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THE PRINCIPLES OF
ELECTRODEPOSITION

(THE ELECTRO-CHEMISTRY OF ELECTRO-PLATING)

BY

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SECOND EDITION

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PREFACE
TO THE SECOND EDITION

THE call for a second edition evidences a measure of usefulness of a book which was originally intended as a mere outline of the more theoretical aspects of electrolysis in its application to Electrodeposition, without any design to constitute a treatise on Electro-chemistry on its much broader basis.

If the advances in Electrodeposition during the past quarter of a century are not by any means so spectacular to the lay mind as other departments of science applied to industry, they are nevertheless outstanding, as is shown by a comparison of the literature of that time with that available to-day.

Extension with simplification and standardization of the methods of Electrodeposition have, in the main, been the product of a wider knowledge and appreciation of the theoretical principles upon which the industry is necessarily dependent for progress comparable with that of other industries. The more intensive research of the past few years has, in the main, been undertaken to solve problems which have found their origin in practice but which nevertheless needed to be investigated from a more purely scientific standpoint.

There seems therefore some justification for the issue of separate volumes dealing with theory and practice, each making frequent contacts with the other.

In the period intervening between the issue of the first edition and the present time, no great change has arisen in our fundamental conception of these processes. The additions now made are therefore on a relatively small scale with the hope that the added detail will help to elucidate the more abstract principles which may at first make little appeal to the practical man.

The whole aim of technical education is, and must be, a wider knowledge and appreciation of the more intensive light which may be focused upon industrial processes with a view to

inculcating a more intelligent outlook in the realm of practice, and with it, a better product to keep pace with the general progress in other and allied industries where these meet.

Renewed and grateful acknowledgement is made for the loan of blocks to Messrs. Baird & Tatlock, Ltd., Messrs. F. E. Becker & Co., Ltd., and The British Drug Houses.

S. F.

PREFACE
TO THE FIRST EDITION

THE contacts with and applications of the principles of Electro-chemistry to the processes of Electrodeposition are both numerous and varied. Recent applications of these principles, and especially those concerned with the deposition of metals, have been largely due to the more scientific exploration of the problems than was formerly the case. This instances the need for some appreciation of these principles by those who are intimately concerned with the problems of Electrodeposition, whether from the experimental or industrial points of view.

Modern works on Electro-chemistry, however, do not, in their necessarily broader treatment of the subject, em-phasize those points of contact which are particularly relevant to Electrodeposition.

The need for some more simple treatment of these prin-ciples has been stressed in the mind of the author by long educational experience, and he essays the task with some trepidation in view of the wide range of knowledge which has to be bridged over in an attempt to present a simple yet convincing account of the deeper problems of the science of Electrodeposition, while avoiding the mathematical treatment called for by the requirements of the more academic student, and which characterizes the modern literature on the subject.

The fact also that educational courses in Electrodeposition require some systematic knowledge of the science of Electro-chemistry seems to justify this more specialized treatment of the subject with an industrial bias, and the knowledge of first principles thus gained should assist in the easier acquisition and appreciation of the new discoveries and points of view which are from time to time coming forward with the advance of the science and art of Electrodeposition.

In the present volume the author has drawn generously from current literature. These numerous sources of information are hereby freely and gratefully acknowledged. This applies particularly to the many tables and diagrams to illustrate and emphasize the essential points in the general argument.

The volume may thus be regarded as the theoretical companion of *Electroplating*, which now passes into its fourth edition. Some little overlapping will be noticeable. This is not only unavoidable, but is even desirable.

Notwithstanding this bias, however, towards the processes of some phases of industrial Electro-chemistry, the volume may still serve a useful introduction to the more general student of Electro-chemistry who may feel unable to plunge at once into the deeper issues of the subject.

Finally, sincere and grateful acknowledgment is due and made to Messrs. Baird & Tatlock, Ltd., Messrs. F. E. Becker & Co., Ltd., and The British Drug Houses for the loan of a number of illustrations.

S. F.

CONTENTS

ABBREVIATIONS

A = Ampere
abs. = Absolute
Ah = Ampere-hour
Amin = Ampere-minute
atm. = Atmosphere
b.p. = Boiling point
B.Th.U. = British thermal unit
C = Centigrade
C = Coulomb
C.E. = Chemical equivalent
cm = Centimetre
cm^2 = Square centimetre
cm^3 = Cubic centimetre
c/s = Cycles per second
dm. = Decimetre
dm^2 = Square decimetre
dm^3 = Cubic decimetre
E.C.E. = Electro-chemical equivalent
e.m.f. = Electromotive force
F = Farad
f.p. = Freezing point
ft = Foot
ft^2 = Square foot
ft^3 = Cubic foot
ft-lb = Foot-pound
g = Gramme
g. cal = Calorie (gramme-calorie)

hr = Hour
in. = Inch
$in.^2$ = Square inch
$in.^3$ = Cubic inch
J = Joule
kWh = Kilowatt-hour
lb = Pound
mg = Milligramme
min = Minute
ml = Millilitre
mm = Millimetre
N = Normal
N.T.P. = Normal temperature and pressure
p.d. = Potential difference
p_H — Hydrogen ion concentration
sec = Second
t = Ton
V — Volt
W — Watt
μ $\dfrac{1}{10^6}$
$\mu\mu = \dfrac{1}{10^{12}}$
Ω = Ohm

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Metal Ind. . . . . . *Metal Industry* (Gt. Britain)
Metal Ind., N.Y. . . . . *Metal Industry* (New York)
Trans. Amer. Electro-chem. Soc. . *Transactions of the American Electro-chemical Society*
Trans. Faraday Soc. . . . *Transactions of the Faraday Society*
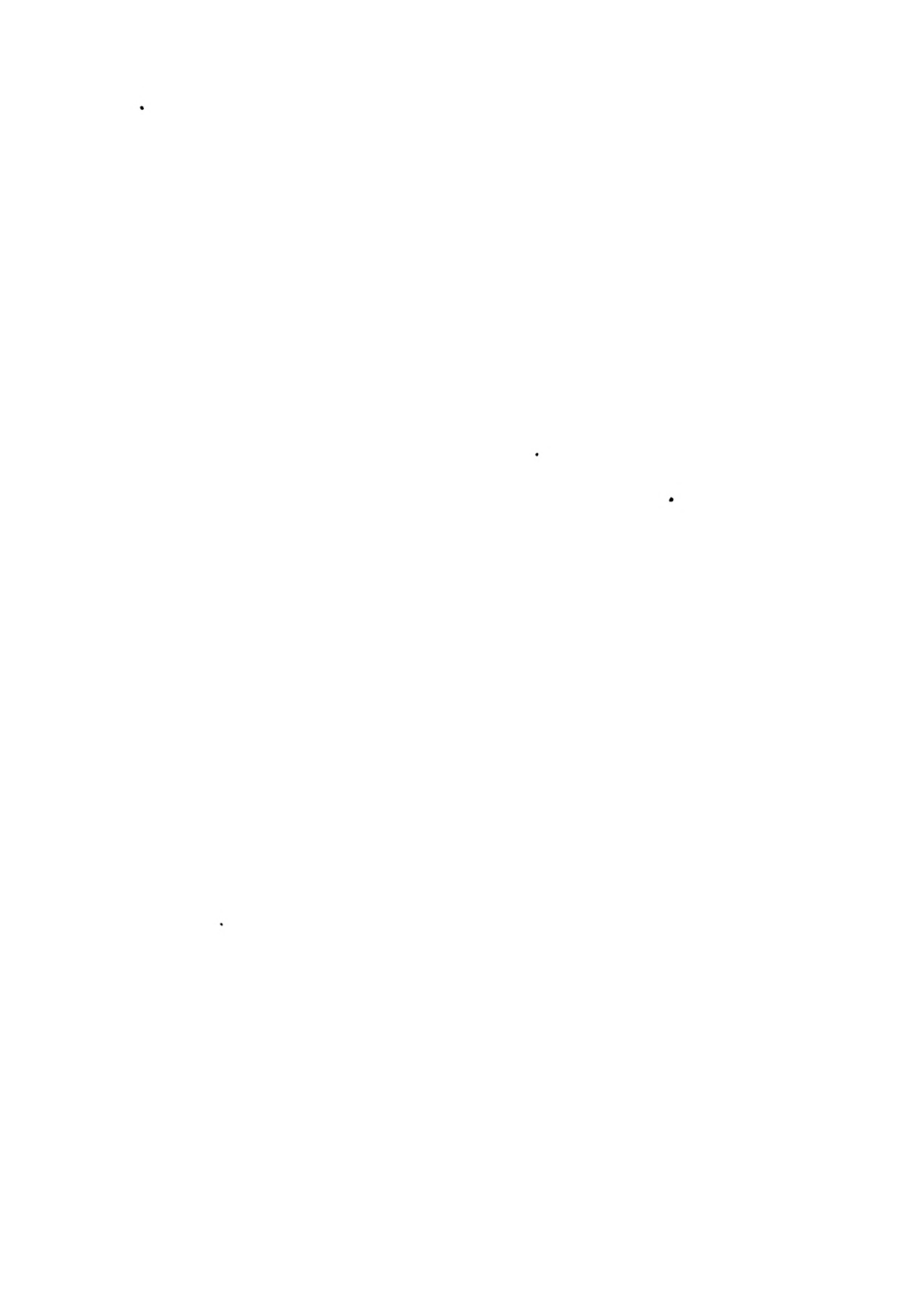
THE PRINCIPLES OF ELECTRODEPOSITION

INTRODUCTION

Progress of Scientific Thought. A survey of the progress of scientific thought during the last 150 years at once reveals the fact that those organized studies into the things of nature which are briefly referred to as the sciences find their origin in comparatively recent times.

The birth of chemistry can only be dated back to the time of Lavoisier who, late in the eighteenth century, laid the foundation of definite knowledge of the composition of many substances, in addition to overthrowing the previously conceived notion of phlogiston as an explanation of the crudely observed facts of the process of combustion. The later conception of chemistry includes the study of (1) the composition of the numerous materials which come within our experience, (2) their properties, especially those which are intimately related to the composition, (3) the interactions possible between these chemical substances under widely varying conditions, and (4) the phenomena which accompany these interactions or, as they are termed, "chemical reactions."

With the accumulation of facts which quickly came to light, there came the need for some simple conception as to the manner by which these observations were to be explained and, on the quantitative side, the atomic theory of Dalton, enunciated in the dawn of the nineteenth century, supplied, to a great extent, that felt need. The science of chemistry cannot therefore be dated prior to about one hundred and fifty years ago. While more modern progress has revolutionized this conception of the structure of the atom, Dalton's simple idea of atoms as the indivisible units in chemical reactions, served a very

useful purpose for an elementary study of chemistry in many of its phases.

Briefly, the atom is now regarded to have a centre or nucleus which accounts for its mass. Around this nucleus revolve in orbits, at comparatively large distances, very much smaller negatively-charged particles which are the units or "atoms" of electricity. These are the electrons. Their mass is about $1/1\,800$ part of that of a hydrogen atom, and is therefore negligibly small. The number of electrons is the atomic number of the element. The massive nucleus is now regarded to be of complex structure, not yet clearly realized. It is composed of almost equal numbers of protons—positively charged and equal in charge to the number of electrons—and neutrons. neutral particles of practically the same mass as protons but not always of the same number. The differing number of neutrons accounts for the existence of isotopes, i.e. elements having the same chemical properties, determined by the number of electrons, but differing masses. The structure of the atom is thus a highly complicated and advanced study, the conception of which is still progressing. As far as our study is concerned, we shall be more interested in the number of electrons which may be lost or gained by an atom or radicle in the process of electrolytic dissociation, this number together with the mass of the atom or radicle determining their chemical, and therefore electro-chemical, equivalents.

Again, a good deal of knowledge was acquired concerning electricity—about the nature of which there was no definite conception—knowledge which was put to considerable industrial use and laying the foundations of the present huge electrical industry.

Sooner or later it became obvious that numerous scientific problems were of an overlapping character, being not too definitely assignable to any one of the then more or less watertight compartments of science into which previous developments had been grouped.

As a result, new borderline sciences began to take shape, but though they found their origin in these early times they did not establish themselves until much later. Illustrative of these borderline studies may be mentioned the fact that Dalton's atomic theory with the then observed quantitative facts were,

in themselves, insufficient to provide an adequate basis for the determination of many molecular and atomic weights, and we had to wait for the enunciation of that important law relative to the quantitative behaviour of gases which is inseparably associated with the name of Avogadro, for a solution to the problem. Atomic and molecular weight determinations thus became problems requiring the experimental work and thought of both the chemist and the physicist. These contacts of physics and chemistry sooner or later gave rise to the subject of physical chemistry.

Similar developments can be instanced in many other cases. The ramifications of chemistry soon became so numerous, diverse, and complex as to necessitate subdivisions and give rise to new departments of science. Thermo-chemistry is, for example, concerned with a study of the thermal changes which accompany chemical change. Photo-chemistry concerns the effects of light energy on chemical change and, in one more practical form, takes charge of the chemical side of photography. Biochemistry is another branch, dealing with the numerous and complex chemical materials and processes concerned with the maintenance of the vitals' functions.

In much the same way there was born the subject of electro-chemistry, when Volta and Wollaston introduced the simplest types of voltaic cell. These were soon followed by the Wollaston pile which provided the first example of cells fitted in series in order to obtain an intensified effect. Then, very early in the nineteenth century, Nicholson and Carlisle effected the first electrolytic decomposition of water by the use of the Wollaston cell, and the process soon extended to the decomposition of many other compounds, notably that of caustic soda by Davy with the first indications of metallic sodium, and the vision that, some day, this and similar processes might be operated on an industrial scale for the production of this and other metals, which up to that time had resisted extraction by chemical methods. This isolation of the alkali metals by Davy emphasized the intimate relationship between the subject of chemistry and electricity, while further impetus to these studies was given by the epoch-marking work of Faraday who, as the results of his painstaking work, enunciated the laws of quantitative electro-chemical change.

On the other hand, the development of conceptions adequate to explain these observed facts was less rapid. While some formulation of a theory of electrolysis was attempted in the earliest history of the subject, it was not until the time of Clausius in 1857 that we had any clear idea given to us of the existence of ions in an electrolyte prior to the impression of the electrical influence, while the more elaborate theory of electrolytic dissociation definitely found its origin in the suggestion of Arrhenius in 1887 that this prior separation of the electrolyte molecules into charged ions was already far advanced in aqueous solutions, and constituted the first step in the process of electrolytic decomposition.

Definitions. In order to proceed to the discussion of even the elements of the new science it becomes necessary to formulate some simple definitions which will embrace the conceptions to be attached to the language employed in the subject. Definitions are notoriously difficult, inasmuch as in them there is the endeavour to compress a wide array of experience in the most compact form. Most definitions are therefore susceptible to criticism, and a limited measure of elasticity must be exercised in their use. Nevertheless, there is the great desirability to adopt language which, by common consent, is the most appropriate, and for this purpose the British Standards Institution undertakes, amongst its numerous duties, that of the formulation of definitions, and those relating to the science of electro-chemistry are embodied in its Glossary of Electrical Terms. It is from this source that the following definitions are mainly drawn.

By electro-chemistry then, is understood that "branch of physical chemistry dealing with the relation between, and mutual transformation of, chemical and electrical energy." Explanatory of this, it may be recalled that all chemical changes are accompanied by changes in energy. This energy is frequently set free in the form of heat. In voltaic cells, however, the arrangement is such that the chemical energy set free by the materials used appears in the electrical form. The reverse transformation is widely possible, while the ordinary accumulator provides an arrangement of chemical materials through the medium of which, during the charging and discharging processes, the transformations of electrical to chemical

and chemical to electrical energy respectively take place. The usual phenomena of electrolysis are included in this conception. The accumulator is essentially an electro-chemical cell.

Electrolytic dissociation (ionization) is "the reversible resolution of certain substances, commonly called electrolytes, into oppositely charged ions." This is exemplified in the case of sodium chloride thus—

$$NaCl \rightleftharpoons Na. + Cl^-$$

and these ions are "atoms or radicals carrying a charge of positive or negative electricity in excess of the charges normally associated with the electrically neutral atom or radical." Thus the sodium ion is a sodium atom carrying a unit positive charge. In terms of the electronic theory this means an atom of sodium which has lost a (negative) electron. An electron carries an exceedingly small charge, requiring the passage of 6×10^{18} (six trillions) per second to represent a current of 1 A. (See page 27.) With the usually accepted mass of the electron (about $1/1\,800$ of that of the hydrogen atom), there is no appreciable difference between the mass of the atom and ion. From the fact that sodium ions are stable in water in which they can exist in considerable concentration, we must attribute to them vastly different properties from those associated with the atom. Similarly, the chlorine ion is a chlorine atom carrying an additional electron (or negative charge).

Some ions are simple while others are more complex. Simple ions are the ultimate products of electrolytic dissociation. Further examples are—

$$CuSO_4 \rightarrow Cu^{..} + SO_4''$$
$$AgNO_3 \rightarrow Ag^. + NO_3'$$
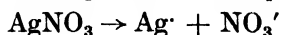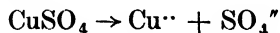
A complex ion is one "which, under suitable conditions, may be further resolved into more simple ions, or results from the association of more simple ions." For example, the dissociation of potassium argento-cyanide proceeds in two stages—

$$AgCN . KCN \rightleftharpoons K. + Ag(CN)_2^-$$
$$Ag(CN)_2^- \rightleftharpoons Ag. + 2CN^-$$
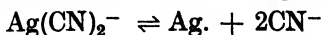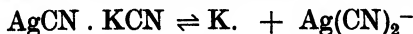
$Ag(CN)_2^-$ is thus a complex ion. $\rightleftharpoons$ is the sign of reversibility. Others frequently used are $\rightleftarrows$ and $\rightleftharpoons$.

Similarly the solution of ferrous cyanide in potassium cyanide involves the formation of a complex ion thus—

$$Fe(CN)_2 \rightleftharpoons Fe.. + 2\ CN^-$$
$$4KCN \rightleftharpoons 4K. + 4CN^-$$
$$Fe.. + 2CN^- + 4CN^- \rightarrow Fe(CN)_6^{----}$$
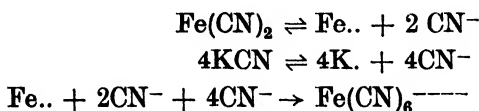
The valency of the ion is usually expressed as the number of charges which it carries. Thus the copper (divalent) ion is represented as Cu^{++} or Cu'', while the divalent SO_4 ion is expressed as SO_4^{--} or SO_4''.

An electrode, in electrolysis, means "a conductor of the metallic class by means of which electrons pass to or from an electrolyte," electrons leaving at the anode and entering at the cathode.

During electrolysis ions move in an orderly manner towards these electrodes. This motion is known as the "migration of ions," those migrating under the influence of an applied p.d. to the anode being anions, while those which simultaneously migrate to the cathode are cathions or cations.

On the basis of these definitions that for electrolysis can now be expressed as "the production of chemical changes by ionic migration and discharge in accordance with Faraday's laws." These laws will be dealt with in detail later (page 26). The term electrolyte can now be regarded as connoting "a conducting medium in which the electric current consists in the migration and discharge of ions in accordance with Faraday's laws." This definition, it will be observed, has no application to such substances as solid copper sulphate, and applies only to the conducting solutions produced in an ionizing medium. Water is a powerful ionizing medium, while solutions of many so-called electrolytes in benzene are non-conducting because they are not then ionized. In common parlance, however, the term electrolyte is frequently applied to the solid substance. An alternative term "ionogen"* has been suggested for the solid indicating that, in solution, it is resolvable into ions.

In view of the fact that portions of the electrolyte suffer different changes in composition in proximity to the anode and cathode, it is proposed to use the term "anolyte" to "that

* *Trans. Amer. Electro-chem. Soc.*, Vol. XLVII, p. 123.

portion of the electrolyte which surrounds or is near to the anode and is changed in chemical composition or concentration by reactions taking place at the anode," while the "catholyte" refers to "that portion of the electrolyte which surrounds or is near to the cathode, and is changed in chemical composition or concentration by reactions taking place at the cathode."

