, 510, 512, 513, leakage, 452, 457, losses in induction furnaces, 452, 455, properties of pure iron, 299
Magnetite, 435 ff, anodes, 151, **153**, 279, 285, 339, 345, 346, 361, 362, **363**
Manganese ; compounds, 206, 214, 227, 396, 443, 444 ; impurity in zinc extraction, 286 ; steel, 462
Manganese dioxide, 398, 399, anodes, 151, 154, 285, depolariser, 199, 206, 208
Mansfeld experiments, 261
Marchese process, 260
Mass action law, **14**, 72, 102, 192, 520
Maximum external or useful work, 78
Meidinger element, 201
Mercury, cathodes, 129, 130, 151, 350 ff, cells, 342, **347 ff**, compounds, 216, 221, 226, 234, 243, 351, hydrogen overvoltage, **113**, **119**, 122, 130, 132, 198, 226, 343, 347, 348, oxygen overvoltage, 226, 351
Metal deposition, 120, fog, 160, **161**, 419, 420, 422, 428
Metallic conductors, 26, 415
Metaphosphoric acid, 500
Migration of ions, **49 ff**, 355 ff, ratios, (see *Transport numbers*)
Moebius process, 258, 266, 269
Molecular concentration, 14, osmotic pressure, 42, weight of dissolved substances, determination, 43 ff
Molten electrolytes, 158 ff
Mond-Langer cell, 217
Monochloracetic acid, 73, 385
Monox, 486, 487
Multiple system, 253 ff, 259
Multipliers, 111

Nathusius furnace, 450, 457

Negative characteristic, 185, 187, 189, electrode or pole, 27, plates, 225, 226, 231, 232, 234, 243
Neotherm cell, 203
Nickel; alloys, 454, anodic behaviour, 292, as catalyst, 385, cathodes, 297, 298, 339, 399, 400, 408, compounds, 134, 221, 234 ff, 292 ff, 320, 327, 339, 401, electrolytic, 124, 136, 294, 295, 297, 298, 300, electrolytic deposition, 121, 126, 293, electrometallurgy, 292 ff, fusion, 454, hydrogen overvoltage at, **118**, **119**, 293, 343, matte anodes, 298, plating, 309, **311**
Nickel anodes, 292, 295, 296, 299, 311, 312; oxygen overvoltage, 131, 132, 134, 145, passivity, 139 ff, 154, 292, 408
Nickel ores, electrothermal treatment, 438, 439, 504, extraction, 292, 296 ff
Nitrates, 129, 283, 479
Nitric acid as forming agent, 224, 225, from air, 479, 505 ff, from nitrous gases, 519 ff, in primary cells, 199, 201
Nitric oxide equilibrium, 24, 506, formation in electrical discharge, 186, **505 ff**, oxidation, 519 ff, technical formation, 510 ff
Nitrites, 479, 505, 520
Nitrobenzene, 127, 129, 385
Nitrogen; absorption by carbide, 472, **479 ff**; fixation, 478; in blast furnace, 435; in fuel combustion, 168; oxidation in arc, 479, **506 ff**; oxidation in silent discharge, 190, 507, 524; oxides, 190 ff, 479, 507, 519, 520, 524; reduction to ammonia, 385, 479
Nitrosobenzene, 127
Nitrosyl-sulphuric acid, 216
Nitrous gases, 519 ff
Noble potential, 96
Nodules on cathodes, 150, 255
Normal electrodes, 95, 105

Oerlikon electrolyser, 387
Oettel chlorate process, 339
Ohm, 6
Ohm's law, **5**, 75
Osmometer, 39
Osmotic pressure, 38 ff
Otto ozoniser, 527
Outhenin-Chalandre cell, **365**, 383
Overvoltage, 118, 129, 145, bromine, 132, chlorine, 132, hydrogen, 118, oxygen, 130, theory, 133 ff
Oxidation, electrolytic, 144 ff, of nitrogen, 505 ff, -reduction cell, 102, -reduction electrode, 101, 196
Oxidising agent, 103
Oxygen, combination with nitrogen, 505 ff, discharge at porous anodes, 345, disturbs zinc condensation, 502, electrode, 131, electrolytic production, 154, 386, from alkali-chlorine cells, 343 ff, 361, in anodic chlorine, 362, 383, overvoltage, 130 ff, 145, ozonisation, 522 ff
Oxygen evolution, 130 ff, in accumulators, 228, 238, in electrolytic oxidation, 144
Ozone, 522; anodic formation, 131, 387, 402, 403; equilibrium, 191, 522; formed in silent discharge, 186, 522 ff; oxidises nitrous gases, 521; technical production, 525 ff; thermal production, 522; tube, 523
Ozonisers (technical), 525