These few terms will suffice as a starting point. Their fuller meaning will become more apparent as a discussion of electrolytic phenomena proceeds. In general, too, an electrolytic cell will be regarded as "a system of electrodes and one or more electrolytes, e.g. a voltaic cell or an electroplating bath."

Early Conceptions. It must be admitted that the salient facts of the application of the electric current to effect chemical change were early and accurately noticed, this excellent work laying the sound foundation of the subject. At the same time there was some attempt to devise a system of terms for the new science. Many of these have persisted to the present, but they have assumed different interpretations with the advance in our knowledge of the fundamental changes in which they play their little part. For example, the term electrolysis from its construction suggests the idea of the analysis or decomposition of chemical compounds by means of the electric current. In the light of more recent conceptions this definition is wholly inadequate.

Far from electrolysis being concerned only with the decomposition of chemical substances, there are numerous electrochemical manufactures to-day in which new chemical compounds are built up through the medium of electro-chemical reactions, while many electro-chemical changes are effected in which the transformation of the chemical energy resident in chemical substances is efficiently transformed into electrical energy and vice versa, this being strikingly instanced in the case of the accumulator. The whole development of the science has called for a more careful scheme of definitions in view of the wide range covered by the observed phenomena, and the task has not proved an altogether easy one.

Early Theories of Electrolysis. Similar remarks apply to theories of electrolysis, expressions of the invisible processes through which the observed phenomena were to be satisfactorily

explained, and which would be broad enough to embrace new discoveries and anticipate expanding thought. No great weight need attach to the early theories of electrolysis. They doubtless served their purpose, but sooner or later were weighed in the balance of further discovery and conception and were found wanting. Thus old terms obtained a new interpretation while many new terms came into use.

Grotthus Theory. Possibly the first real attempt at a theory of electrolysis was that associated with the name of Grotthus,
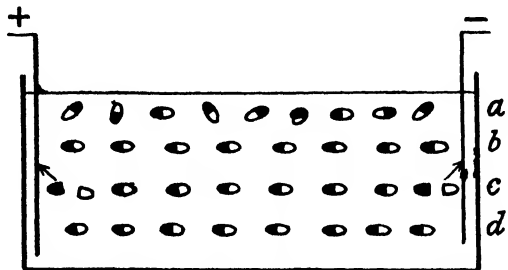

FIG. 1. GROTTHUS'S CONCEPTION OF ELECTROLYSIS

according to whom molecules were double-ended units with different electrical charges, the metal or basic end being positively charged and the acidic end negatively charged. The first application of a potential difference upon conducting plates immersed in the electrolyte caused the molecules to arrange themselves systematically. An increase in the p.d. sooner or later effected the decomposition of these molecules, especially those adjacent to the electrodes. The change throughout the solution was then to be explained by a succession of molecular effects between adjacent molecules, the reaction thus proceeding from pole to pole, or poles to the centre. The conception is depicted in Fig. 1 in which the bipolar molecules are first shown without the influence of electrical conditions (a) and, secondly, after the application of a p.d. (b).

Sooner or later this p.d. was assumed to attain a value requisite for the decomposition of the molecules nearest the electrodes (c), thus setting free ions which immediately attack contiguous molecules so that the action proceeds from the electrodes through the solution (d). In the absence of an

alternative suggestion, this theory for a time held the field, and investigators were, at that time, rather more concerned with the accumulation of facts than in formulating a theory of the mechanism through which they were realized.

Grotthus's view, however, had its weaknesses. Obviously, time would be involved in the completion of the chain of action between the two electrodes, while later observation showed that in, for example, a U-tube with a long horizontal limb (Fig. 2) the passage of current was instantaneous with


Fɪɢ. 2. Iɴsᴛᴀɴᴛᴀɴᴇᴏᴜs Eʟᴇᴄᴛʀᴏʟʏsɪs

the closing of the circuit. Secondly, electrolysis began to take place before the attainment of any definite e.m.f. such as might be required for the decomposition of molecules. Thirdly, it must be difficult to attach properties to the temporarily liberated ions which would enable them to decompose the next molecules and at the same time liberate other ions of exactly the same kind.

Clausius Theory. Some advance in the conception of electrolysis was made by Clausius in 1857, who urged that probably the molecules were not so extraordinarily stable, but that the act of solution loosened the two parts of the molecule and even allowed of the temporary separation of the two parts, which immediately combined with dissimilar parts from other molecules. In other words, at any moment a relatively small number of molecules were in a state of dissociation, and the influence of the "current" attracted away to the electrodes these temporarily disengaged ions, their withdrawal being immediately followed by the formation of others. This view would seem to account for the immediate effects observed with the application of a p.d. to the electrodes. Thus to what may be called the inherent movement of the ions, that is, the ordinary vibratory motion attributable to all molecules and

current. Of these ions those of hydrogen remain, as it were, to keep the SO_4 ions company, while the HO ions are discharged thus—

$$2OH = H_2O + O$$
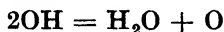
The accumulated acid is due mainly to the migration of the SO_4 ion. If any difficulty appears in this explanation by reason of the very small amounts of ionic water present, it is removed when we remember that these dissociation processes are almost instantaneous, so that the removal of the ions of water leads to the immediate dissociation of more water.

The electrolysis of the dilute acid yields the two gases roughly in the proportion—as anticipated—of two volumes of hydrogen to one of oxygen. There are, however, immediate deviations from this simple proportion. Both gases are soluble in the liquid. The greater solubility of oxygen accounts in part for the observed smaller volume of this gas, and the correct proportion of 2 : 1 is more nearly obtained when anolyte and catholyte are saturated with their respective gases.

With an increase in the strength of the acid, however, the volume of oxygen is further deficient. Examination of the evolved gas reveals a reaction with potassium iodide-starch paper indicating the presence of ozone. Moreover, the anolyte gives evidence of the presence of hydrogen peroxide while with acid of still greater strength persulphuric acid is definitely found. This latter product might readily be accounted for by the ionization of the acid as follows—

$$H_2SO_4 \rightleftharpoons H. + HSO_4{}^-$$

while the following equations may express the secondary chemical reactions already indicated—

$$2HSO_4 + 2H_2O = 2H_2SO_4 + H_2O_2$$
$$6HSO_4 + 3H_2O = 6H_2SO_4 + O_3$$
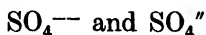$$2HSO_4 = H_2S_2O_8$$
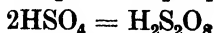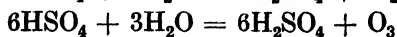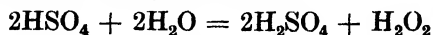
Reactions similar to the last of these are well known to occur in the electrolysis of strong sulphate solutions, and manufacturing methods for persulphates are based on the reaction.

Alternative methods of representing the hydrogen ions are—

$$H \cdot \text{ and } H^+$$

while for SO_4 and other negative ions the following signs are alternatively employed—
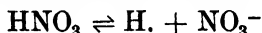
$$SO_4^{--} \text{ and } SO_4''$$

In the case of sulphuric acid, therefore, the reaction can hardly be regarded as simple, and with the complications indicated there would appear to be some difficulty in employing the electrolyte for coulometers (page 32).
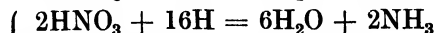
It seems possible that all these reactions are likely to take place at all dilutions. In general, however, the simple evolution of hydrogen and oxygen occurs with dilute acid, and the secondary products result from the use of the stronger acid. This in turn seems to indicate progression in the ionization of the acid, this taking place in two stages—

(1) $$H_2SO_4 \rightleftharpoons H. + HSO_4^-$$

(2) $$HSO_4^- \rightleftharpoons H. + SO_4^{--}$$

Nitric Acid. The acid ionizes as follows—

$$HNO_3 \rightleftharpoons H. + NO_3^-$$

Following the example of sulphuric acid, the evolution of hydrogen and oxygen at cathode and anode respectively may be anticipated, and this takes place in acid of low concentration. With an increase in strength, however, the evolution of hydrogen is largely replaced by the reduction of the acid on one or more of the following lines—

$$2HNO_3 + 2H = 2H_2O + 2NO_2$$
$$2HNO_3 + 4H = 3H_2O + N_2O_3$$
$$2HNO_3 + 6H = 4H_2O + 2NO$$
$$2HNO_3 + 8H = 5H_2O + N_2O$$
$$2HNO_3 + 10H = 6H_2O + N_2$$
$$\begin{cases} 2HNO_3 + 16H = 6H_2O + 2NH_3 \\ 2HNO_3 + 2NH_3 = 2NH_4NO_3 \end{cases}$$
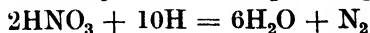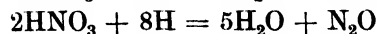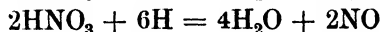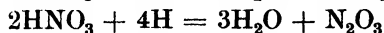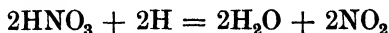
The evolution of brown oxides of nitrogen is a common occurrence in the use of nitric acid in the Bunsen and Grove cells, while the presence of ammonium compounds can readily be shown. There appears to be no special example of the electrolysis of this acid in industry.

Hydrochloric Acid. This again would appear to be a simple matter, with apparently only two products. The usual form of "voltameter," however, soon shows a great deficiency in the volume of chlorine evolved at the anode due to the solubility of the gas. Chlorine, however, is much less soluble in strong solutions of chlorides and there is a much better chance of obtaining the two gaseous products in their correct proportion from a strong solution of calcium chloride to which strong hydrochloric acid has been added.

Alkalis. The course of the reaction with the caustic alkalis in aqueous solution is simple and it will be apparent that with aqueous potash the ions are K. and OH^-, the former at the cathode remaining in solution as the hydrogen ion is preferentially displaced, while at the anode oxygen is evolved—

$$KOH \rightleftharpoons K. + OH^-$$
$$2K. + (2H. + 2OH^-) = 2(K. + OH^-) + H_2$$
$$2OH = H_2O + O$$
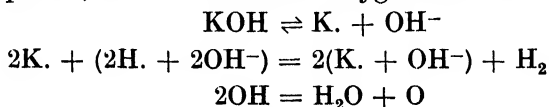
This is an example which finds large application in cells for the production of electrolytic hydrogen and oxygen, the absence of complicating secondary reactions ensuring the permanence of the electrolyte which, when strong, is an excellent conductor. It has application, too, in some forms of gas coulometer (see page 34).

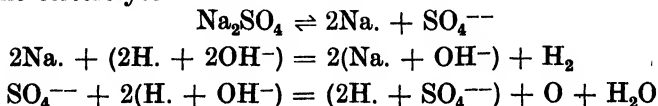**Neutral Alkali Salts.** A solution of sodium sulphate may be taken by way of example and electrolyzed in a usual type of "voltameter" (Fig. 3). The solution is coloured with neutral litmus. Electrolysis yields hydrogen and oxygen at their usual electrodes and in their usual proportion, while the anolyte turns red and the catholyte blue. These are things seen which at once appear to be the result of the following unseen changes in the electrolyte—

$$Na_2SO_4 \rightleftharpoons 2Na. + SO_4^{--}$$
$$2Na. + (2H. + 2OH^-) = 2(Na. + OH^-) + H_2$$
$$SO_4^{--} + 2(H. + OH^-) = (2H. + SO_4^{--}) + O + H_2O$$

These reactions are not to be taken to represent quantitatively the yield of products unless adequate steps are taken to ensure their complete separation. They indicate the chemical course of the reaction. The accumulations of acid at the anode

and alkali at the cathode indicate similar reactions with the electrolysis of sulphuric acid and caustic soda respectively, though in these latter cases the changes of concentration of the electrolytes would not be shown by mere indicators.

Again, sodium chloride presents a case of special interest and considerable industrial importance. Its ionization is simple—

$$NaCl \rightleftharpoons Na. + Cl^-$$

The general observations are that sodium hydroxide is formed at the cathode with the evolution of hydrogen, while chlorine is evolved at the anode. These are results which may reasonably be anticipated. By design of plant it can be imagined that the process could be turned to industrial account, and large quantities of these materials are produced on this principle, one of the chief requirements of the process being that of the separation of the two products, and the collection of the caustic soda sufficiently free from common salt. These, however, are points with which we are here not greatly concerned.

But chlorine and caustic soda are susceptible to a number of secondary reactions. If the electrolysis proceeds under conditions which permit of the mixture of the products, the production of sodium hypochlorite follows. This product is unstable at elevated temperatures and thus, if the electrolysis is carried out at a temperature of 60° C. with the mixing of the anolyte and catholyte, the production of sodium chlorate results. These reactions are well known to take place chemically when chlorine is passed into caustic alkali, thus—

Cold. $2NaOH + Cl_2 = NaClO + NaCl + H_2O$

Warm. $6NaOH + 3Cl_2 = NaClO_3 + 5NaCl + 3H_2O$
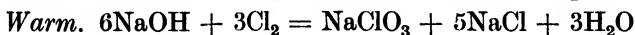
These reactions in the electrolytic cell are carried out on a large scale for the formation of hypochlorites for bleaching and disinfecting purposes and for chlorates for use in explosives. It is, however, not suggested that the reactions take the simple course which has here been outlined. The end results appear to be reached by more devious electro-chemical routes. The simple principle has been given as indicative of important industrial possibilities. Further, by the electrolysis of chlorates, perchlorates result from what we shall here term the anodic oxidation of the chlorates.

For hypochlorites and chlorates the admixture of anolyte and catholyte is obtained usually by the appropriate disposition of the electrodes. For the production of caustic alkali and free chlorine the separation of the two parts of the electrolyte is achieved gravitationally in some processes, while others effect the separation of the anode and cathode reactions by the use of partitions or diaphragms which, in some cases, are porous and non-conducting, and in others are non-permeable and conducting. This is a subject which will be returned to later.

Metallic Salts. For a large number of metallic salts, electrolysis with an insoluble anode proceeds on anticipated lines, the metal ions being deposited while the acidic ions remain in the solution in the form of their respective ionized acids with the evolution of oxygen in the case of nitrates and sulphates, and chlorine in the case of chlorides. Table I summarizes a number of these reactions, though other secondary products could be included.

Thus in the case of copper sulphate a deposit of copper appears on the cathode with the evolution of oxygen and the

TABLE I

PRODUCTS OF ELECTROLYSIS

Electrolyte	Products			
	At Anode		At Cathode	
	Primary	Secondary	Primary	Secondary
H_2SO_4	SO_4	H_2SO_4; O_2	H	H_2
HNO_3 .	NO_3	HNO_3; O_2	H	H and oxides of nitrogen
HCl	Cl	Cl_2	H	H_2
NaOH	OH	O_2; H_2O	Na	NaOH; H_2
NaCl	Cl	Cl_2	Na	NaOH; H_2
$CuSO_4$	SO_4	H_2SO_4; O_2	Cu	Cu
$AgNO_3$	NO_3	HNO_3; O_2	Ag	Ag
CuCN . 2 KCN	$Cu(CN)_3$	CuCN; 2 CN	K	Cu
AgCN . KCN	$Ag(CN)_2$	AgCN; CN	K	Ag
K_2CO_3	CO_3	CO_2; O_2	K	KOH; H_2
$ZnSO_4$	SO_4	H_2SO_4; O_2	Zn	Zn
$CdSO_4$	SO_4	H_2SO_4; O_2	Cd	Cd
$Pb(C_2H_3O_2)_2$	$C_2H_3O_2$	$H.C_2H_3O_2$; O_2	Pb	Pb

formation of sulphuric acid at the anode. It would appear that by this process the whole of the metal might be extracted from the solution which will finally contain the corresponding acid. Reactions of this type have considerable application. In electrolytic analysis the metal is recovered quantitatively and then weighed, while in electrolytic extraction processes the reaction follows the same course, except that the quantitative removal of the metal is not necessary, and the resulting solution containing some of the metallic salt and a large proportion of the acid is again used to extract further quantities of the metal from suitably prepared materials such as ores, the acid liquor being thus used cyclically with relatively small losses such as are unavoidable in industrial operations. Copper and zinc provide two prominent examples of this type of industrial electrolytic extraction processes.

Further, a number of secondary reactions may safely be anticipated. In the case of the electrolysis of a lead salt some production of lead dioxide at the anode occurs, this being instanced in the lead accumulator reaction. A detailed explanation of these electro-chemical processes will be found on page 223.

Insoluble Anodes. Anodes which are unaffected by the current, that is, do not form ions, are said to be insoluble. Electrodeposition processes are usually concerned with soluble anodes for the maintenance of the composition of the solution. There are, however, notable exceptions. Special cases include the deposition of metals such as zinc and copper in their respective electrolytic extraction processes (pp. 39 and 213) when the aim is the recovery of the metal and the cyclical use of the electrolyte for the extraction of further quantities of the metallic compound from ores or other products.

Another case of interest is that of chromium deposition. Cast chromium anodes could be made but they are not required. They dissolve anodically with practically 100 per cent efficiency, while that of deposition is of the order of only $12\frac{1}{2}$ per cent. Thus for every gramme of metal deposited there would be an accumulation of 7 g of the metal in the solution. Further, all chromium is made with difficulty and high cost from CrO_3.

· Again, cadmium anodes dissolve with a full 100 per cent efficiency, while deposition is at the rather lower figure of 95

per cent. This might lead to an accumulation of cadmium in the solution which may be offset by the substitution of a part of the anode surface with insoluble iron or steel.

In yet other varying conditions, insoluble anodes are preferred in alkaline stannate baths for tin deposition. The most coherent deposits are made in the absence of stannite compounds which result from the use of soluble tin anodes. Insoluble steel anodes are therefore preferred, and periodic additions of sodium stannate made to the solution.

Use of Soluble Anodes. By this term is meant the solution of the metal anode under electrolytic influence. Thus a copper anode with any sulphate solution will produce copper sulphate at the anode, which is the equivalent of the production of copper ions instead of the evolution of oxygen, and this makes the production of copper ions from the metal an example of oxidation. Many other metals behave similarly, the metal being taken into solution at the anode at a rate approximating to that of its deposition at the cathode. This is the principle involved in the numerous examples of metal deposition in industry, so that the strength of the electrolyte remains approximately constant and the process thus becomes continuous with the addition of more anode metal to replace that dissolved away.

Anodic Oxidations. Many other examples might be given in which anodic oxidation results in the formation of well-known and much required compounds. Thus the electrolysis of chromium sulphate—for example in the form of chrome alum —leads to the production of chromic acid (CrO_3) at the anode. This compound is much used in the oxidation of organic products required in the formation of dyestuffs, and the reduced material, again in the form of chromium sulphate, is reoxidized cyclically by returning it to the anode compartment of an electrolytic cell.

A similar reaction takes place in the usual chromic acid solution for the deposition of chromium. There are always—and essentially—some trivalent chromium ions in the solution. They are constantly being formed at the cathode and may easily be formed there in excess of the desirable proportion. At the anode, however, they are re-converted into the hexa‑ valent form, thus to some extent maintaining a desirable

balance in the solution. Any accumulation of the trivalent form can be rectified by a manipulation of the electrodes to increase the anodic oxidation. A type of apparatus for this purpose is called a "de-chromator."

Similarly manganese compounds are capable of oxidation to permanganates. In one simple case the electrolysis of potassium carbonate solution with an anode of manganese or ferromanganese results in the production of potassium permanganate which can be, on account of its relatively low solubility, crystallized out from the electrolyte.

Numerous other examples are forthcoming in which similar oxidation processes are made available in commercial electrolysis. On the same basis the conversion of a soluble anode to one or other of its salts provides an example of oxidation, this term connoting an increase in the active valency of the metal, rather than the mere addition of oxygen to which the term oxidation was originally applied, and which is now altogether inadequate to our conception of oxidation.

Cathodic Reductions. Similarly at the cathode many reducing reactions are industrially exploited. We may readily understand the deposition of a metal from its salt as an example of reduction. The term reduction, however, covers a much wider range of reactions. For example, in an acid solution nitrobenzene is converted at the cathode to aniline—

$$C_6H_5NO_2 + 6H = C_6H_5NH_2 + 2H_2O$$
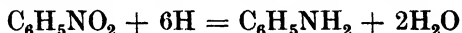
while the electrolysis of ferric compounds does not immediately result in the deposition of the metal. Before this can take place it becomes necessary to reduce the ferric compound to ferrous—

$$FeCl_3 + H = FeCl_2 + HCl$$
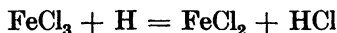
from which the metal may then be deposited.

Production of Compounds. While the term electrolysis was originally intended to represent the splitting up of chemical compounds by electricity, it has, in its modern meaning, a much wider significance and covers also the production of numerous compounds. For example, the electrolysis of a solution of potassium chlorate and potassium carbonate with a lead anode results in the temporary formation of soluble lead chlorate which, in contact with water and the soluble carbonate,

is transformed into insoluble basic carbonate of lead of the composition conforming to that of the product known as white lead, and electrolytic methods for the production of this important paint constituent have long been explored with varying degrees of success, the greater difficulty experienced being that of the production of the material not altogether of the correct chemical composition but having the desired degree of opacity.

The course of the reactions would seem to be expressed in the following equations which represent merely the chemical and not the electro-chemical changes, so that the electrical charges are omitted from the equations—

$$6KClO_3 \rightarrow 6K + 6ClO_3$$

$$3Pb + 6ClO_3 \rightarrow 3Pb(ClO_3)_2$$

$$3Pb(ClO_3)_2 + 3K_2CO_3 + H_2O$$
$$\rightarrow 2PbCO_3 . Pb(OH)_2 + CO_2 + 6KClO_3$$

$$6K + 6H_2O \rightarrow 6KOH + 3H_2$$

$$6KOH + 3CO_2 \rightarrow 3K_2CO_3 + 3H_2O$$
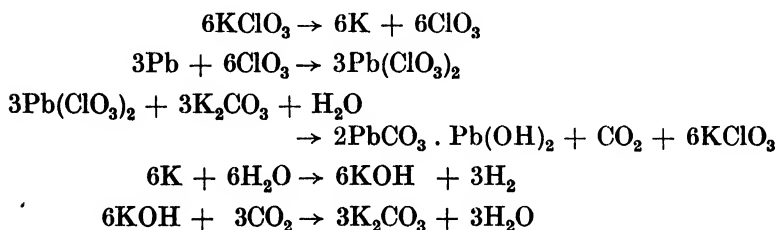
These equations show that the process is maintained by a sufficiency of lead anode and the addition of CO_2.

Similarly, the electrolysis of a neutral salt with an anode of cadmium produces a soluble cadmium salt into which the passage of sulphuretted hydrogen effects the precipitation of yellow cadmium sulphide with its well-known pigment properties.

There would therefore appear to be endless possibilities of carrying out relatively simple electrolytic reactions for the production of many important compounds. Upon these reactions industrial electro-chemistry has been developed.

Electrolysis of Complex Salts. Many complex compounds are likewise amenable to electrolysis. The double cyanides provide a case in point. Of these, reference may be made to the compounds containing copper, silver and gold of the following respective formulae : copper potassium cyanide ($CuCN . 2KCN$), silver potassium cyanide ($AgCN . KCN$), and the gold compound ($AuCN . KCN$). From these solutions the metals are obtained in the usual deposition processes, while much gold is originally

recovered from auriferous quartz by extracting the metal in weak cyanide solution—

$$O + 2Au + 4KCN + H_2O = 2AuCN.KCN + 2KOH$$
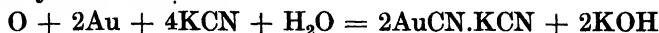
subsequently electrolyzing the weak gold cyanide solution with insoluble iron anodes and lead cathodes upon which the gold is deposited and subsequently recovered by cupellation.

In these and similar cases it has been shown that the course of the ionization is as follows—

$$AgCN \cdot KCN \rightleftharpoons K. + Ag(CN)_2^-$$
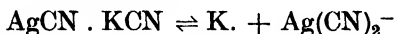
the complex $Ag(CN)_2^-$ ion migrating to the anode while the metal is deposited at the cathode as the result of a secondary reaction which was first represented simply, but not altogether accurately, thus—

$$K + AgCN \cdot KCN = Ag + 2KCN$$

Again, there is no reason to imagine this reaction which involves the continuous loss and then re-formation of potassium ions. The more reasonable explanation lies in the conception of a limited dissociation of the $Ag(CN)_2^-$ ion as follows—
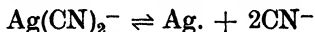
$$Ag(CN)_2^- \rightleftharpoons Ag. + 2CN^-$$

the silver ions being preferentially discharged and others formed by the practically instantaneous dissociation of more of the complex $Ag(CN)_2$ ion.

In explanation of the appearance of metallic silver at the cathode in the electrolysis of its double cyanide it has already been recorded that by a two stage dissociation some, though only a few, silver ions are present, amounting to only 1 g of silver ions in 1 000 000 000 000 litres of the solution. Again, as previously explained in the case of sulphuric acid, the removal of these silver ions leads to the instantaneous production of others, thus maintaining the usual concentration while the silver is being deposited.

Similar reasoning applies to all these double cyanide solutions which are so largely used in practical deposition.

In fact, it was the unusual concentration of the silver compound at the anode which led to the discovery of the mechanism of this electrolytic change.

Similar reactions take place with the double cyanide compounds of copper and gold with the alkali metals sodium and

potassium, these reactions · being taken advantage of in the commercial deposition of these metals.

Electrolysis of Organic Compounds. Numerous organic compounds, especially the acids and their salts, are susceptible to electrolysis. Their ionization in water provides the preliminary stage and in some cases this is conspicuous, while in others it is feeble. The alkali salts of acetic acid, for example, are freely dissociated while the acid, well known to be a poor conductor, is only slightly dissociated at moderate dilutions.

With potassium acetate we have—

$$CH_3COOK \rightleftharpoons K. + CH_3COO^-$$

At the cathode, therefore, the evolution of hydrogen and the formation of alkali occur. At the anode the reaction depends somewhat upon the concentration. In weak solutions there is the regeneration of the acid with the evolution of oxygen, while in strong solutions ethane and carbon dioxide are among the gaseous products thus—

$$2CH_3COO \rightarrow C_2H_6 + 2CO_2$$
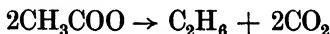
and ethane may be prepared by this method after passing the anode gases through caustic alkali for the absorption of the carbon dioxide.

Similarly, from sodium propionate (C_2H_5COONa) there is the production of alkali and hydrogen at the cathode and the evolution of butane (C_4H_{10}) and carbonic acid gas at the anode thus—

$$2C_2H_5COO \rightarrow C_4H_{10} + 2CO_2$$
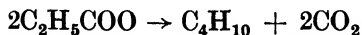
Similarly, from the succinic acid series, hydrocarbons of the olefine group are produced—

$$\begin{matrix} CH_2COOH \\ CH_2COOH \end{matrix} \rightarrow 2H. + \begin{matrix} CH_2COO^- \\ | \\ CH_2COO^- \end{matrix}$$

and

$$\begin{matrix} CH_2COO \\ | \\ CH_2COO \end{matrix} \rightarrow C_2H_4 + 2CO_2$$
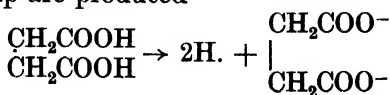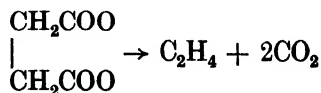
With increasing complexity of the anion there is the tendency to the formation of other substances, an experience well known in organic chemistry. In addition to these relatively simple

examples of electrolysis of organic compounds in which the compound undergoes dissociation, there will be numerous examples in which organic compounds are either oxidized or reduced at the anode or cathode respectively when suitably introduced into the anolyte or catholyte of a cell containing an inorganic electrolyte.

Organic compounds are of frequent and increasing use in electrodeposition, especially in the form of addition agents. Formaldehyde (H.CHO) and sodium formate (H.COONa) are both used in bright nickel solutions. Gelatine, phenol, glycocoll and tartrates find application in copper deposition. Dextrose and peptone are of service in the deposition of zinc and lead respectively. While a number of these substances are essentially non-conducting, there is the possibility of their combination with the electrolytes or ions and thus migration towards one or other of the electrodes. Examples will be dealt with in greater detail later (Chapter XX).

Alternating Current Electrolysis. The application of a.c. to an electrolyte would seem unlikely to effect any appreciable permanent change, as whatever chemical work was done by the current in one direction would seem to be counterbalanced by a reversed change with the rapid reversal of the current. This in many cases is quite true: a.c. applied to a copper sulphate solution makes no obvious change with either a copper or platinum anode. This fact is applied in the use of a.c. for conductivity measurements (see page 79).

There are, however, some cases, and not a few, in which marked changes do occur. If a.c. is applied to copper electrodes in a solution of an alkali cyanide, the metal disappears from both plates. In fact, it almost appears that a weak cyanide copper solution for plating purposes could be prepared in this manner. This would seem to indicate a very rapid change from the copper ions first formed into the complex ion common to those solutions. Such an almost instantaneous change is in harmony with the stability of these solutions due to the very small proportion of copper ions present.

Further, some application has been made of the superimposition of a.c. in electrolytic cells with a view to assisting essential anode solution.

QUANTITATIVE ELECTROLYSIS

Introduction. In approaching the subject of quantitative electrolysis it is well to recall that well over a century ago it came to be recognized, as the result of accumulating evidence, that chemical action is controlled by quantitative laws. The laws of chemical combination are known to every student of chemistry, and equally familiar will be the conception of Dalton, known for so long as the atomic hypothesis, put forward in order to account for these quantitative relationships. For example, 23 parts by weight of sodium are always combined with 35·5 parts by weight of chlorine in the compound which we call common salt. This definiteness of chemical composition is a feature of chemical compounds. If electrolysis is concerned with changes of composition of these substances by the agency of electrical energy, it will be reasonably anticipated that similar definiteness will mark the quantities of the resulting products.

With a few ill-designed experiments in electrolysis we might at first be inclined to doubt the accuracy of this assumption, but it will be recognized that in order to track accurately any conceived relationships it will be necessary to apply accurate methods of manipulation and measurement. Where the products are weighable, accurate balances are available, while gas volumes are easily measured. Accuracy of an equal order in manipulation, however, may not be so easily assured. For example, it is useless to "put current" through any solution containing copper and expect quantitative deposition. It will be appreciated that there is some choice in the selection and concentration of the electrolytes to be used for coulometric work.

Faraday's Laws. The pioneering work in this direction is universally credited to Michael Faraday a century ago. Arranging a number of cells in series with the moderately accurate instruments then available and using a large variety of electrolytes, Faraday made two important discoveries embodied in

laws associated with his name. The first related the masses of the products to the current passed and the time, or, in other words, to the coulombs. Now while the heating effect of a current is proportional to the product of the square of the current passed and the time, that is, $H \propto I^2t$, the chemical effect was found to be proportional to the product of the current and time. This is Faraday's First Law, that the quantities of substances concerned in electrolysis are proportional to the coulombs passed. "Quantities concerned" puts the matter very comprehensively and includes therefore metal deposits, anode corrosion, acids and alkalis formed at the anode and cathode respectively, gases evolved, and other chemical changes which may take place in the solution.

Next, Faraday found that the same number of coulombs passing through a succession of different electrolytes gave products proportional to their chemical equivalents. This might reasonably be regarded as the only possible proportion in which they could appear. If electrolysis is the electrical decomposition of chemical substances formed by the combination of definite quantities of simpler substances, then these materials can only appear in the proportions in which they combined. Up to Faraday's time no one had definitely shown by experiment that this actually was the case. Faraday found that the quantities of substances concerned in electro-chemical change were always proportional to their chemical equivalents. This constitutes the Second Law of Quantitative Electrolysis. In order, however, to attain these quantitative results it needed a considerable amount of work to determine the best conditions to secure the translation of all the coulombs passed into the desired products, and nowadays this quantitative translation of coulombs into desired products is only achieved under the special conditions aimed at in coulometric work. The usual processes of electrodeposition, refining and extraction frequently fall short of this quantitative ideal.

Based on the acceptance of these laws it is now possible and usual to define the ampere in terms of the chemical work which it will effect, and thus it becomes the unvarying current which, under ideal conditions, will deposit 0·001 118 g of silver per second or 4·024 g per hour.

This apparently unnecessarily complicated figure is due to

the fact that the practical ampere derives its origin from a unit based on ·electromagnetic phenomena, this latter unit being ten times as large as the one now being defined.

Chemical Equivalents. For an appreciation of the subject there must be some familiarity with the quantities which chemically are known as "chemical equivalents," and relevant data appear in Table II. The table includes only elements, and some slight inaccuracy in the figures must be allowed for in the fact that many of them are expressed to only three significant figures.

TABLE II

CHEMICAL AND ELECTRO-CHEMICAL PROPERTIES OF ELEMENTS

Element	Symbol	Atomic Weight	Valency	Chemical Equivalent*	Electro-chemical Equivalent† (mg.)	Grammes per Ampere-hour
Cadmium	Cd	112	2	56	0·58	2·088
Chromium	Cr	52·5	6	8·75	0·091	0·327 6
Copper .	Cu	63·6	2	31·8	0·329	1·182
Cobalt .	Co	59	2	29·5	0·305	1·098
Gold .	Au	197	3	65·6	0·676	2·436
Hydrogen	H	1	1	1	0·010 4	0·037 6
Iron .	Fe	56	2	28	0·29	1·044
Lead .	Pb	207	2	103·5	1·071	3·86
Nickel .	Ni	58·6	2	29·3	0·303	1·09
Oxygen .	O	16	2	8	0·082 8	0·298
Silver .	Ag	108	1	108	1·118	4·024
Tin. .	Sn	118	2	59	0·615	2·21
Zinc .	Zn	65	2	32·5	0·338	1·22

These atomic weights are not taken to the last degree of accuracy, but are generally accepted as close approximations.

Valency may be regarded as the number of atoms of hydrogen combining with or displaced by one atom of the element. It is also the number of electrons gained or lost per atom during electrolytic dissociation.

This and similar tables will always require comment. The figure for chromium, for example, assumes the production of the metal from the tri-oxide solution. That for gold refers to

* *Chemical Equivalent* is the mass of a substance chemically equal to 8 parts by weight of oxygen.

† *Electro-chemical Equivalent* is the mass associated with one coulomb.

the chloride solution, whereas the deposition of gold for electro-gilding is usually from the double cyanide solution with potassium ($AuCN . KCN$), in which compound the gold is monovalent and its equivalent is then the atomic weight.

Further illustrative of the operation of these laws in a number of well-known electro-chemical reactions, the following examples will be taken, these having been referred to qualitatively in the preceding chapter.

Electrolysis of aqueous salt solution—

$$\underset{58\cdot5}{NaCl} + \underset{}{H_2O} = \underset{40}{NaOH} + \underset{1}{H} + \underset{35\cdot5}{Cl}$$
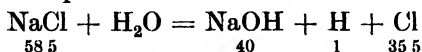
The quantities expressed are obviously the equivalents, and a simple calculation will therefore show that the ampere-hour yields of these products are 1·49 g of sodium hydroxide and 1·325 g of chlorine from the decomposition of 2·18 g of sodium chloride.

Production of potassium chlorate—

$$\underset{74\cdot5}{KCl} + \underset{48}{3O} \rightarrow \underset{122\cdot5}{KClO_3}$$
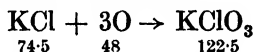
The simple equation shows 6 equivalents; the chemical equivalent of $KClO_3$ (as a product of this type of oxidation) is therefore 122·5/6 and the theoretical yield per ampere-hour is 0·76 g.

Oxidation of chromic compounds to chromic acid (CrO_3). Simple equation—

$$\underset{}{Cr_2O_3} + \underset{48}{3O} \rightarrow \underset{2(100\ 5)}{2CrO_3}$$
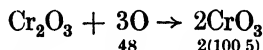
The chemical equivalent of chromic acid (judged either by the oxidation process by which it is produced from chromic compounds or its action as an oxidizing action) is therefore 201/6 = 33·5, the theoretical yield per ampere-hour being 1·25 g.

Similarly, white lead may be given the formula—

$$2PbCO_3 . Pb(OH)_2$$

the molecular weight being 775. It is electrolytically produced from 3Pb and its equivalent becomes 775/6 = 129·1 with a theoretical yield (and also a good commercial one too) of 4·8 g/Ah or, by a simple conversion, 10·68 lb/1 000 Ah.

Electrode Efficiency. The figures calculated according to Faraday's laws represent the quantities to be attained only under ideal conditions of electrolysis. Seldom in commercial work are these ideal conditions realized. In the decomposition

of the salts of many metals there is the simultaneous deposition of hydrogen with a corresponding lack of metal. Generally speaking, the conditions for quantitative metal deposition include strong electrolytes in motion, so that metal ions are always present on the surface of the cathode to be turned out quantitatively. These conditions are not naturally present as practical solutions may rlot be saturated, and, in any case, the rate of migration of the metal ion falls far short of the rate at which the metal is deposited. There is also in many other examples the possibility of secondary changes occurring which limit the yield of the main and desired product. These defects in the case of the metals, for example, occur at both the anode and cathode, and thus we get some idea of what is called percentage "cathode efficiency" as follows—

$$\text{Cathode efficiency} = \frac{\text{Wt. metal deposited} \times 100}{\text{Wt. by Faraday's law}}$$

Similarly—

$$\text{Anode efficiency} = \frac{\text{Wt. metal dissolved} \times 100}{\text{Wt. by Faraday's law}}$$

Similar expressions apply to all electro-chemical operations. In the usual processes of metal deposition these efficiencies are not far short of 100. For continuity of operation these efficiencies, if short of ideal, should be as nearly alike as possible, there then being no depreciation or appreciation of the metal content of the solution. Where they are not, some correction of the metal content needs to be made from time to time.

Another convenient term is "electrode efficiency," representing the relative efficiencies at anode and cathode thus—

$$\text{Electrode efficiency} = \frac{\text{Anode efficiency}}{\text{Cathode efficiency}}$$

which may be expressed either as a fraction or a percentage. Thus in the case of the deposition of cadmium from the usual double cyanide [$Cd(CN)_2 2NaCN$] solution, the electrode efficiency usually exceeds unity as cadmium anodes dissolve practically in accordance with Faraday's law while the cathode efficiency is short of 100. In addition, there is the fact that under the influence of the air and solution some cadmium dissolves chemically, though this reaction takes place also at the cathode.

It is usual in this case, in which the electrode efficiency exceeds unity, to introduce a part of the anode surface in the insoluble form by the addition of a limited area of iron, from which current passes without taking cadmium into the solution. These are points which need attention in the more practical examples of deposition as well as in other cases of commercial electrolysis. Further illustrative of his principle is the boosting up of the current in the anode compartment of mercury diaphragm cells for the production of alkali from the electrolysis of alkali chlorides (page 332).

The Faraday. The electro-chemical equivalent of silver is 0·001 118 g, while the chemical equivalent is 108. To deposit the gramme-equivalent of silver will therefore require the passage of—

$$\frac{108}{0·001\ 118} = 96\ 600\ \text{C}.$$

Similarly for copper, the chemical equivalent of which is 31·8 and the electro-chemical equivalent 0·000 329 g, we have—

$$\frac{31·8}{0·000\ 329} = 96\ 600\ \text{C}.$$

This figure naturally applies to all other electro-chemical products. This constant quantity of electricity required to effect the separation of the gramme-equivalent is called the "Faraday." In the units of everyday work it represents—

$$\frac{96\ 600}{3\ 600} = 26·8\ \text{Ah}.$$

Again, 96 600 is a very good approximation and also a simple figure. The figure depends upon the exact value of the atomic weights of the elements and therefore their electro-chemical equivalents.