Parallel connections, 148
Parkes process, 284, 301, 302, 305, 503
Partition coefficient, 22
Passivity, 139 ff
Pasted plates, 223, 225
Pattinson process, 301
Pauling process, 512, **514**, 516, 519, 520
Perchlorates, 341, **401**, 403
Perchloric acid, 224, 225, 401, 402
Periodicity, 181
Permanganates, 398 ff
Permeability of diaphragms, 156, 369 ff, 376
Persulphates, 402 ff
Persulphuric acid, 283, 285, 402 ff
Petroleum coke, 494, 495
Phase, 16, difference, 180, 511, rule, 17
β-phenyl hydroxylamine, 127
Phosphorus, electrothermal production, 497, 498, **500**; furnaces, 500, 501, 503; in ferro-alloys, 462, ferrosilicon, 464; removal from steel, 443, 459
Pinch effect, 453
Planté plates, 223
Platinised platinum electrodes; mechanically weak, 151, 152, 329, 345; overvoltage at, 131, 132, 133, 318
Platinite solution, 315
Platinum; black, 213, 217, 339, 345; catalyst, 404; cathode, 151; electrolytic, 124; hydrogen overvoltage, 118 ff, 151, 342; -iridium electrodes, 151, 329, 331, 333; oxide, 131, 133, 390; plating, 315
Platinum anodes, acid formed at, 367, attached by anodic gases, 151, 152, 274, 285, 404, bromine overvoltage at, 132, 390, chlorine overvoltage at, 132, 133, 153, 318, 345, oxygen overvoltage at, 131, 132, 154, 318, 345, 402, passivity, 139, 151, 152, 274, technical, 151

Poggendorff cell, 202

Polarisation, 106 ff, discharge curve, 113, 228, in conductivity measurements, 60, voltage or E.M.F., 113, 256, 267, 304, 348, 383

Pole, 27, plates, 457, 458, reagent paper, 28

Porosity of carbon anodes, 153, 331, 345, depolarisers, 198, diaphragms, 156, 370, 376

Positive column, 186 ff, 523, electrode or pole, 27, plates, 223, 225, 232, 235, 240

Potassium chlorate, 364, 402, electrolytic production, 338 ff

Potassium chloride, 104, 162, 338, 340, 349, 364, 402, 417, 422, electrolysis of, 344, 356 ff, 361

Potassium chromate, prevents cathodic reduction, 322, 327, 340, 394, 397, 403

Potassium compounds, 57, 146, 159, 199, 202, 285, 312, 313, 314, 319, 340, 391, 393, 394, 395, 398, 399, 401, 402, 404

Potassium cyanide, 270, 276 ff, 312 ff, 398, 480

Potassium hydroxide, 221, 234, 236, 386, 388, electrolytic liquors, 364, 376, electrolytic production, 342 ff

Potential difference, 5

Power, 5, factor, 179, production, 8 ff

Preheating of charge, 438, 439, 440, 499, 503, 514, 517

Primary cells, 3, 195, circuit, 451

Producer-gas cells, 211

Purification of brine, 375, 380

Pyridine, 130

Pyrrhotite, 438, 439

Quantity of electricity, 5, measurement, 31

Quartz, 496

Quartzite, 464

Quinone, 130

Radiation losses from furnaces, 172, 518

Rapid forming, 224

Rathenau furnace, 465

Rathenau-Suter sodium process, 408, 412

Reactance, 182

Reaction resistance, 12, 121, 136, 144, 146, 250, velocity effect, 114, 121, 128, 139, 141, 142, 201, 206, 395

Red lead, 226

Reducing agents, 103

Reduction, electrolytic, 126 ff

Refractory ores, 169, 442, 504

Regeneration of chromic acid, 395, depolariser, 199, 203, electrolyte, 257, 267, 269, 270, 274, 279, 284, 291, 304, 340, 397

Regulation of arc discharge, 187

Resinate, 323

Resistance, 5, determination, 59, 60, depolarisers, 198, 207, 236, diaphragms, 157, 369, 375, electrolytes, 58 ff, furnaces, 167, 170, 174, heating, 167, 169, 171, primary cells, 198, 201 ff, 208, 209, secondary cells, 229, 237, technical cell, 150

Resorcinol, 126

Reversible process, 78

'Reversible' reaction, 12

Rhodin cell, 354

Röchling-Rodenhauser furnace, 450, 452, 454, **456 ff**, 459 ff

Roesing process, 284

Rössler-Edelmann process, 284

Rotating arcs, 510, 512, cathodes, 270, 286, 287, 316, 317, furnaces, 446, 475, magnetic field, 510