Now physicists have determined by several and widely different methods that there are 60×10^{22} molecules in the gramme-molecule of any substance. This is known as the Avogadro number. Accordingly, there is the same number of atoms in the gramme-atom. The gramme-atom of monovalent hydrogen, the gramme-equivalent, is associated with the Faraday, that is, 96 600 C, from which it follows that the charge on the hydrogen ion is $96\ 600 \div (60 \times 10^{22}) = 16 \times 10^{-20}$ C.

This charge is increased proportionally with the valency. This charge may sometimes be given as one-tenth of this quantity, the unit then having the electromagnetic origin previously referred to.

Coulometers. Electro-chemical work often necessitates the accurate measurement of current. It, moreover, more frequently calls for the measurement of an average of a slightly varying current over long or comparatively long periods. The possibility of averaging a large number of readings on an ammeter is quite out of the question, and in the experiments in question the maintenance of a uniform current would require constant personal attention and even then not be altogether satisfactory.

A solution of the problem is the insertion into the circuit of an electrolytic cell in which the translation of the coulombs passing into products capable of easy and accurate measurement is possible. Such cells will necessarily involve reactions which can be carried out with ideal efficiency and the products obtained and measured with similar accuracy. Such electrolytic cells used for this purpose are called coulometers, this term replacing the older and cruder term voltameter.

In them, gases may be produced, the volumes of which are easily and accurately measured. Alternatively, metals such as silver and copper may be deposited and subsequently weighed. In all cases a number of essential requirements must be met. In them (1) every coulomb must be translated into the desired product (in other words there must be a full 100 per cent efficiency whether at the anode or cathode); (2) the products must be capable of quantitative collection and measurement; and (3) it is desirable that the products, if solid, should have a large equivalent mass.

The first condition will in many cases be met by the careful choice of electrolyte and control of the rate of deposition to avoid all possibility of secondary reactions. The second is met by the production of metal deposits or the collection of easily measurable volumes of gases, either hydrogen, oxygen, or a mixture of the two, while the third condition finds its answer in the choice of metals with high chemical equivalents giving relatively large masses for the number of coulombs passed, while the item of cost may necessitate the choice of a cheaper

metal like copper in spite of the fact that its equivalent is less than one-third of that of silver.

Gas Coulometers. The electrolysis of many acids, alkalis, and neutral salts with insoluble electrodes gives rise to the evolution of oxygen at the anode and hydrogen at the cathode. These gases are easily collected and measured. The quantitative aspect may best be considered by taking the case of hydrogen alone. Taking the E.C.E. as 0·000 010 4 g and the mass of 1 cm^3 at N.T.P. (see page 55) as 0·000 09 g, we have an evolution of—

$$\frac{0 \cdot 000\ 010\ 4 \times 60}{0 \cdot 000\ 09} = 6 \cdot 93 \text{ cm}^3/\text{A min.}$$

Exactly one-half of this volume of oxygen will be simultaneously evolved at the anode. Our immediate consideration does not call for the adjustment of such conditions as slight daily variations in barometric pressure, and we shall at the same time omit the correction required for the fact that the collected gases are saturated with water vapour. Allow then that the temperature of the gases is of the order of 16° C., and we have the volume of mixed gases per ampere-minute as—

$$6 \cdot 93 \times \frac{3}{2} \times \frac{273 + 16}{273} = 11 \text{ cm}^3$$

This is a principle which is applied in a number of types of gas coulometer, two of which are shown in Figs. 5 and 6, the former being designed for the collection of the two gases separately and the latter for the mixed gases.

In the latter case the cell need be of only very simple construction, gas-tightness being the essential condition. Two nickel electrodes are employed when the electrolyte is an alkali, while platinum electrodes will be necessary when an acid electrolyte is used. In either case the internal resistance of the cell is reduced by shaping the electrodes in spiral form so that a comparatively large area of electrode may be used with very small inter-electrode distance. The mixed gas is then collected in a suitable measuring cylinder, the volume being measured against the time of evolution with care not to commence the time measurement until gas appears in the collecting cylinder. When the apparatus has been set up and run for a short time

to make sure of gas-tightness, there should afterwards be no delay in the appearance of the first bubbles of gas in the measuring cylinder.

The choice of electrolyte, however, demands attention. It has already been pointed out that moderately strong sulphuric acid is subject to secondary reactions which are responsible for a reduction in the volumes of gases evolved, while with the
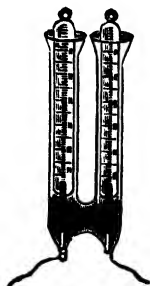

FIG. 5. SEPARATE   FIG. 6. MIXED GAS COULOMETER
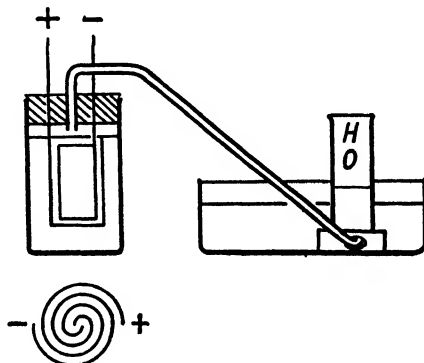GAS COULOMETER

more dilute acid we are still up against the problem of the solubility of the gases. Nevertheless in some types of gas coulometers dilute sulphuric acid would be used. An alternative choice is that of phosphoric acid which is much less susceptible to secondary changes.

For practical work, however, this difficulty is surmounted by the use of alkali solutions. These are comparatively free from any secondary reactions. It is essential that the alkali should be free from chlorides and similar impurities as these give rise to anode corrosion and hence loss of gas. These are the precautions which also become necessary in setting up the electrolytic cells for the commercial production of hydrogen and oxygen, in this case the electrodes being of iron or a nickel-iron alloy.

Such gas coulometers, however, involve the consumption of something of the order of two volts. They can be put into the circuit and the total volume of gas measured over either a long or short time, the volumes being readily converted into current.

Thus the evolution of 50 cm³ of mixed gas in the course of 10 minutes represents an average current of—

$$\frac{50}{10 \times 11} = 0\cdot454 \text{ A.}$$

Copper Coulometer. From a strong copper sulphate solution with the addition of free sulphuric acid the deposition of the metal takes place almost ideally, and with some control over the composition of the solution and the conditions of deposition the cathode efficiency can be regarded as 100 per cent. For this purpose the following solution is recommended—

Copper sulphate crystals . . .	150 g
Sulphuric acid	50 g
Alcohol	50 g
Water	to 1 litre

The addition of alcohol is made to prevent the re-solution of the deposit under the combined action of the air and acid. It also improves the physical character of the deposit. Current density should not exceed 10 A/ft² (approx. 1 A/dm²). Thin copper cathodes are easily and accurately weighed. Prior to final weighing the deposit is rinsed with cold and then hot distilled water and dried in an oven. From the weight of copper deposited and the duration of the deposition, the average current is calculated by the application of the E.C.E. of copper, which is 0·000 329 g. Such a cell

FIG. 7. COPPER COULOMETER

admits of the measurement of relatively large currents with materials of low cost. The internal resistance of the cell is low, and with practically 100 per cent anode efficiency there is little or no "polarization." Only a small e.m.f. is thus absorbed in the cell (Fig. 7). Thus a deposit of 5 g of copper in 2 hr represents an average current of—
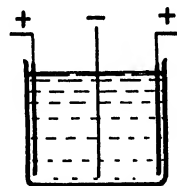
$$5/(2 \times 1\cdot182) = 2\cdot115 \text{ A.}$$

Silver Coulometer. One disadvantage of the copper coulometer is the relatively low chemical equivalent of copper. Other metals with higher equivalents are therefore preferable if they fulfil the requirements previously stated. A number of metals are available for this purpose, their relevant data being set out in Table III, p. 36.

TABLE III
PROPERTIES OF COULOMETER METALS

Metal	Chemical Equivalent	Milligrammes per coulomb
Copper . · .	31·8	0·329
Mercury . .	100	1·034
Lead . . .	103·5	1·071
Silver . .	108	1·118

Of these metals silver has found extended application, and when set up and used with control, provides one of the most accurate methods of coulometry. The method involves the electrolysis of a strong solution of silver nitrate. This necessitates the use of a platinum cathode. The anode is of fine silver, which must be enclosed in filter paper to prevent the possibility of silver, which may become detached from the anode by disintegration, from floating about in the electrolyte and possibly being enclosed in the cathode deposit.

In a usual form (Fig. 8) the apparatus comprises a silver crucible or dish which, after cleaning and weighing, constitutes the cathode and holds the solution of silver nitrate, which is of the order of normal strength. A small silver anode can be shaped to follow the contour of the dish or a small disc of the metal will suffice. Only a low current density of the order of 0·02 A/in².

FIG. 8. SILVER COULOMETER

is permissible. The deposit is crystalline and with a higher rate of deposition the crystals are liable to become detached and then require more careful handling in the subsequent washing and weighing processes. While the method admits of considerable accuracy it can only be used for relatively small currents. A deposit of 0·198 g of silver in 35 min = 0·198/(0·001 118 × 60 × 35) = 0·084 A.
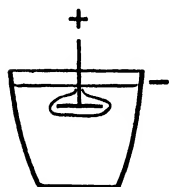
Other Metal Coulometers. There are, however, other possibilities in metals which, with high equivalents, are of lower cost than silver. Thus Betts and Kern* suggested the use of the lead silico-fluoride bath which finds commercial application in the electrolytic refining of lead on a considerable scale.

* *Trans. Amer. Electro-chem. Soc.* (1904), Vol. VI, p. 67.

Again, the use of lead perchlorate solution was proposed by Mathers.* The solution has the following composition—

Lead (as perchlorate)	.	.	.	.	50 g
Perchloric acid (free)	.	.	.	.	50 g
Peptone	.	.	.	.	0·5 g
Water	.	.	.	.	. to 1 litres

The small addition of peptone is essential to the production of a coherent deposit. In comparison with the silver coulometer, Mathers found that this lead cell gave a cathode efficiency of 99·8 per cent, and this inaccuracy of 2 parts per 1 000 may be regarded as a tolerable allowance in many cases in which the lower cost of the materials and the larger scale in which the cell may be used are obvious advantages.

Still further, the use of silver perchlorate was suggested by Cahart, Willard and Henderson† on the grounds that the deposit is more coherent and the substance more stable than the nitrate.

Reference may also be made to the use of mercury compounds which are employed in some types of electrolytic meters, in which a small and known proportion of the current to be measured is by-passed through a high resistance and a solution of a mercury salt. The deposited mercury is collected in a graduated cylinder calibrated so that the volume of mercury collected may at once be read off in terms of the kilowatt-hours passing through the meter. This principle has found application in industrial and domestic electric supplies, of which that of Wright is a well-known example.

Another substance suggested for coulometric work is iodine, set free at the anode by the electrolysis of iodides and readily estimated by titration with standard sodium thiosulphate.

Power Calculations. The added data regarding bath voltage now enable us to calculate the energy (or, as it sometimes erroneously called, the power) consumption in the bath. Thus—

Ampere-hours × volts = watts

watts/1 000 = kilowatts

Adding the time factor,

1 kWh = 1 000 × 3 600 = 3 600 000 watt-sec or joules.

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* *Trans. Amer. Electro-chem. Soc.* (1910), Vol. XVII, p. 261.
† *Trans. Amer. Electro-chem. Soc.* (1906), Vol. IX, p. 375.

When this is done the energy consumption should be referred to that from the original source of supply. This is usually a.c., the conversion to d.c. being made by rotary converter, rectifier, or motor-generator, in each of which cases there will be definite loss as in conversion and subsequent transmission to the bath. · Costs of energy must naturally be referred back to the equivalent energy at the source and the subsequent losses charged to the operation in the bath.

EXAMPLES

1. How many kilowatt-hours will be required to deposit 1 t of copper from the sulphate solution with a bath voltage of 0·3 V and 100 per cent current efficiency?

31·8 g Cu deposited by 26·8 Ah at 100%. Kilowatt-hours per ton with 0·3 V

$$= \frac{2\,240 \times 454}{31\cdot8} \times \frac{26\cdot8 \times 0\cdot3}{1\,000} = 257$$

2. If 96 600 C deposit the gramme-equivalent of a metal, what weights of nickel and silver respectively will be deposited by 10 A in one hour? (*City and Guilds Inter. Exam.*, 1937.)

10 Ah $= 10 \times 3\,600 = 36\,000$ C.

C.E. of Ni $= 58\cdot6/2 = 29\cdot3$

Wt. of Ni per 10 Ah

    $= (29\cdot3 \times 36\,000)/96\,600 = 10\cdot92$ g.

C.E. of Ag $= 108$.

Wt. of Ag per 10 Ah

    $= (108 \times 36\,000)/96\,600 = 40\cdot2$ g.

3. In an experiment, the increases in weight of the cathodes in three cells connected in series and containing (*a*) copper sulphate, (*b*) copper cyanide and (*c*) nickel sulphate were (*a*) 2·36 g, (*b*) 2·13 g and (*c*) 2·08 g. Assuming the cathode efficiency in the first cell to be 100 per cent, what were the efficiencies in the other cells? (*City and Guilds Inter. Exam.*, 1935.)

C.E. of Cu (sulphate) $\doteqdot 63\cdot6/2 = 31\cdot8$

C.E. of Cu (cyanide) $= 63\cdot6$

C.E. of Ni (sulphate) $= 59\cdot6/2 = 29\cdot3$

Copper cyanide bath,

$$\text{Cathode Eff.} = \frac{2 \cdot 13}{2 \cdot 36 \times 2} \times 100 = \underline{45 \cdot 1\%}$$

Nickel bath,

$$\text{Cathode Eff.} = \frac{2 \cdot 08}{2 \cdot 36 \times 29 \cdot 3 / 31 \cdot 8} \times 100 = \underline{95 \cdot 7\%}$$

4. You are required to deposit an average thickness of $\frac{1}{8}$ in. of copper from the acid solution on to a surface of 3 ft² in area. Assuming the density of copper to be 8·9 and the E.C.E. of copper to be 0·000 329 g, (1) how many ampere-hours will be required and (2) if the tank voltage is 1 and the converter plant efficiency 75 per cent how much would the current cost at 1d. per kWh? (*City and Guilds Inter. Exam.*, 1938.)

(1) $1 \text{ in}^3. = 6 \cdot 45 \text{ cm}^3$

Wt. of Cu deposit $= 3 \times 144 \times \frac{1}{8} \times 6 \cdot 45 \times 8 \cdot 9$

                     $= 3\ 100 \text{ g.}$

Ampere-hours required

          $= 3\ 100 / (0 \cdot 000\ 329 \times 3\ 600) = \underline{2\ 620}$

(2) Cost of current at 1d. per unit—

$$= \frac{2\ 620}{1\ 000} \times 1 \times \frac{100}{75} = \underline{3 \cdot 5\text{d}}$$

5. If the current efficiency of a chromium plating process using chromic acid solution with insoluble anodes is 15 per cent, what weight of chromic acid must be added per 1 000 Ah to replace the chromium removed by deposition? (*City and Guilds Final Exam.*, 1937.)

$$\underset{100 \cdot 5}{\text{CrO}_3} \equiv \underset{52 \cdot 5}{\text{Cr}}$$
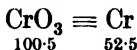
E.C.E. of $\text{Cr} = 0 \cdot 000\ 091$ g.

E.C.E. of $\text{CrO}_3 = 0 \cdot 000\ 091 \times 100 \cdot 5 / 52 \cdot 5$

                     $= 0 \cdot 000\ 174\ 2$ g.

Wt. of CrO_3 required

    $= 1\ 000 \times 3\ 600 \times 0 \cdot 000\ 174\ 2 \times 15 / 100 = \underline{94 \text{ g.}}$

6. In the electrolytic extraction of zinc (page 213) the solution entering the cells contains zinc as sulphate and some free sulphuric acid to impart conductance. As it flows through the series, the zinc content

decreases with a proportionate increase in the acid concentration. The equation—

$$ZnSO_4 + H_2O = Zn + O + H_2SO_4$$
$$\ 65 \ 98$$
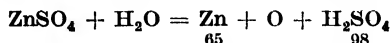
gives the exact quantities, from which it will be seen that the metal and acid are roughly in the proportion of $1 : 1\frac{1}{2}$. Assume the original liquor to contain 10 g of zinc and 3 g acid per 100 cm³ and that the process is continued until the zinc content has fallen to 3 g and the acid increased to $1.3\frac{1}{2}$ g per 100 cm³. Alternatively, the extraction of the zinc might be carried down to 2 g with the acid increase to 15 g per 100 cm³. In the former case, the tons (volume)* of liquid required for 1 t of zinc will be $100/7 = 14$ approx ; while, with the decrease of zinc down to 2 g per 100 cm³, the tons (volume) of liquor required per ton of zinc extracted will be $100/8 \div 12\frac{1}{2}$. The larger the extraction, the smaller the bulk of liquor to be handled in all stages with consequent lower costs. The weaker zinc solution will, however, result in a much lower current efficiency and consequent increase in the cost of electrical

TABLE IV

ELECTROLYSIS OF PURE ZINC SULPHATE—SULPHURIC ACID SOLUTION

Composition of solution in g/100 cm³—

In Zinc 8·0, Acid 3·0
Out Zinc 4·6, Acid 8·91
Current Density = 28 A/ft²

Cell No.	Zinc Deposit (g)	Current Efficiency	P.D.	Composition (g/100 cm³)		Kilowatt-hours per ton
				Zinc	Acid	
1	171·7	96·8	4·63	7·83	3·26	3 991
2	171·2	96·5	3·69	7·48	3·78	3 195
3	171·9	96·9	3·64	7·13	4·30	3 139
4	171·7	96·8	3·40	6·79	4·82	2 935
5	170·7	96·3	3·24	6·44	5·34	2 814
6	169·2	95·5	3·21	6·10	5·84	2 810
7	168·6	95·1	3·18	5·77	6·35	2 794
8	167·8	94·7	3·17	5·43	6·85	2 799
9	165·1	93·1	3·13	5·18	7·34	2 810
10	160·5	90·5	3·08	4·78	7·83	2 845
11	152·6	87·0	3·04	4·47	8·30	2 922
12	150·8	85·0	3·01	4·16	8·76	2 939
Average		93·7	3·37			3 001

* Ton volume = volume of 1 t of water
   1 ft³ water = 62·5 lb.
 1 ton volume = 2 240/62·5 = 35·8 ft³.
The term is here used as a relative figure only.

energy. The decision as to the degree of extraction can therefore only be arrived at by a balancing of the costs, together with other items which need not be mentioned here.

In any case, as the process proceeds, decreasing zinc means decreasing current efficiency with increased electrical costs, but there is a somewhat counterbalancing increase in the conductance of the solution with a decreased p.d. to maintain the required current density and thus a reduction of "power" costs. The data shown in Table IV, from an experiment in which the solution passed through a series of 12 cells, may be taken as fairly representative of these varying conditions.
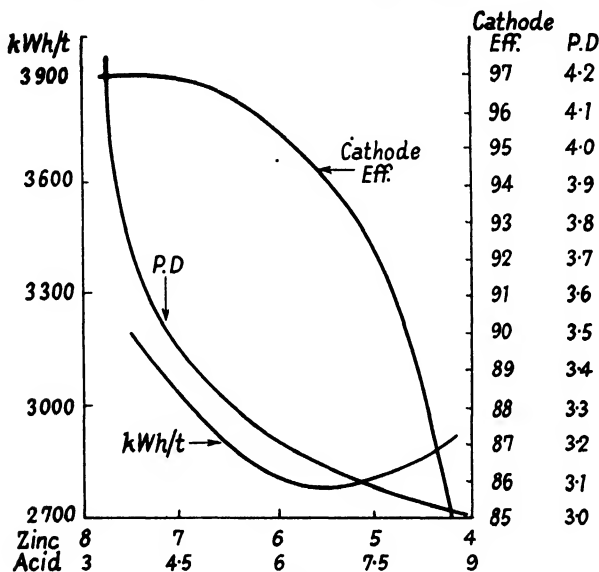

kWh/t	Cathode Eff.	P.D
3 900	97	4·2
	96	4·1
	95	4·0
3 600	94	3·9
	93	3·8
	92	3·7
3 300	91	3·6
	90	3·5
	89	3·4
3 000	88	3·3
	87	3·2
	86	3·1
2 700	85	3·0
Zinc 8 7 6 5 4		
Acid 3 4·5 6 7·5 9		

Fig. 9

From the p.d. and cathode eff. data calculate the kilowatt-hours as follows—

Ampere-hours per ton $= 2\ 240 \times 454/1{\cdot}22 = 833\ 000$

$$\text{Kilowatt-hours per ton} = \frac{\text{Ampere-hours per ton} \times \text{p.d.} \times 100}{1\ 000 \times \text{cathode eff.}}$$

Check the figures for kilowatt-hours per ton in the sequence of tanks. Plot the data in three curves showing (1) cathode eff., (2) p.d. and (3) kilowatt-hours per ton, all against the composition of the solution in the corresponding tanks. The curves as shown in Fig. 9 result, from which it will readily be seen that

kilowatt-hours decrease with the first increases in the acid content but later increase due to the more rapidly decreasing current efficiency. Other factors being also taken into consideration, particularly that of the volumes of solution to be handled in a number of stages, and the plant required, the choice of the composition of the original solution and that leaving the tanks and to be used cyclically for treating fresh quantities of roasted ore will be determined by the cost of "current" per ton of zinc extracted.