Salom process, 306

Sault Ste. Marie experiments, 438, 442

Savelsberg-Wannschaff process, 297

Schmidt electrolyser, 387

Schönherr-Hessberger process, 512, **516**, 518, 519

Schoop electrolyser, **387**, 388

Schuckert electrolyser for hypochlorites, **331**, 334, for hydrogen and oxygen, 388

Secondary cells, 220 ff, circuit, 451, 457

Self discharge, 226, 227, 238, induction, 181, 452, 457

Semi-permeable membrane, 38

Series system, 253, **258**, 387

Short circuiting, 222, 302, 428

Shunt circuit, 351, current losses, 258, 327, 329, 331, 340, 387

Siemens-Halske processes for copper, **262**, 264, 284, gold, 277, zinc, 284; ozoniser, **525**, 527

Silent discharge, **186**, 507, 522

Silica, 172, 174, 447, 463 ff, 486 ff, 493, 496

Silicon carbide, 486, 487, 488 ff; furnaces, 488; monoxide, 486, 487, 490; oxycarbide, 486; technical production, 487

Siloxicon, 172, 486 ff, **492**, 494 ff

Silundum, 492

Silver anodes, 266, 269, 313, cathode, 266, cathodic, 125, 266, 267, 268, 269, compounds, 159, 221, 252, 266 ff, 274 ff, 313, coulometer, **32**, 266, electrolytic refining, 265 ff, extraction, 270, hydrogen overvoltage, 118, plating, 313, -zinc alloy, 284, 503

'Slimes,' 277

Sodium; alloys, 342; amalgam, 122, 342 ff; bicarbonate, 338, 378; bichromate, 202, 338; carbonate

355, 377, 383, 384, 389, 393, 395, 412, 433, 483, 520; chlorate, 319, 338 ff, 388, 389, 402; chromate, 329, 389; deposition from aqueous solution, 122, 342, 343, 347 ff, from fused caustic, 408 ff, from fused salt, 413 ff; hypochlorite, 199, 319 ff; hyposulphite, 404 ff; -lead alloy, 342, 414, 415, 432; nitrate, 159, 408, 478, 520; phosphate, 146, 398; resinate, 323, 332; salts, 57, 199, 226, 315, 393, 398, 401 ff, 410, 415, 429, 480, 520, 521; sulphate, 310, 349, 389, 390, 406; sulphide, 287, 298, 305; sulphite, 312, 404; technical production, 408 ff
Sodium chloride, 162, 255, 286, 298, 338, 363, 389, 391, 393, 416, 417, 421 ff, 427, 480, 483, 489 ff; caustic soda from, 342 ff, 431; chlorate from, 335 ff; electrolysis of, 318 ff, 342 ff, 413 ff, 431 ff; electrolysis of acid solutions, 338, of alkaline solutions, 336 ff; hypochlorite from, 318 ff; sodium from, 413 ff
Sodium hydroxide, 199, 203, 288 ff, 334, 386, 426, 520, 521; diffusion, 361; molten, 408 ff, 414 ff, 431 ff, electrolysis, 408 ff; technical production, 347 ff, 362 ff, 371 ff, 431 ff
Solid depolariser, 197, 198, solution, 18, 121, 133, 134, 136 ff, 241, 492
Solubility product, 73
Solution laws, 39 ff
Solvay cell, **352**, 354
Specific conductivity, 58 ff
Stable arc, production, 187, 516
Standard cell, 6, electrode, 104
Stannic compounds, 56, 288 ff
Stannous compounds, 288, 289
Stassano iron furnace, 437, steel furnace, 167, 444, **445**, 461, 503
Steam, 363, 374, 377, 432, 480; power, 10
Steel; electric, 434, 442 ff; electric refining, 434, 442 ff, 459 ff; furnaces, 7, 172, 174, 444 ff, 454 ff, 459 ff; losses in steel furnaces, 447, 448, 450, 455, 459, 460; refining process, 443
Sublimation pressure, 18
Sulphate ion, 134, 349, 397, 403
Sulphating, 231
Sulphide anodes, 260, 261, 298
Sulphur, 499, 500, chloride, 385, dioxide, 215, 224, 262, 272, 488
Sulphuretted hydrogen, 306
Sulphuric acid, 202, 255, 274, 306, 309, 311, 315, 386, 387, 395, 396, 520, for hydrogen peroxide, 404, for lixiviating ores, 262, 284, in chromic acid regeneration, 396, 397, in Jungner cell, 215, in lead accumulator, 221 ff, in primary cells, 199, 201, 202
Swinburne-Ashcroft process, 421, **423**

'Tailings,' 277
Tantalum, 143
Tapping furnaces (carbide), 476
Tapping of furnaces (electrical method), 467, 476, 488
Taylor furnace, 498
Technical electrolytic bath, 148 ff
Temperature coefficient of electromotive force, 83, of Daniell cell, 84, 200, of fuel cell, 212, of iron accumulator, 237, of lead accumulator, 227
Temperature; effect on ammonia equilibrium, 23, anode effect, 164, 165, bath voltage, 150, carbide equilibrium, 470, 471, chlorate formation, 337, 338, combination of nitric oxide and oxgyen, 519, condition of cathodic deposits, 125, copper refining, 246, 256, electrolytic dissociation, 69, electrolytic oxidation, 145, electrolytic reduction, 129, 130, equilibrium, 23, furnace efficiency, 170, hypochlorite concentration, 325, 326, 337, molten sodium hydroxide electrolysis, 408, 415, nitric oxide equilibrium, 24, 506, overvoltage, 120, 132, 133, ozone production, 522 ff, passivity, 140, 271, quality of anodic chlorine, 346, specific conductivity of electrolytes, 64, 158, steel refining, 443, 444, 459; of arc discharges, 189, 190, 506, 508, 509, of electric heating, 169, of fuel heating, 169
Testing of carbon anodes, 346, of diaphragms, 156
Thermal efficiency of electric furnaces, 170, of fuel fired furnaces, 170, of zinc distillation, 501
Thermite process, 3, 462
Three-phase currents, 439, 440, 446, 448, 450, 452, 458, 466, 477, 478, 518
Tin, 138, 250, 288, 309; anodic behaviour, 289, cathodes, 129, 288, 342, electrolytic, 124, 125, 291, electrometallurgy, 287 ff, hydrogen overvoltage at, 118, 119, 290, 342, ores, 504
Titaniferous iron ores, 438, 443
Titanium compounds, 130, 199, 426, 438
Total energy decrease, 78, of fuel combustion, 209
Townsend cell, 155, 375, **378**, 383, 384
Transformer, 451, losses, 451, 452
Transport of ions, 49, numbers, 52 ff, 528

Transportable accumulators, 230, 234, 238
Trinitrochloro-benzene, 385
Tudor plates, 224, 226
Two-phase currents, 441, 499
Tyndall-de Vries ozoniser, 526

Unsaturated fatty acids, 385, glycerides, 385

Vanadium salts, 130, 199, 216, 323
Vertical diaphragms, 370
Volt, 6
Voltage, 6, dependent on furnace charge, 464 ff, 473, gaseous discharges, 185 ff, losses in leads and contacts, 150, 256, 424, 474, measurement, 111, series, 96, technical electrolysis, 148, 149
Voltage gradient in alkali-chlorine cells, 367 ff, diaphragms, 369, electric gaseous discharges, 186, 189, 191, 509
Voltmeter, 111, calibration, 111, for current measurement, 31
Volume changes in accumulator plates, 225, 226, 234
Vosmaer ozoniser, 526

Water; action on nitrous gases, 519; coulometer, 33, 36; dissociation constant, 117; electrolysis, 132, 386; power, 9
Watt, 6, second, 6
Wavellite, 500
Welsbach accumulator, 221
Wet galvanising, 310
Wheatstone's bridge, 59
White lead, 302, 303, **388**
Whiting cell, **352**, 383
Wildermann cell, **354**, 383
Wohlwill process, **271 ff**, **275**, 278
Working cell, conductivity, 62, voltage, 110
Wright electricity meter, 34
Wrought anodes, 135
Wünsche cell, 391

Zinc, 250, 277 ff, 302, 309, 404 ff, 502, 503, amalgamated, 36, 198, 201, 208, 221, anodes, 198 ff, 221, 284, cathodes, 36, 129, 130, 284, 334, 340, cathodic deposition from aqueous solution, 120, 122, 126, 280 ff, chemical extraction, 281, 497, 501, chloride, 199, 206 ff, 286, 310, 418, 421 ff, compounds, 133, 199, 200, 221, 283 ff, 310, 313, 404, 421, 424, 502, 503, distillation, 502, electrodeposited, 282, 284, 285, 286, 287, electrolytic extraction, 154, **284 ff**, 421 ff, electrothermal production, 498, **501 ff**, from fused zinc chloride, 407, **421 ff**, furnaces, 503, 504, hydrogen overvoltage, 118, 282, 405, refining, 284, vapour condensation, 502, 503

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