These are general principles only, so much depending upon the local cost of current and the size and cost of plant and its operation for the varying quantities of liquor handled per ton of zinc.

7. Bright nickel deposits are made (page 292) from a mixed solution of the sulphates of nickel and cobalt, the deposit usually containing about 15 per cent of cobalt. Using a nickel anode and making periodical additions of cobalt sulphate, calculate the weight of the latter substance which should be added per 1 000 Ah with a current efficiency of 95 per cent. For this purpose the approximate atomic weights of both the metals may be taken as 59, the chemical equivalent being 29·5.

$$1\ 000\ \text{Ah (Ni.Co)} = 1\ 098\ \text{g.}$$

With cathode eff. 95 per cent and 15 per cent Co in deposit—

Wt. of Co deposit $= 1\ 098 \times 0·95 \times 15/100$ g.

$$\frac{CoSO_4 \cdot 7H_2O}{Co} = 281/59$$

Equiv. Wt. of $CoSO_4 = 1\ 098 \times 0·95 \times 15 \times 281/(100 \times 59)$
$$= 745\ \text{g.}$$

This would apparently involve an accumulation of nickel sulphate of like amount. In practice this is withdrawn by "drag-out," necessitating also the addition of a larger amount of cobalt sulphate than that calculated above.

PROPERTIES OF GASES

Introduction. The molecules of a solute are, relatively speaking, widely scattered throughout the solvent. A study of their properties would seem to be simplified by a knowledge of the properties of another attenuated form of matter as exemplified in gases. The properties of gases provide a helpful introduction to those of solutions. In a simple way we regard a gas as a form of matter requiring support in all directions or exerting pressure in every direction. This is a simple idea but, as will later be seen, inadequate. A study of the properties should first be made and then an attempt at a definition.

Properties of Gases. The compressibility of gases and their change of volume with change of temperature are well known. In each case these variations are expressible quantitatively. There is a uniformity in both cases which is capable of concise statement or, in other words, as a law.

Boyle's Law. The change of volume of a gas with change of pressure was quantitatively studied and stated by Boyle in 1662, who summarized his results in a statement, known as Boyle's law, as follows: "At constant temperature the volume of a gas varies inversely as its pressure." In other words, at constant temperature the product of the volume and pressure of a given mass of gas is constant. Ordinarily a gas is under atmospheric pressure (14·7 lb/in.^{2}; 760 mm Hg. or 1 033 g/cm^2). Double the pressure and the volume is reduced to one-half. These results are clearly expressed by simple graphs as illustrated in Figs. 10 and 11.

Fig. 11 shows the product PV constant at all pressures. Expressed in simple mathematical terms—

$$P \times V = c \text{ or } P \propto \frac{1}{V}$$

This statement and these expressions cover the general behaviour of all gases. Some deviations will be referred to later.

Charles's Law. All gases expand on heating and contract on

43

cooling. These variations of volume with change of temperature are common to all gases. They were quantitatively determined by Gay Lussac and Charles in 1801, and are stated in a simple law known as Charles's law, which takes several forms. In passing, it must be noted that these volume changes are first observed at constant pressure. The law then states that: "At constant pressure the volume of a gas varies to the extent of 1/273 of its volume at 0° C. for each degree in
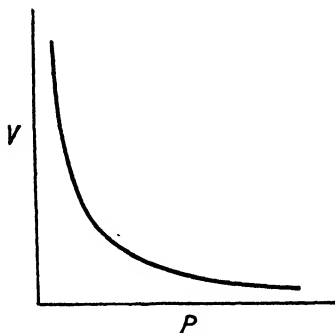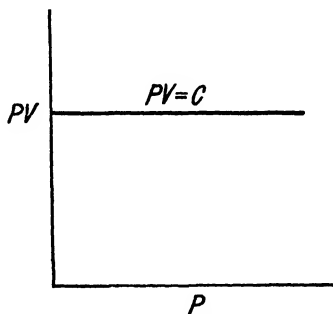

FIG. 10. BOYLE'S LAW   FIG. 11. BOYLE'S LAW

temperature variation on the centigrade scale." Thus 273 cm³* at 0° C. become 274 cm³ at 1° C., 275 cm³ at 2° C. and $(273 + t)$ cm³ at $t°$ C. It must be realized that the fraction 1/273 applies only to the volume at 0° C. If we take 1° C. as the standard temperature, then the expansion fraction or coefficient of expansion would be 1/274. In the following table we have the variations over a given range of temperature—

Deg. C. .	.	− 200	− 100	0	50	100	273
Vol.	.	73	173	273	323	373	546

From these figures it might appear that at the temperature of − 273° C. the gas would cease to show volume. It will, however, be obvious that even if this temperature were attained

* cm³ = cubic centimetre now frequently replaced by ml = millilitre. The litre was at first defined as the volume of a kilogramme of water at normal pressure (760 mm Hg.) and 4° C. (temperature of maximum density). Later determinations showed that the standard kilogramme was inaccurate and was, in fact, 1 000·027 g, so that the litre is 1 000·027 cm³, and 1 ml = 1·000 027 cm³. The difference is negligibly small except for the most accurate work. The two quantities, cubic centimetres and millilitres, will be used interchangeably.

the gas would refuse to be squeezed out of existence. Some variation in the contraction must occur at very low temperatures prior to liquefaction and, in general, it must be noted that there are usually limits to the ranges over which such laws apply. It must not be assumed that simple changes which take place within our limited experience will necessarily apply under all extreme conditions. Again, this fraction 1/273 is very slightly different for different gases, but the fraction may for simple purposes be taken as applicable to them all.

In another case, however, the volume of a gas may be kept constant by confining the gas in a vessel while being heated and then the pressure changes. The same fractional change takes place with pressure as with volume under constant pressure and thus: "At constant volume, the pressure of a gas varies 1/273 of that at 0° C. for each degree C. variation in temperature." Following the same reasoning as with the volume variation, it might appear that at $-273°$ C. the gas would cease to exert pressure. This unthinkable contingency again does not arise, but it does appear that this—shall we say— hypothetical temperature of $-273°$ C. provides a useful point at which a new scale of temperature might be made, and this is largely done in scientific work. The new scale is called the Absolute scale, which is compared with the centigrade scale in the following figures—

Absolute Scale	.	0	100	200	273	373
Centigrade Scale	.	-273	-173	-73	0	100

These variations of volume with temperature are graphed in Fig. 12. They are expressed as follows—

$$\text{At const. pressure}: \ V_t = V_0(1 + \alpha t)$$

where V_t is the volume at $t°$ C.,

V_0 is the volume at 0° C.

and α is the coefficient of expansion.

Further, on the absolute scale we have—

$$\frac{V_1}{T_1} = \frac{V_0}{T_0} = \text{const.},$$

where V_1 and T_1 represent volume and corresponding absolute temperature.

Again—

At const. volume: $P_t = P_0(1 + \alpha t)$

and

$$\frac{P}{T} = \text{const.}$$

Charles's law can then be restated thus: (1) At constant pressure the volume of a gas is proportional to its absolute temperature; (2) At constant volume the pressure of a gas is proportional to its absolute temperature.
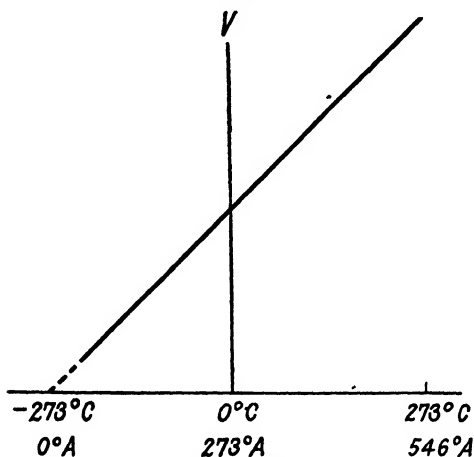

FIG. 12. CHARLES'S LAW

For the moment the general conformity of all gases to this law is important. Slight variations will be dealt with later.

Constitution of Gases. Now science is concerned not only with the accumulation of information but also with the formulation of adequate explanations for the observations made. Why do all gases obey the laws of Boyle and Charles, or in other words, why is there such uniformity of behaviour of gases? The answer is supplied in the simple conception that gases are constituted of molecules which, in comparison with their size, are widely separated. Their recognized volume is really the space in which they collectively move, and the pressure they exert is the sum of the numerous collisions of the vibrating molecules with the walls of the containing vessel.

This is generally known as the "Kinetic theory of gases." Now heat is defined as molecular motion. On heating, molecular vibration is increased and is reduced on cooling. When a gas with freedom to expand is heated, the more rapidly moving molecules require and take up more room. This constitutes expansion. If the gas is confined in a constant volume, then increased molecular vibration results in more molecular collisions on the side of the containing vessel. Hence the greater pressure. This is a simple view of the constitution of a gas and for the moment seems adequate, at least qualitatively.

Combining Boyle's and Charles's Laws. It now becomes possible to combine variations of volume due to both pressure and temperature changes in a single expression. Assume that a gas at V_0, T_0 and P_0 undergoes a change involving variation of all three factors, say to V_1, T_1 and P_1. Follow the change in two stages—

(1) Keep the temperature constant and vary the pressure from P_0 to P_1. Then the new volume will not be V_1, as this is only attained when the temperature has altered to T_1. Call this new volume v.

Then $$P_0 V_0 = P_1 v \text{ and } v = \frac{P_0 V_0}{P_1}$$

(2) Now vary the temperature to T_1 when—

$$\frac{v}{T_0} = \frac{V_1}{T_1}$$

Substitute the value of v thus—

$$\frac{P_0 V_0}{P_1 T_0} = \frac{V_1}{T_1}$$

Hence $$\frac{P_0 V_0}{T_0} = \frac{P_1 V_1}{T_1} = \text{const.}$$

That is, with a given mass of gas the product of the volume and pressure divided by the absolute temperature is constant. The expression takes the usual form of $PV = cT$. In this expression $c = $ a constant, the value of which depends upon the units of volume and pressure taken. Thus pressure might be referred to as grammes per square centimetre or pounds per square inch, while volume might be taken in terms of cubic

feet, cubic inches, or cubic centimetres. Also different quantities of the gases might be taken. Later all these possible variations will be replaced by constant units and quantities.

Avogadro's Law. In the foregoing we have not had any definite quantity of gas in mind. Avogadro in 1811 put forward the suggestion that the common behaviour of gases could only be due to a quantitative similarity. He expressed his conclusions as follows: "Under similar conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules." This original suggestion or hypothesis has been so abundantly established, and has provided one of the chief methods for the determination of the molecular weights of volatile substances, that it has long passed from the region of hypothesis to that of a well-established law. Imagine separate litre volumes of a number of gases. Each contains a very large, but according to Avogadro's law the same, number of molecules. The relative weights of the equal volumes are thus the relative weights of the individual molecules, a first important step in the determination of molecular weights.

Note that the law states "similar"—not necessarily exactly the same—conditions of temperature and pressure. Thus in two cases one gas, say hydrogen, might be at N.T.P.* Another gas, say oxygen, might, however, be under different individual conditions, with, for example, an increased pressure (reducing the volume) with a corresponding increase of temperature (increasing the volume), thus restoring the original volume. This compensation arises from the fact that Charles's law is a proportional law while Boyle's law is one of inverse proportion.

Determination of Molecular Weights. This may be dealt with briefly in passing. Without adducing the evidence, it may be stated that the molecule of hydrogen contains two atoms. Molecular hydrogen is therefore H_2. Take the atomic weight of hydrogen as unity. (More exactly it is 1·008 when the oxygen standard of 16 is adopted as is now the rule.) The molecular weight of hydrogen becomes 2. Now oxygen is sixteen times as heavy as hydrogen. Its molecular weight is therefore $16 \times 2 = 32$ and thus of a gas—

$$\text{Molecular weight} = \text{Density}_{(H = 1)} \times 2$$

* N.T.P. = Normal temperature and pressure, i.e. 0° C. and 760 mm Hg. pressure.

The Gas Constant. Now consider a molecular weight of a gas in grammes. This is briefly referred to as the gramme-molecule. This is 2 for hydrogen, 32 for oxygen, 28 for nitrogen and 44 for carbonic acid gas. The weight of a litre of hydrogen at N.T.P. is approximately 0·09 g. One gramme of hydrogen therefore occupies $1/0·09 = 11·11$ litres. The volume of the gramme-molecular weight is therefore $11·11 \times 2 = 22·22$ litres, from which it follows that the volume of a gramme-molecule of all gases at N.T.P. is 22·22 litres. This is a very important generalization arising from Avogadro's law.

Taking the gas equation—

$$PV = cT$$

we can now find the value of c, taking the gramme-molecule and standard units of pressure and volume. For the former, grammes per square centimetre, and for volume, cubic centimetres are adopted. For normal temperature and pressure—

$$P = 1\ 033\ \text{g/cm}^2,$$
$$V = 22\ 220\ \text{cm}^3$$

and $$T = 273°\ \text{A.}$$

Hence $$c = \frac{PV}{T} = \frac{1\ 033 \times 22\ 220}{273} = 84\ 000\ \text{approx.}$$

This gramme-molecular constant is usually designated R. The gas equation for the gramme-molecule becomes $PV = RT$ where $R = 84\ 000$. R is now a constant figure because definite units of volumes and pressures are used and also a constant quantity of the gas, viz., the gramme-molecule. Another point may in passing be noted. As

$$P = \frac{\text{grammes}}{\text{square centimetres}} \text{ and } V = \text{cubic centimetres}$$

$$PV = \frac{\text{grammes} \times \text{cubic centimetres}}{\text{square centimetres}} = \text{gramme-centimetres}$$

This quantity gramme-centimetres will be recognized as of like character with the foot-pound, and is thus a measure of work done during the expansion of a definite quantity of the gas under definite conditions. This is another matter which need not here be pursued in detail.

Definition of a Gas. We have now reached a point at which

a more accurate definition of a gas can be given. A gas has now to be regarded as that form of matter which conforms to this general gas equation and thus "obeys" the laws of Boyle, Charles, and Avogadro. If it *should* be found that a substance dissolved in water conforms to this equation there will be no alternative to regarding it as a gas, contained within the solvent.

Apparent Deviations from the Gas Laws. Now according to the law of Boyle, $PV = c$ and PV plotted against P gives the
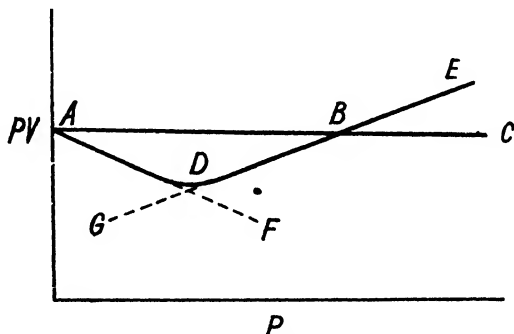

FIG. 13. DEVIATIONS FROM GAS LAWS

horizontal line represented as AC in Fig. 13. With high pressures, however, there are marked deviations from this straight line. These deviations are typified in the line $ADBE$. The exact form varies with different gases. The deviations merit some attention if only for the sake of correcting the simple notion of the constitution of the gas which we have already adopted.

From the curve $ADBE$ the descending portion AD represents a lower PV value. From D to E some opposite effect is apparent. At D these two effects exactly balance one another. It would appear that the portion AD is part of a curve which is continued with the dotted line DF while the portion DE requires completion with the dotted line GD. Let us briefly inquire into these new observations. We have so far assumed that the measured volume of the gas is the space in which the molecules are vibrating. Let us exaggerate the case. Suppose that the measured volume is 10 and the actual volume of the molecules

is 1. Then the space in which the molecules vibrate is only $10 - 1 = 9$. Presumably, therefore, we ought to be using $V - b$, where b represents the volume of the molecules instead of V. This would account for the depression. Moreover, with increased pressure or smaller volume there will be a larger proportional reduction accounting for the descent of the line.

Again, the individual molecules of all substances attract each other. In a solid this attraction gives the rigidity. In a gas there is very much less attraction between the widely separated molecules, but this is considerably increased with the diminution of inter-molecular distances accompanying reduction of volume occasioned by high pressures. On a molecule completely surrounded by other molecules, these attractive forces balance, but it may be imagined that with molecules on the surface of the containing vessel there is not this balancing effect. The inner molecules are pulling the outer ones and thus adding pressure to them over that observed of the pressure gauge. It appears then, that the observed pressure should be increased, giving an increased PV which becomes very prominent at high pressures. Hence the volume correction is more conspicuous from A to D where it is balanced by the pressure correction, after which the latter overtakes the volume correction. A quantitative treatment of these deviations due to Van der Waals is not called for here. It suffices for us to recognize that in the pursuit of scientific law simple ideas gathered over our first limited experience not infrequently need elaboration with widened experience. Too sweeping generalizations must not be made on limited data.

Thermal Dissociation. Another type of deviation from the usual gas behaviour is that occurring when the heated gas undergoes decomposition. Many substances decompose on heating and the products do not recombine on cooling. The reactions are not reversible. From the formula of sulphuric acid it might be assumed that the density of the acid vapour should be $98/2 = 49$. As a matter of fact it is only $24\cdot5$. This points to the vapour occupying twice the anticipated volume under standard pressure and temperature conditions. It is known that when the acid is boiled it undergoes decomposition as follows—

$$H_2SO_4 = H_2O + SO_3$$
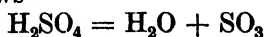
These products recombine on cooling. This reversible decomposition is called thermal dissociation, reversibility being expressed as follows—

$$H_2SO_4 \rightleftharpoons H_2O + SO_3$$
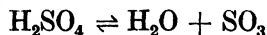
In the decomposed state there are twice as many molecules as would be anticipated. This, in accordance with the law of Avogadro, gives twice the volume and the observed density of one-half of that calculated from the formula.

Thus the method of determining molecular weights of volatile substances from their densities is only possible when vaporization takes place without decomposition. Numerous examples of thermal dissociation might be given, but we shall take one only for quantitative treatment.

Nitrogen peroxide at 22° C. is a light brown gas with a density of 46 (H = 1) and corresponding, therefore, to the formula N_2O_4. At 140° C. the density (after allowing for thermal expansion) is only 23, corresponding to the formula NO_2. The colour of the gas at this point is dark brown. Intermediate temperatures and densities are given as follows—

Deg. C.	22	26·7	60	100	140
Density $(_{H = 1})$	46	38	30	24	23

It would be of interest to know the degree of dissociation at the intermediate temperatures.

For a simple calculation let α represent the fraction dissociated. Then $1 - \alpha$ represents the undissociated portion. In this case—

$$N_2O_4 \rightleftharpoons 2NO_2$$
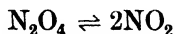
so that each dissociated molecule produces two molecules. The total number of molecules in the partly dissociated substance will then be—

$$1 - \alpha + 2\alpha = 1 + \alpha$$

These densities are being measured under constant pressure. According to Avogadro's law, molecules represent proportional volumes. With increased volume there is decreased density. Let D = original density (46 at 22° C.) and d the observed density of the partly dissociated gas. Then—

$$\frac{D}{d} = \frac{1 + \alpha}{1}$$

from which $\qquad \alpha = \dfrac{D - d}{d}$

and at 60° C. $\qquad \alpha = \dfrac{46 - 30}{30} = 0{\cdot}533$

Similarly, ammonium chloride on heating sublimes. During its passage from the solid through the gaseous and back to the solid state, it undergoes thermal dissociation thus—

$$NH_4Cl \rightleftharpoons NH_3 + HCl.$$

This is easily demonstrated by the fact that red litmus, held at the top of the tube in which the substance is being heated, turns blue, due to the presence of ammonia by reason of its more rapid rate of diffusion.

In a more general case, however, we may regard one molecule of the dissociated substance producing n molecules of products. The total number of molecules then becomes—

$$1 - \alpha + n\alpha = 1 + (n - 1)\,\alpha.$$

The degree of dissociation then becomes—

$$\alpha = \dfrac{D - d}{d(n - 1)}.$$

When $n = 2$, $n - 1$ becomes unity, and thus disappears, as is the case with nitrogen peroxide.

All these principles governing the behaviour of gases will find some application in a study of the properties of solutes. They affect, too, a wide range of operations some of which are of considerable industrial importance. Even steam is dissociated at 2 200° C. into its constituent gases. Hence these gases presented to each other at this elevated temperature show no sign of combination, let alone violent explosion. Further, in the oxyacetylene flame the temperature of which exceeds that of the dissociation of steam, the hydrogen of the acetylene remains free until the temperature of the flame is reduced, as it is in the outer zone. Hence the main reaction responsible for the exalted temperature of the flame is—

$$C_2H_2 + O_2 = 2CO + H_2$$
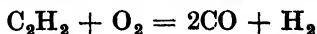
representing approximately equal volumes of acetylene and oxygen, a matter of well-known practice.

Partial Pressures. As solutions in some of which we are particularly interested are mixtures of substances, it may be of interest and value to consider the properties of mixtures of gases.

A simple case will be that of air which will be regarded as a mixture of oxygen and nitrogen in the usually stated proportions of one to four. We need to clarify our ideas as to the interpretation of this proportion. It is, for example, evident that both gases are equally diffused throughout each other. Put in another way, we may, indeed must, regard a litre of air as containing litres of each of the gases, the oxygen component being at one-fifth of an atmosphere pressure and the nitrogen at four-fifths of an atmosphere. Only when these components are withdrawn and each brought to atmospheric pressure are their volumes one-fifth and four-fifths of a litre respectively.

Obviously it is more correct to consider any volume of mixed gas as containing the same volume of each of the components, each with its particular or partial pressure. Moreover, the behaviour of these components is in many properties dependent upon these partial pressures. Take, for example, the solubility of the air in water.

At normal pressure oxygen and nitrogen separately dissolve in water to the extent of 4·8 and 2·0 cm³ respectively in 100 cm³ of water at 0° C. In air the oxygen is only under a pressure of one-fifth of an atmosphere and its solubility (measured in actual mass of the gas) or volume measured at normal pressure is only $\frac{1}{5}$ of 4·8 = 0·96 cm³, while that of nitrogen is $\frac{4}{5}$ of 2·0 = 1·6 cm³. Thus the total volume of air dissolved is 2·56 cm³, the dissolved air having the composition of—

$$\text{Oxygen } \frac{0·96}{2·56} \times 100 = 37·5 \text{ per cent}$$

$$\text{Nitrogen } \frac{1·6}{2·56} \times 100 = 62·5 \text{ per cent.}$$

It is thus generally stated that the solubility of a gas from a mixture is dependent upon its partial pressure. Shake a volume of air with water. Its oxygen is, in part, dissolved. Now add a considerable quantity of nitrogen, thus increasing the total internal pressure. The solubility of the oxygen remains

unchanged in spite of the increased total pressure, as the component, or part of the pressure due to oxygen and under which only oxygen dissolves, is unchanged. This independence of the constituents of a mixture is a phenomenon of considerable application in other mixtures, including solutions.

[NOTE. The volume of a gramme-molecule of a gas at N.T.P. is frequently stated to be 22·22 litres, while in other cases the figure 22·32 litres may be found. The former figure is based on the weight of a litre of hydrogen (at N.T.P.) being 0·09 g, while the latter figure finds its origin in the weight of a litre of hydrogen being taken as 0·089 6 g.]

PROPERTIES OF SOLUTIONS

Introduction. For present purposes a solution may be defined as a molecular mixture of two or more substances. Those of immediate interest will be mainly composed of solids and liquids, and occasionally gases, in some liquid solvent. This will therefore cover a wide range of electrolytic substances. With a dissolved solid the terms solvent and solute are clear. With two liquids such as sulphuric acid and water we must be a little more elastic in the use of these terms. More recently it has become the custom to refer to the solvent as the "dispersion phase," the solute then being called the "disperse phase." This wider definition admits of the application to colloids, in which the dispersed particles are not down to molecular dimensions and the mixtures are therefore not to be regarded as true solutions. (See Chapter XX.)

The Process of Solution. Some simple, yet very important, observations can be made when a quantity of salt is put into water. These are—

(a) *The Cooling Effect.* This is common to all examples of solution except those in which there is definite chemical action (such, for example, as the addition of sulphuric acid to water or the hydration of dehydrated copper sulphate). The preparation of the usual forms of freezing mixture involves this principle, and by the addition of salt to ice-cold water the temperature may easily fall to $-10°$ C. This cooling or absorption of heat would appear to be due to a change of state involving the transformation of sensible heat into molecular energy. One gramme of ice at $0°$ C. melts to water without rise in temperature with the absorption of 80 g. cal. This is the latent heat of fusion of ice. Further, 1 g of water at $100°$ C. absorbs 537 g. cal during its conversion to steam without increase in temperature. This is its latent heat of evaporation. The decrease in temperature during the process of solution would therefore suggest a change of state from the solid to, possibly, a form analogous to that of a gas.

(b) *Diffusion.* Solutes diffuse throughout the solvent in a manner akin to that of the spread of one gas either into a vacuum or throughout another gas. Gaseous diffusion is relatively rapid because of the freedom of the molecules. The diffusion of solutes is naturally very much slower on account of the much finer intermolecular spaces in the solvent as evidenced by the very small degree of compressibility of water.

Briefly, then, it may be said that it is a reasonable suggestion that a solid, in dissolving, assumes a form which appears to be similar to that of a gas.

The question arises: Is the solute in a gaseous form? If so, it will be amenable to the usual gas laws, including those of Boyle, Charles, and Avogadro. The real test lies in the application of the gas constant. To obtain this constant, a number of values are required. These include temperature (easily measured on a thermometer), volume or space in which the solute molecules move—this will be the volume of the solution, or possibly the volume of the solution, less the volume of the solute—the mass which is readily obtained, and, finally, the pressure exerted by the solute molecules. This last value seems to present the difficulty.

Osmosis. Now the diffusion of the solute is obvious. The solute spreads throughout the solvent through some inherent pressure. How is this to be determined? Gas pressure is only measured by preventing gas diffusion, either by the height of a mercury column or the strength of the spring of a gauge. If, for the moment, we accept the usual notion of the existence of ether,* then the gas whose pressure we measure seems like the solute in ether, which is the solvent. Measurement of gas pressure involves the use of a diaphragm impermeable to the gas but permeable to the ether. Is it possible to produce a diaphragm which will be able to prevent the passage of a solute while giving freedom of passage to the solvent and therefore not acquiring any of the solvent pressure? Such "semi-permeable" diaphragms, as they are called, are well known. They prevent the passage of the solute and thereby pick up the solute molecular bombardment, but allow of the

* A hypothetical but very attenuated medium by which radiant energy is transmitted from the sun and supposed to pervade all space and permeate all substances. Its existence provides a very useful working hypothesis in explaining a number of phenomena.

passage or "osmosis" of the solvent. The term osmotic pressure is defined as the pressure required to prevent osmosis. Osmosis is therefore primarily an effect of the solvent in or near the semi-permeable partition. An apparatus designed to show osmotic phenomena is called an osmotic cell, while if this is designed to record osmotic pressure it becomes an osmometer.

The Osmotic Cell. Many substances exhibit semi-permeable properties. These include copper and zinc ferrocyanides, silicic acid and calcium phosphate. Copper ferrocyanide was used for this purpose by Pfeffer in 1875. A film of this substance has no inherent strength with which to withstand the pressures to be measured. It is therefore prepared within the wall of a porous rigid substance, the purpose of which is merely to reinforce it.
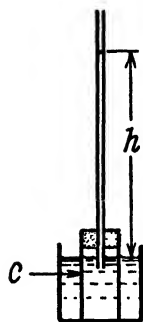
FIG. 14
OSMOTIC CELL

A simple type of osmotic cell is shown in Fig. 14. This consists of a small and clean porous cell (c) from the pores of which the air has been removed by boiling with water or preferably subjecting to diminished pressure under a pump. On releasing the suction, water takes the place of the air. This operation should be done as completely as possible. On it depends the continuity and therefore effectiveness of the semi-permeable partition to be produced within the walls of the cell.

The cell is now filled with a weak solution of potassium ferrocyanide (3 per cent) and stood in a beaker containing copper sulphate of equal strength. These liquids permeate the walls of the cell and, meeting, develop a thin film of copper ferrocyanide. Time must be allowed for the development of a sufficiently thick deposit, and special methods are followed to ensure this. Subsequently the cell is emptied and most thoroughly washed to remove all traces of the two salts. It is kept by standing in distilled water. Such films are readily observed when the cell is broken.

Into the cell is placed a 1 per cent solution of sugar. The cell is tightly sealed with a rubber stopper and is conveniently sealed with wax to, a depth of, say, half an inch from the top, where it is likely that the ferrocyanide film has been only imperfectly developed. Through the rubber stopper is a glass

tube as shown. The whole is now stood in water so that the levels outside and inside the cell shall be approximately the same. Assuming the success of the production of the semi-permeable membrane, there will be observed a rise of liquid within the tube. Normally we should allow this to proceed to completion, that is, until the column becomes stationary. The column of liquid within the tube must have been the result of the entry of liquid through the copper ferrocyanide film, thus developing pressure within the cell. The stationary column (h) represents the hydrostatic pressure to prevent the further flow of solvent into the cell and is therefore a measure of a difference of pressure which occasioned this flow. Quite astonishing heights of columns are obtained. For example, a 1 per cent solution of sugar would, under the best conditions, give rise to a column no less than 20 ft high, though more exact figures will be given later.

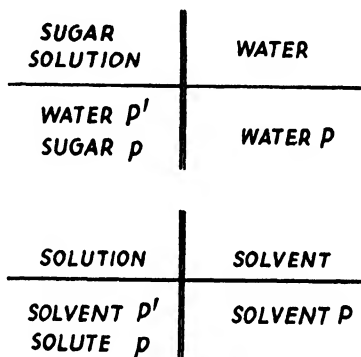| SUGAR SOLUTION	WATER
WATER p' SUGAR p	WATER P
SOLUTION	SOLVENT
SOLVENT p' SOLUTE p	SOLVENT P

FIG. 15

We trace the origin of this pressure in the following manner: The water on the outside of the cell is a single substance (Fig. 15). The solution inside has two components, water and sugar, each part of the mixture developing its own or partial pressure. In the first instance their total pressures are the same, say, P. The original pressure of the water on the solution side is obviously less. Call this P' and the pressure exerted by the solute p. Then—

$$P = P' + p, \text{ i.e. } p = P - P'$$

Thus water passes through the membrane under a pressure equal to that exerted by the solute, and this is therefore measured as the hydrostatic pressure of the stationary column of liquid, which prevents further osmosis. This hydrostatic column is obviously inconvenient in its height, and it may be replaced by a mercury column reducing the height by a figure expressing the density of mercury, viz. 13·6 (Fig. 16). Mercury

can be added to the longer limb of the tube to maintain liquid at its original level, thus preventing osmosis. Alternatively, especially where very high osmotic pressures are concerned, a pressure gauge is substituted, and these osmotic pressures sometimes go up to some hundreds of atmospheres. The manipulative details are, however, not of immediate interest.

The interpretation of the results is of greater importance in the development of the study of electrochemistry.

As far back as 1875 Pfeffer made measurements on these lines. Working with different sugar solutions at constant temperature he obtained the following results—
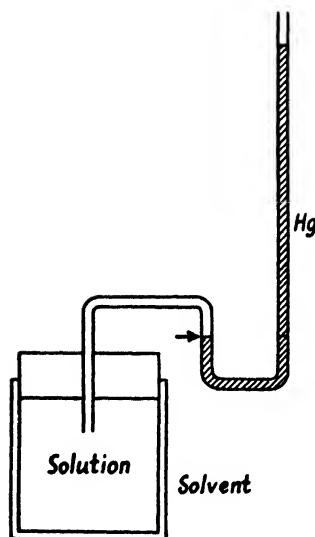
Per cent Sugar	Os. P. (cm. Hg.)
1	53·6
2	101·6
4	208·2
6	317·5

Fig. 16

from which it will be seen that the osmotic pressure is proportional to the concentration of the solute. Now concentration increases as the volume containing the same mass decreases, and thus we can say that the osmotic pressure is inversely proportional to the volume of a given mass of the solute. This, with a little thought, will be recognized as conforming to Boyle's law, indicating that the solute is probably in the gas form.

Similar experiments were made with a solution of constant strength but varying the temperature. Pfeffer obtained the following results—

Temp. ° C.	Os. P. (cm. Hg.)	Os. P. / Abs. Temp.
6·8	50·5	0·180
13·5	52·1	0·182
14·2	53·1	0·185
22·0	54·8	0·186

from which it becomes apparent that osmotic pressure increases with the absolute temperature, again agreeing with the behaviour

of gases. These results have been abundantly confirmed by many experimenters using many other solutes. They definitely lead to the conclusion that a solute is behaving in an atmosphere of the solvent in exactly the same manner as the molecules of a gas in the ether.

Much more elaborate methods were later worked out for a more detailed investigation of the phenomena and Table V gives some more accurate results which were obtained by Morse

TABLE V

OSMOTIC PRESSURES OF SOLUTIONS OF CANE SUGAR (MORSE)

Conc. (Gramme-molecules per 1 000 g Water)	Osmotic Pressures at Different Temperatures (Atm)				
	0° C.	10° C.	20° C.	30° C.	40° C.
0·2	4·72	4·89	5·06	5·04	5·16
0·4	9·44	9·79	10·14	10·30	10.60
0·6	14·38	14·85	15·40	15·71	16·15
0·8	19·48	20·16	20·90	21·37	21·80
1·0	24·83	25·69	26·64	27·22	27·70

with solutions of cane sugar of different concentrations and at different temperatures. Simple calculations will show how closely they conform to the behaviour which might be anticipated if the solute is in a form analogous to that of a gas.

Application of the Gas Law to Solutes. The matter can be tested quantitatively by ascertaining if the usual gas constant holds for molecular quantities of the solute. Take from the figures given above the following: A 1 per cent solution of cane sugar at 6·8° C. gives an osmotic pressure of 50·5 cm of Hg. The 1 per cent solution may be taken as containing 1 g of the sugar in 100 cm³ of solution. The gramme-molecule would therefore be contained in ($C_{12}H_{22}O_{11}$ = 342) 34 200 cm.³ The osmotic pressure is 50·5 × 13·6 g/cm.² From the gas equations we have to find the value of the constant

$$R = \frac{PV}{T} = \frac{50 \cdot 5 \times 13 \cdot 6 \times 34\,200}{(273 + 6 \cdot 8)} = 83\,900$$

and this must be taken as a sufficiently close agreement to justify the conclusion that, by the most exact definition of a

gas, the behaviour of the sugar solute confirms the suggestion that it is in a quantitatively analogous form. This idea is of considerable value in the development of the conception of the processes of electrolysis.

Determination of Molecular Weights. Here, it would appear, is a method for the determination of molecular weights of substances which, on account of decomposition at elevated temperatures, that is before or on volatilization, are not amenable to the application of the law of Avogadro to the substance in the form of a gas obtained by thermal methods. Thus in solution form, the molecular weight will be that mass which dissolved in 22·22 litres of water will at 0° C. give an osmotic pressure of one atmosphere.

Militating against the application of the method, however, is the difficulty of preparing semi-permeable membranes of sufficient continuity and strength to withstand the pressures involved, and this method is therefore one only capable of manipulation in the hands of the expert.

Definitions. We have already used the term "osmotic pressure" in a manner indicative of the pressure under which a solute diffuses from a stronger to a more dilute solution. This is, perhaps, a loose application of the term. It will be appreciated from the method of measurement that this diffusion is determined not directly, but indirectly by opposing the passage of the solvent into the stronger solution. In fact it could be argued that osmotic phenomena are not exhibited without the presence of a semi-permeable membrane, and are in fact the changes occurring about that semi-permeable partition. Thus osmosis may be more correctly defined as the passage of solvent through a semi-permeable membrane from a dilute to a stronger solution, this definition therefore including the case of the pure solvent as an extremely dilute solution. Osmotic pressure thus becomes the pressure necessary to prevent osmosis in a given system. Though the numerical expression of the osmotic pressure is independent of the definition, the latter expression of the phenomena seems more correctly to fit the observed facts. The term osmotic pressure is, however, frequently used to indicate diffusion pressure and should occasion no misconception in this application.

A simple explanation of the process of osmosis is that the semi-permeable membrane acts as a filter, allowing the passage of the smaller solute molecules and not the larger solute molecules. This is called the "sieve" theory. It is inadequate in that many solutes and ions which are also present are not sensibly larger than the somewhat complex solvent molecules. An alternative suggestion is that the membrane acts by the process of selective solubility. The solute molecules are soluble in the membrane, are absorbed by it, and thus pass through, while the solute is insoluble in the material of the membrane. There appears to be some experimental support for this idea. Into a vessel introduce successive layers of chloroform, water, and, on the top, ether. Chloroform and ether are miscible but separated by the water. Chloroform is immiscible with water, while ether is slightly soluble in water. The ether at the top is absorbed by the water and passes on to the chloroform. The top layer of ether slowly diminishes, while the layer of chloroform increases in depth by reason of the ether which has passed through the water. This seems a reasonable explanation, even if it has no immediate application.

MEASUREMENT OF HIGHER OSMOTIC PRESSURES

For the measurement of greater osmotic pressures, Morse and Fraser took more care in the preparation of their ferrocyanide membranes. They employed the method of passing a current through the two solutions contained inside and outside the porous pot, this method more effectively bringing together the copper and ferrocyanide ions within the walls of the pot. The production of thicker and better diaphragms enabled these workers to measure much greater osmotic pressures and thus to extend the range of observation to much stronger solutions with, as will be seen, some interesting and useful results.

A further development of the osmometer is due to Earl Berkeley and E. G. J. Hartley, whose apparatus is diagrammatically shown in Fig. 17. This diagram is sufficiently explanatory, and from it it will be realized that the solution surrounding the semi-permeable partition is subjected to pressure in order exactly to balance the tendency of the water within the

tube to pass by osmosis into the solution. The results obtained by this method checked up with those of Morse and Fraser, and took the investigation of osmotic phenomena into the realm of very strong solutions, the apparent abnormalities of which will call for attention in the solution of problems which are outside the range of the simple laws first observed.

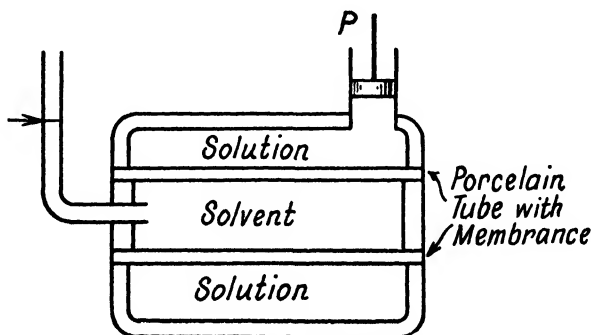**Abnormal Osmotic Pressures.** We must apparently always be on the look-out for abnormal behaviour of certain classes of

FIG. 17. BERKELEY'S AND HARTLEY'S OSMOMETER

compounds. These abnormalities call for extensions of our conceptions, when they can be seen to fit in with the general scheme. With osmotic pressure such abnormalities are of two general types. There are, for example, those which are slightly in excess of the values anticipated by the application of the gas laws, while with other examples the excessive values are considerable.

Illustrative of the first type the figures shown in Table VI may be given. This table includes results which have been obtained experimentally together with others which have been calculated. On the latter point, however, there arises the difficulty as to whether we ought to take the volume of the solvent or that of the solution. The figures include those calculated by both methods. Column (5) gives the calculated results on the assumption that the sugar occupies the same volume as the solvent, while column (4) gives the calculated results on the assumption that the solute occupies the volume

of the solution. It will be seen that the former are nearer the results obtained experimentally.

TABLE VI

SUCROSE $[C_{12}H_{22}O_{11}]$ AT $15°$ C.

Gramme-molecules per 1 000 g Water	Gramme-molecules per 1 000 cm^3 Solution	Osmotic Pressures (Atm)		
		Observed	Calculation I	Calculation II
0·1	0·098	2·48	2·31	2·36
0·2	0·192	4·91	4·53	4·72
0·4	0·369	9·78	8·71	9·44
0·6	0·533	14·86	12·58	14·16
0·8	0·684	20·07	16·14	18·88
1·0	0·825	25·40	19·49	23·63
(1)	(2)	(3)	(4)	(5)

Further, excessive osmotic pressures may be due to the possible combination of the solute with some of the water, there then being less water functioning as solvent. There is considerable evidence of the existence of such loose compounds in aqueous solutions, and from the decreased solubility of certain gases in water to which a solute has been added it is possible to calculate what is called the degree of "hydration" (see page 310). A more general term is that of "solvation," implying the loose combination of any solute with the solvent. This aspect can be considered later, but it would account for osmotic pressures somewhat in excess of those anticipated.

Osmotic Pressure of Electrolytes. The second case concerns substances which in aqueous solution form electrolytes, that is, they conduct electricity, generally with concomitant chemical change.

These abnormalities are considerable. For example, a normal solution of potassium chloride (containing 74·5 g KCl per litre) gives an osmotic pressure of the order of 39 atm. Ordinarily, we should expect a much smaller value, which is obtained in the following manner: If the gramme-molecule of KCl occupied 22·32 litres, then at $0°$ C. it should give a gas pressure and therefore osmotic pressure of 1 atm. In the solution containing one gramme-molecule of KCl in 1 litre there

should be a corresponding increase in pressure to 22·32 atm. The observed figure, however, is more nearly 39 atm. Similarly, a normal solution of copper sulphate shows an osmotic pressure which is nearly one and a quarter times that anticipated from calculation based on the known behaviour of simple organic substances such as sugar, from which the simple laws of osmotic pressure were deduced. In the case of these two substances, these abnormal osmotic pressures vary between the theoretical value and twice that figure. Potassium sulphate, on the other hand, gives excessive results up to, but not exceeding, three times the theoretical value. Moreover, these abnormalities increase with dilution.

The simple explanation of this behaviour is that such molecules are separated into ions in water solution. These ions, as separate entities, function as molecules. These charged masses in the case of sodium chloride can never exceed twice the number of the original molecules, and this maximum is only approached in very dilute solutions. Again, the following expression—

$$K_2SO_4 \rightleftharpoons 2K^+ + SO_4^{--}$$
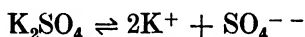
indicates that each molecule of potassium sulphate gives rise by "electrolytic dissociation," as the process is called, to not more than three ions. Finally it might be possible from the excessive osmotic pressure to compute the extent to which such dissociation has taken place. This is a matter which can be referred to later to greater advantage, but we have at least some reasonable suggestions to account for the abnormal behaviour of some substances when examined from the point of view of osmotic pressure.

Freezing-point of Solutions. It is well known that the freezing-point of a solution is markedly lower than that of the solvent. Salt solutions can be taken down to $-20°$ C. or lower without freezing, and it is common practice to make an addition to the water of a radiator of a motor-car to prevent freezing with its accompanying damage.

The phenomenon has been exhaustively explored, and a number of simple laws enunciated.

The method of Beckmann is standard for exploring this effect. The apparatus is shown in Fig. 18. The inner tube

contains the solution under investigation, into which is immersed the bulb of a thermometer reading to 0·01° C. A stirrer is also provided to maintain constancy of temperature.

Cooling is effected by a freezing mixture contained in the outer glass jar containing broken ice with a good sprinkling of common salt. With this a temperature of $-10°$ C. can easily be obtained, and this suffices for most purposes. A Beckmann thermometer is an adjustable thermometer in which the quantity of the mercury can be varied according to the range of temperature over which it is to be used. This variation of the mercury contents of the bulb is readily effected, a larger quantity being required for lower temperatures, while a smaller amount suffices for the measurement of higher temperatures. The thermometer scale usually covers a range of about 5° C. Distilled water, previously cooled down near to its freezing-point, is introduced into the tube immersed in the freezing mixture. Cooling must be accompanied by stirring. The temperature of the distilled water falls, and sooner or later

Fig. 18

becomes stationary. This usually represents super-cooling. Rapid stirring or, more usually, the introduction through the side limb of a small crystal of ice, then effects freezing with a temperature rise until it becomes stationary, this being the freezing-point of the water. On removing the tube, ice crystals will be observed. This stationary temperature is noted. The ice crystals are then allowed to melt and the freezing process repeated to obtain a more accurate average of two or three
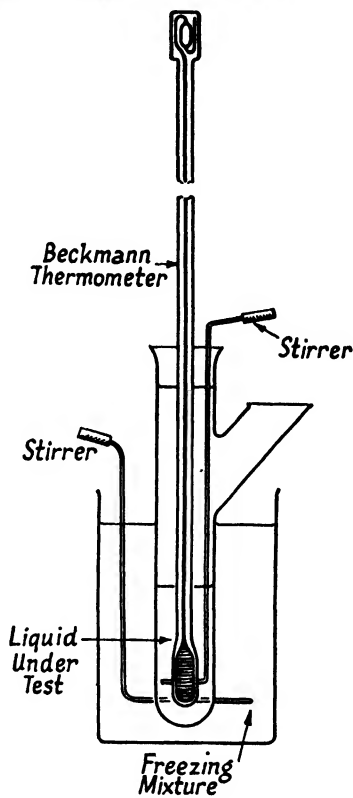
observations. This represents on the thermometer scale 0° C. The thermometer is thus calibrated.

The distilled water is now replaced by the solution under test, and the cooling and freezing process repeated. A larger degree of super-cooling will probably be observed, but a constant freezing-point will be readily obtained and checked by a repeated test. The thermometer records this temperature from which the depression of freezing-point is obtained by subtraction.

The first law expresses the fact that the depression or lowering of the freezing-point of a solvent is proportional to the
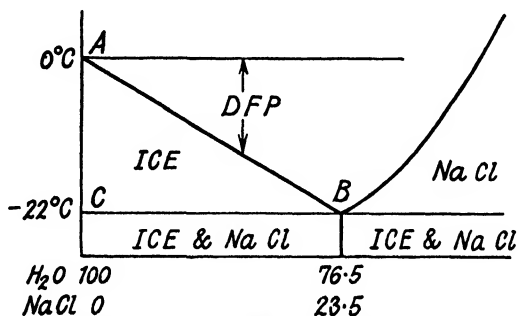
FIG. 19. FREEZING-POINTS OF SODIUM CHLORIDE SOLUTIONS

concentration of the solute. This in the case of sodium chloride is illustrated by the line AB in Fig. 19.

Secondly, there is a maximum depression, which in this example is indicated by the point B, corresponding to a solution containing 23·5 per cent of salt in 76·5 per cent of water.

With still stronger solutions the freezing-point is again raised, but freezing consists in the separation of salt and not solvent. This is the well-known process of crystallization.

Again, all solutions of sodium chloride below 23·5 per cent strength have two definite freezing-points, the higher one at which ice begins and continues to form, and a lower one at which the whole of the unfrozen materials, both solute and solvent, freeze out together. The higher of the two freezing-points is reduced with increasing concentration of solute, while the lower is constant for all mixtures. The particular

composition which has this one and only lowest freezing-point is known as the "cryohydrate." Below this concentration freezing first consists in the crystallization of the solvent, in this case, water as ice. Above this concentration freezing consists in the separation, or crystallization as it is more usually called, of the solute. Thus the area ABC represents the conditions for the separation of ice.

These phenomena have their almost exact analogue in the case of a number of mixed metals or alloys, in which the first desirable property of a solder is that it should have a melting-point considerably lower than that of the metal to be soldered.
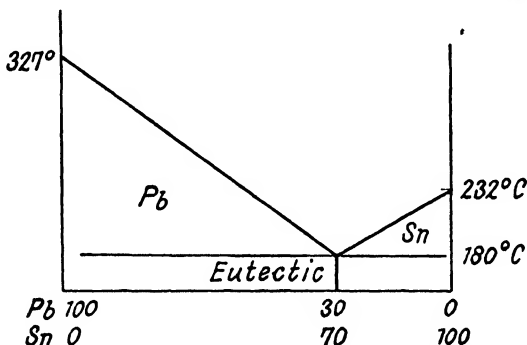
FIG. 20. FREEZING-POINTS OF LEAD-TIN ALLOYS

The behaviour of the lead-tin series of alloys is shown in Fig. 20, and is in almost every sense exactly comparable with the behaviour of common salt solutions. Here the alloy with the lowest melting-point is known as the "eutectic," and in this case is one containing approximately 70 per cent of tin and 30 per cent of lead. It will be seen from the diagram that the addition of relatively high melting-point lead appreciably lowers the melting-point of the lower melting-point tin. Proportionality with the addition of each to the other is indicated by the sloping straight lines, the eutectic melting at about 180° C. With less than 70 per cent tin, freezing consists of the crystallization of the lead in excess of the eutectic composition, while with more than 70 per cent tin freezing is first the crystallization of the tin which is in excess of this eutectic composition. The choice of a solder for tin goods is definitely

limited to the eutectic mixture, the usual composition being that of two parts of tin to one of lead. Again the mixture of two parts of lead to one of tin for plumber's solder is determined by (1) the lower melting-point of this alloy in comparison with that of lead, and (2) a definite range of temperature from 250° to 180° C. during which the alloy passes from the liquid to the solid state, giving the plumber time to "wipe" his joint.

Reverting to solutions, however, it was next observed that what are called equi-molecular solutions give the same depression of freezing-point. One interpretation of "equi-molecular" is that in separate litres of water, gramme-molecular quantities of various substances are dissolved. Molecular quantities by mass represent equal numbers of molecules. Another interpretation of the term, however, is that of a solution in which there is an equal number of molecules of both solute and solvent. This interpretation may be of use in the general theoretical treatment of the subject, but will, of course, be outside the range of practical work, involving the solution of a gramme-molecular weight of sugar ($C_{12}H_{22}O_{11}$) or 342 g in a gramme-molecular weight of water or 18 g. The former interpretation will be applied in the present consideration.

Raoult's Law then states that equi-molecular solutions give the same depression of f.p. For example, 342 g of cane sugar dissolved in 1 litre of water will provide a solution of the same freezing-point as that of a solution containing 180 g of a sugar of the $C_6H_{12}O_6$ type. This depression of freezing-point is 1·86° C. If we exclude electrolytes, the law has a very general application. Given an accurate method of determining freezing-points, we are provided with a method of determination of the molecular weights of many substances which cannot possibly, owing generally to decomposition, be subjected to vapour density methods, and by the freezing-point method the molecular weight will be that weight which, dissolved in 1 000 g of water, will give a solution with a freezing-point of —1·86° C. This figure, 1·86° C., is called the "molecular depression" of freezing-point of water.

Further, the same phenomena are observed with other solvents, bringing into the range of freezing-point determination many organic substances which are not soluble in water. Each of these solvents has its own molecular depression (K), these

values, all in terms of the gramme-molecule of the substance in 1 000 g of solvent, being shown in Table VII.

TABLE VII

MOLECULAR DEPRESSION OF FREEZING-POINT

Solvent	F.P. (° C.)	K	$\dfrac{0 \cdot 002 T^2}{L}$
Water	0	1·86	1·86
Benzene . . .	5·5	5·12	5·07
Acetic acid . .	17	3·90	3·82
Phenol	39	5·30	5·05
Naphthalene . .	80	6·90	6·95

The expression in the end column of this table was derived by Vant Hoff by thermodynamical reasoning as the relation of the molecular depression of freezing-point with other physical properties of the various solvents. In the expression T represents the freezing-point on the absolute scale, while L represents the latent heat of fusion. In the case of water the calculation is as follows—

$$\frac{0 \cdot 002 \cdot T^2}{L} = \frac{0 \cdot 002 \times 273 \times 273}{80} = 1 \cdot 86$$

this being a remarkably close agreement with the experimentálly determined figure.

Electrolytes and Freezing-points. It is to the behaviour of electrolytes that we must give the greater attention. Again, they behave abnormally, giving excessive molecular depressions of freezing-points, and, moreover, from these excessive depressions it is possible to estimate with accuracy the degree to which this dissociation has taken place. The depression of freezing-point is proportional to the number of molecules and ions present.

In the case of a simple electrolyte like NaCl we have—

$$\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$$

each dissociated molecule producing two ions. Let α be the fraction of the whole which is dissociated.

$$\underset{1-\alpha}{\text{NaCl}} \rightleftharpoons \underset{\alpha}{\text{Na}^+} + \underset{\alpha}{\text{Cl}^-}$$
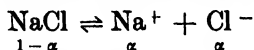
That undissociated is therefore $1 - \alpha$ which, with 2α ions,

give a total of $1 + \alpha$ individual parts. If the molecular depression of the electrolyte is t'° C. while that of a non-electrolyte is t° C. then—

$$\frac{t'}{t} = 1 + \alpha$$

from which

$$\alpha = \frac{t' - t}{t}$$

The figures given (Table VIII) will provide an illustrative case for sodium chloride—

TABLE VIII

FREEZING-POINTS AND DISSOCIATION OF NaCl

Normality of Solution	Freezing-points		Degree of Dissociation
	Calculated for Non-electrolytes	Observed	
0·001	0·001 86	0·003 7	0·989
0·01	0·018 6	0·035 4	0·903
0·1	0·186	0·342	0·839

Inasmuch as these freezing-point determinations are susceptible of great accuracy, the course of dissociation can be readily followed by this method. We shall have occasion to revert to this subject. It will be seen that in the case of electrolytes producing two ions these observed depressions lie between that for non-electrolytes and twice this value, while for electrolytes producing three ions the observed values lie between the theoretical (non-electrolytes) and three times this value.

A method is therefore available for tracing with accuracy the progress of dissociation with dilution. There ought to be other methods giving completely confirmatory results. One of these will be forthcoming by a study of the conductance of these electrolytes.

Boiling-point of Solutions. In passing, reference may also be made to the fact that solutions boil at temperatures in excess of those of their solvents. The phenomena have been studied on the same lines as those of the depressed freezing-points with, it may be said, much the same results. Boiling-points are

elevated proportionally to the concentration of the solute, and are subject to much the same laws as regards molecular concentrations, except that the values differ sometimes markedly. For example, a gramme-molecule of a substance in 1 000 g of water gives an elevation of boiling-point of 0·52° C. as against the depression of freezing-point of 1·86° C. Further, electrolytes give similar abnormalities due to dissociation. The principle is not, however, amenable to the same degree of experimental accuracy, as the determination of a boiling-point involves some loss of the solvent with a corresponding change of concentration.

The elevation of boiling-point and also the depression of freezing-point can be deduced from the reduced vapour pressure of the solvent in association with the solute, in view of the attractive forces of the solute molecules, thereby increasing the difficulty of separating the solvent molecules either by evaporation on boiling or crystallization on freezing.

ELECTROLYTIC CONDUCTANCE

Introduction. A study of the conductance of electrolytes naturally constitutes an important step in the development of any conception of the mechanism of the process of electrolysis. For this purpose a clear statement and definition of a number of relevant terms is essential.

Conductance in solids is termed metallic or electronic conductance, and is due to the movement of electrons from atom to atom. Electrolytic conductance is concerned with the movement of comparatively massive ions, of which electrons form a very small part. There are, however, some peculiar cases. The silver halide compounds are solid, yet conduct electrolytically: while in the case of β silver sulphide, which is stable below 179° C., 80 per cent of its conductance is electrolytic and 20 per cent metallic. A similar phenomenon is met with in a number of metallic compounds at elevated temperatures below 200° C.

Both electrolytic dissociation and ionization may be more correctly regarded as the acquisition by the ions, always existent in the solid, of greater mobility and, therefore, freedom of action by the processes of fusion, vaporization, and solution, giving rise to electrical conductivity in the three different states.

Definitions. By resistance is generally understood the opposition offered by all substances to a greater or lesser extent to the passage of electricity. It is expressed in terms of ohms, the ohm being defined as the resistance of a column of mercury 14·45 g in mass, of uniform cross-sectional area, and 106·3 cm in length at 0° C. In terms of Ohm's law it is expressed as E (volts) $\div I$ (amperes) or as volts per ampere. For the purposes of reasonable comparison a dimensional value is taken when the resistance of a centimetre cube (a length of 1 cm with any uniform cross-section of 1 cm²) is adopted, the resistance of this shape of a substance being known as its specific resistance. An alternative term, not much used, is

resistivity. For the metals the values are small and conveniently expressed in millionths of an ohm or microhms, the value for copper being $1 \cdot 6 \mu\Omega$. Those of solutions are sufficiently large to justify the use of the ohm as the unit.

As is well known, the resistance of a conductor is proportional to its length and inversely proportional to its cross-sectional area. Hence—

$$\text{Resistance (ohms)} = \frac{\text{Specific resistance (ohms)} \times l}{a}$$

all dimensions being expressed on the centimetre scale. Conversely, the term conductance may be regarded as expressing the facility with which electricity flows through a conductor. It will be the reciprocal of the resistance. Hence—

$$\frac{K}{\text{(conductance)}} = \frac{1}{R} = \frac{1}{E/I} = \frac{I}{E}$$

Conductance is therefore expressed as the amperes per volt, this unit being more briefly referred to as the Mho. All conductance figures will carry this conception of amperes developed per volt applied. For the specific conductance, that is, the conductance per centimetre cube, there is the alternative term, and one which is most commonly used, of conductivity, this always and only referring to the conductance per centimetre cube. Conditions of length and sectional area are embodied in the following expressions—

$$\frac{k}{\text{(conductivity)}} = \frac{K \times l}{a},$$

where K is the current developed per volt in a given volume of the substance. The specific resistances and conductivities of a number of metals, and solutions of normal strength, are given in Table IX.

From these figures there is no difficulty in differentiating between the magnitudes of metallic and electrolytic conduction, the data showing that the conductance of copper is 3 000 000 times that of normal sulphuric acid. The resistance of metals generally increases with a rise in temperature. The fractional increase per degree C. over that at 0° C. is called the temperature

coefficient. On the other hand, that of carbon decreases, as also do those of electrolytic solutions.

TABLE IX

SPECIFIC RESISTANCES OF METALS, ALLOYS, AND SOLUTIONS

Metal	Specific Resistance ($\mu\Omega$/cm^3)	Temperature Coefficient	Specific Conductance (mho)
Silver . .	1·6	0·004	602 000
Copper . .	1·6	0·004 3	602 000
Gold . .	2·06	0·004	467 000
Aluminium .	2·9	0·003 8	332 000
Zinc . .	5·75	0·003 7	167 500
Platinum .	8·9	0·003 8	108 200
Nickel . .	12·4	0·006 2	77 700
Lead . . .	20	0·004 3	48 160
Mercury .	100	0·000 9	9 632
Manganin .	53	nil	18 200
Platinoid .	42	0·000 25	23 000
N. H$_2$SO$_4$.	5 050 000		0·198
N. KOH .	5 430 000		0·184
N. KCl .	10 180 000		0·098 2
N. NaCl .	13 450 000		0·0743 5

A unique feature of metallic conduction is the fact that a number of metals at a very low temperature—of the order of $-268°$ C. to $-270°$ C.—seem to lose electrical resistance almost entirely. This fact was observed by Onnes in 1911. Among these metals are lead, tin, aluminium, and zinc. The phenomenon is called super-conductivity. At these very low temperatures, these metals conduct very heavy current densities without showing appreciable heating effects.

Measurement of Conductance. It will be assumed that the student is familiar with the usual methods of measuring resistance. For a coil of wire a simple and approximate method is that of noting the p.d. required to produce 1 A in the coil. Obviously from Ohm's law, any voltmeter and ammeter readings across the coil will yield the required result. Much more accurate results are, however, to be obtained by the application of the principle of the Wheatstone bridge which, with its variants, provides the basis of most resistance

measurements. In any case some care must be taken to maintain constant temperature, and this involves thermostatic control of the material under test. The application of the principles to the determination of the resistance of electrolytes needs some little explanation, especially as, in the case of these substances, the passage of current, with changes of composition or concentration of the electrolyte, introduces difficulties not met in the case of conductors of the metallic class.

Use of Direct Current. Imagine a cell fitted as shown in Fig. 21. It is of glass and contains copper sulphate solution, two parallel copper electrodes at opposite ends filling the section of the cell, and these electrodes are at an easily measurable · distance from each other. An ammeter and voltmeter give the required readings while the uniform sectional area of the solution may be more accurately measured by dividing the volume (cubic centimetres) by the inter electrode distance (l). The following are typical figures obtained with a copper sulphate solution of normal strength—

FIG. 21. CONDUCTIVITY BY DIRECT CURRENT

$$E = 4 \cdot 65 \text{ V}$$
$$I = 0 \cdot 15 \text{ A}$$
$$l = 20 \text{ cm}$$
$$\text{and } a = 25 \text{ cm}^2$$

from which the conductivity is—

$$k = \frac{I}{E} \times \frac{l}{a} = \frac{0 \cdot 15}{4 \cdot 65} \times \frac{20}{25} = 0 \cdot 025 \, 8 \text{ mho}$$

The method, however, is of very limited use. At least two adverse circumstances militate against its reliability. However small the current, there are changes in the concentrations of the solutions near the electrodes. That at the anode becomes stronger, making it somewhat more difficult for copper to pass into solution. That at the cathode becomes weaker, making it
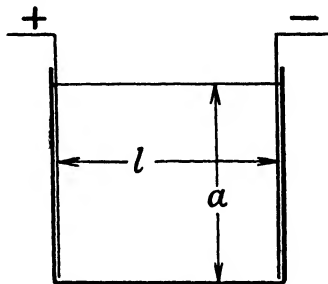
more difficult to deposit copper. This combined difficulty is something more than that of the ohmic resistance of the solution. It is called "concentration polarization," to which later reference must necessarily be made.

Again, the assumption is made that the reactions at, say, the anode are exactly those anticipated, viz. that copper is dissolving according to Faraday's law and therefore that no alternative chemical action is occurring. This is seldom realized. In all but a very few cases, other chemical actions occur at the electrodes, introducing what is generally known as "chemical polarization." For the purpose of measuring resistance these polarizations should be entirely absent and no
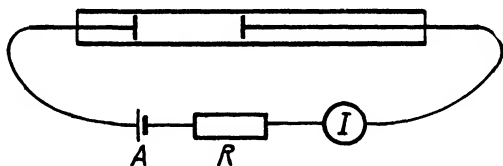
FIG. 22. CONDUCTIVITY BY DIRECT CURRENT

resistance should be present save that of the ohmic resistance of the electrolyte.

Alternative Method. An alternative method with a view to removing or at least considerably diminishing these defects is that of the use of a long tube (Fig. 22) containing the electrolyte with electrodes filling the section of the tube and being adjustable with reference to inter-electrode distance. The diagram also shows an adjustable resistance (R) with current indicator (I) and source of current (A). The average diameter of the tube is calculated from the length of a known volume of solution put into it. The electrodes are placed at a convenient distance and current generated to give a reasonable reading on the indicator. The inter-electrode distance is measured and the electrodes then moved further apart. This increases the resistance and reduces the current shown on the indicator. Resistance is now taken out by the adjustable rheostat (R) until the current is restored to its former value, when the total resistance of the circuit has also been brought back to its original value. The resistance taken out represents the added resistance by the further spacing of the electrodes. In an

experiment with normal copper sulphate, a reduction of resistance by 132 Ω was necessary to restore the original current when the inter-electrodes space was increased by 6 cm in a tube of 1·5 cm diameter.

$$R = r \times l/a \text{ or } r = R \times a/l$$

$$r = \frac{132}{6} \times \frac{22}{7} \times \frac{3}{4} \times \frac{3}{4} = 38\cdot8 \, \Omega$$

$$\therefore \quad k = 1/r = 1/38\cdot8 = 0\cdot025\,8 \text{ mho}$$

In both cases the current is the same and any deviations from Ohm's law by slight polarizations may be taken as the same in both cases. The added resistance of the solution is therefore a truer value of the resistance of the added length of solution from which the specific resistance can be calculated.

Thus, the addition of a further 10 cm of normal copper sulphate solution into the inter-electrode space in a tube of 1 cm^2 in section will necessitate the withdrawal of 388 Ω from the resistance box equivalent to 38·8 Ω per centimetre length and square centimetre in section. This, therefore, is the specific resistance of the solution.

With this refinement, however, the applications of direct current are still very limited, and recourse must therefore be made to the use of alternating current.

The A.C. Method. This follows the lines of the Wheatstone bridge method, with the substitution of a suitable induction coil in place of the battery cell and of the use of a telephone in place of the galvanometer or other current-detecting device.

Alternative arrangements of the apparatus are diagrammatically shown in Fig. 23, in which *ab* represents the standard uniform wire, *R* is the cell of which the resistance is required, while *IC* is the induction coil replacing the battery cell, *T* the telephone and *SR* standard resistances. Resistances of electrolytic solutions generally run into high figures, hence the usual replacement of the slide wire bridge with some type of Post Office box, the details of which are available from other sources.

For electrolytic measurements the induction coil should develop a high-pitched audible note of a frequency of 500 to 1 000 c/s. With low frequencies there would be the possibility of slight electrolytic action at one or both of the electrodes.

With such rapid reversals of the current chemical actions are reduced to negligible amounts, and the only resistance measured is therefore that of the electrolyte.

It must not, however, be supposed that the troubles attaching to the accurate determination of electrolytic conductance are solved by the use of any induction coil. These not infrequently give unsymmetrical currents and thus introduce the possibility
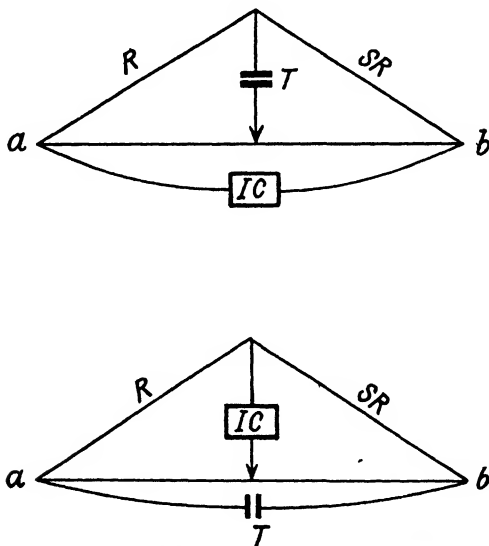

FIG. 23. CONDUCTIVITY BY A.C. (DIAGRAMMATIC)

of a limited degree of polarization. The telephone is a noisy instrument to use and there is difficulty in determining when the noise is at a minimum.

The use of the induction coil for conductivity measurements is thus open to criticism in that (1) it is difficult to maintain constant frequency, and (2) it is not easy to produce an exactly symmetrical wave. Hence, more recently, it has been replaced by the thermionic valve, which can be adjusted to give an almost purely sine wave current.

In the circumstances, therefore, it is not surprising that very considerable refinements have been introduced in the method both in the means of producing the right type of alternating

current with a suitable frequency and in the detecting of the neutral point. These are details, very essential in experimental work, which need not be entered into in this more rapid survey of the results which have been obtained and the conclusions drawn therefrom.

Conductivity Cells. A number of types of these cells containing the solution under test are shown in Fig. 24. In every

(a)   (b)   (c)   (d).
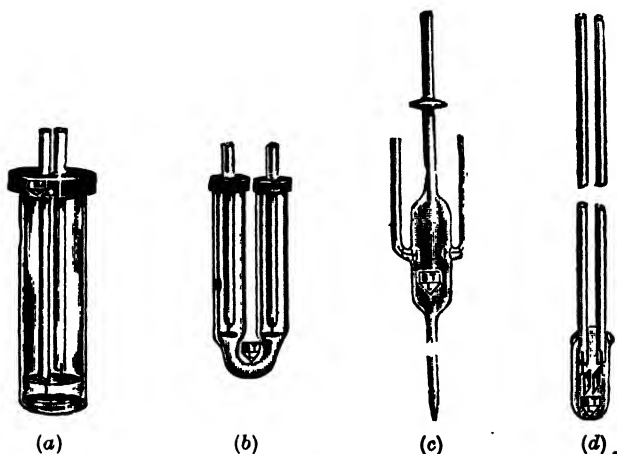
FIG. 24. CONDUCTIVITY CELLS

case the electrodes are of platinized platinum, these minimizing by absorption the effect of any trace of gases which might be evolved. The electrodes are usually platinized by making them cathodes in a solution of platinum chloride containing lead acetate, subsequently thoroughly washing them (page 82). In cell (a) the electrodes are relatively large and close together, while in cell (b) they are small and farther apart. By this method allowances are made for the widely diverse electrolytes which come up for consideration. Cell (c) shows a convenient type suitable for taking samples of liquids from manufacturing conditions and rapidly substituting them in the resistance measuring circuit. Cell (d) shows a type for dipping into liquids of high resistance. In other cells the electrodes are adjustable with marks on the limbs of the tubes to admit

of reproducibility. Connections with the electrodes are invariably made through mercury contacts contained in side limbs into which the platinum wire of the electrode is fused. A few drops of mercury provide the connection between the electrode and the external connecting wire.

Conductance Cell Electrodes. For the electrode metal in these resistance measurements platinum is naturally selected. It has, however, a slight fault in that it does not entirely eliminate polarization. Platinized platinum is a more effective electrode. These electrodes are prepared by the deposition of platinum from a solution of chloroplatinic acid containing a small proportion (from 0·02 to 0·03 per cent) of lead acetate. A finely divided form of platinum is deposited on the electrodes without, however, the deposition of lead. The finely divided platinum presents a very large surface area in comparison with its weight, and this appears to act catalytically in promoting the combination of hydrogen and oxygen which are formed with the rapid reversals of the current. This was the method adopted by Kohlrausch, who, in 1879, made classical researches on the conductance of electrolytes. The electrodes, after platinizing, must be washed free from the solution, otherwise chlorine ions would be introduced into the electrolytic solution under test.

For conductivity measurements with weak electrolytes, cells should at least be made of high-resistance glass, while for handling alkalis and acids the fused silica cell is to be recommended. In any case, where conductivities are low allowance must be made for the conductance of the water which comprises the solvent.

Cell Constant. From these illustrations of the cells it will be seen that there can be no definite knowledge of the inter-electrode distance or length, or of the sectional area of the solution through which the current passes. In all cases current is produced between all parts of one electrode and all parts of the other in much the same way as deposition occurring upon what may be called the back of a cathode. These individual dimensions, the length and sectional area, are not separately required. Their ratio, that is, l/a, is, however, all important. It is called the "cell constant" and is obtained in the following manner. Suppose that any one solution, for example a normal solution of potassium chloride, has its specific resistance

determined with accuracy in a carefully dimensioned cell. This might, for example, be done in a perfectly rectangular cell with electrodes completely occupying the opposite walls of the cell. Alternatively, a wide tube could be used with circular electrodes occupying the area of the cell so that the inter-electrode distance may be varied at will. In either case the current between the electrodes will be "rectangular," that is, at right angles to the electrodes, and not occupying any stray path, which is the case when such geometric proportions are not observed. This involves careful work, but it has only to be done once and the value agreed upon. The determined specific resistance of N . KCl at 18° C. is 10·18 Ω. Its reciprocal is the conductivity. This value for normal KCl at 18° C. is 0·098 22 mho. The solution is then put into a conductivity cell and the resistance, and hence the conductance, determined. From the equation—

$$k = K \times \frac{l}{a}$$

it will be seen that—

$$\frac{k}{K} = \frac{l}{a}$$

and thus the cell constant l/a is determined. This is an important value and needs to be accurately determined. It will vary with the different types of cell but will be very definite for each individual cell. Subsequently any solution under investigation is put into the cell and its resistance, and hence conductance, determined, and from the equation the conductivity is readily calculated. For cells with variable electrodes this ratio needs to be determined for each inter-electrode distance at which the cell is subsequently to be used.

As an example let R, say 5 Ω, be the resistance of the standard electrolyte in the conductance cell, the carefully pre-determined specific resistance of the solution (N . KCl) being 10·18 Ω.

Then—

$$R = r \times \frac{l}{a}$$

$$\frac{l}{a} = \frac{R}{r} = \frac{5}{10·18} = 0·491 = \text{cell constant}$$

By these methods which have been outlined, it becomes possible to determine with accuracy the conductivity of any solution, and we are now in a position to examine these conductivities with a view to the elucidation of any harmonies which may exist, and thus to formulate the laws of electrolytic conductance.

Effect of Temperature. It is well known that an increase of temperature of an electrolyte is accompanied by an increase in conductance. The following table shows the results which have been obtained with normal KCl solutions—

TABLE X

TEMPERATURE AND CONDUCTIVITY (N . KCl)

Temperature (° C.)	Conductivity
15	0·092 52
18	0·098 22
20	0·102 07
25	0·111 8

The standard temperature adopted is 18° C. Hence from 18° C. to 25° C. the percentage increase in conductance per degree Centigrade is—

$$\frac{0{\cdot}111\ 8 - 0{\cdot}098\ 22}{0{\cdot}098\ 22 \times (25 - 18)} \times 100 = 2 \text{ per cent}$$

For different solutions the figure varies between 1·5 and 2·5 per cent. Advantage is taken of this increase in conductance when many electrolytic solutions are warmed. Resistance is reduced with a proportionate reduction in the p.d. required to overcome ohmic resistance, and, in large-scale operations, this may mean the saving of considerable electrical power. This effect is more obvious with solutions of high resistance and where conducting constituents cannot be added. Where large currents are being used, the temperature is practically maintained by the heat generated by overcoming ohmic resistance. Another advantage is the increased solubility of comparatively insoluble anodic compounds. Most simple cyanides thus require a smaller proportion of free cyanide in solutions which are used warm.

Equivalent Conductance. For general purposes the specific resistances of substances are all that is required. This, it will be remembered, is a dimensional value relating specifically to the centimetre cube. The electro-chemist, however, needs to relate conductance to chemical quantities of the various chemical substances. For this purpose the choice of the gramme-equivalent is reasonable. All electrolytic reactions are concerned with equivalent quantities (Faraday's second law), and we are therefore concerned with the amount of conductance obtainable from the gramme-equivalent.

Take a simple case, that of N . KCl. A centimetre cube is placed between electrodes 1 cm. apart (Fig. 25). The sectional area of this unit volume of liquid is therefore 1 cm.^{2} Across these electrodes a p.d. of 1 V develops a current of 0·098 22 A. With a normal solution 1 gramme-equivalent is contained in 1 000 cm^3 of the solution. Between these electrodes and under these conditions the current will be increased one thousand-fold and 0·098 22 × 1 000 = 98·22 A will result. This quantity is called the *equivalent conductance,* meaning the amperes per volt obtainable from 1 gramme-equivalent placed between these electrodes 1 cm apart. Thus—
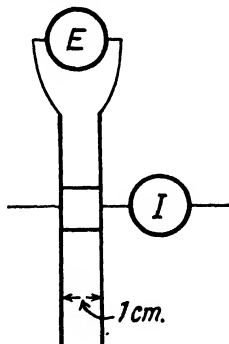
FIG. 25. CONDUCTIVITY AND EQUIVALENT CONDUCTANCE

Equivalent conductance
    = k × cubic centimetres per gramme-equivalent

It is obviously an important electro-chemical value. Such values are shown for a number of electrolytes in the following table (XI). A number of these figures should be checked in order to familiarize the student with the principles involved.

All the values given are for normal solutions. They are generally well recognized and accepted. From various sources slight deviations may be detected, but it must be remembered that they are all experimental values and therefore subject to slight experimental error. Though the actual quantities of sulphuric and hydrochloric acids markedly differ, yet they

agree in each containing 1 g of replaceable hydrogen, and this is the basis of their equivalency.

TABLE XI

CONDUCTIVITY AND EQUIVALENT CONDUCTANCE

Electrolyte	Grammes per Litre	Specific Resistance Ω	Conductivity (mho)	Equivalent Conductance
H_2SO_4 . .	49	5·05	0·198	198
HCl . .	36·5	3·32	0·301	301
HNO_3 . .	63	3·226	0·310	310
$H . C_2H_3O_2$.	60	757	0·001 32	1·32
KOH .	56	5·43	0·184	184
NaOH . .	40	6·37	0·157	157
NH_3 (Soln.) .	17	1 121	0·000 89	0·89
K_2CO_3 . .	69	14·14	0·070 7	70·7
Na_2CO_3 . .	53	21·98	0·045 5	45·5
KCl .	74·5	10·18	0·098 2	98·2
NaCl . .	58·5	13·45	0·074 35	74·35
NH_4Cl . .	53·5	10·31	0·097	97
$CuSO_4 . 5 H_2O$.	124·8	38·7	0·025 8	25·8
$AgNO_3$ . .	170	14·79	0·067 6	67·6

Table XII gives similar values for a number of electrolytes in common use in electrodeposition.

TABLE XII

EQUIVALENT CONDUCTANCES OF COMMON COMPOUNDS

Electrolyte	N	0·5 N	0·1 N
HF		24·7	35·7
KCN	121·8	130·6	142·8
H_3BO_3 (Mol.) . . .	0·014 3	0·016 3	
NaF	54	68	82·6
$ZnSO_4$ . . .	31·1	37·6	52·4
$CdSO_4$ . . .	26·3	32·2	47·6
$FeSO_4$ . . .	31·6	37·6	55
$NiSO_4$ . . .	29·1	37·6	51·3
$NiSO_4 . (NH_4)_2SO_4$ . .		102·6	155
$AgCN . KCN$ . . .		125	

Conductance of Electrodepositing Solutions. The solutions used in electrodeposition differ in composition from those mentioned in Tables XI and XII and therefore in conductance,

but the values given in the tables may be of some value as indicative of the magnitude of these conductances. Usually the metallic compounds required to supply the ions for deposition are relatively poor conductors. Conducting agents are therefore frequently added. To the usual copper sulphate there is a notable addition of sulphuric acid, sufficient to make the conductance more nearly that of the acid than that of the copper salt. This is shown quantitatively in a later section (page 97). As will be seen, such additions may serve other useful purposes, generally in the maintenance of the anodes in a clean condition, in the improvement of the physical properties of the deposit, and also in the improvement of the throwing power of the solution.

Again, many deposition processes involve relatively small consumptions of electrical energy in comparison with the total cost of the process. Nevertheless, it is common practice to take advantage of the decreased resistance of the solution when warmed. In more industrial processes, such, for example, as copper refining, the cost of electrical energy is a notable proportion of the overall cost, and definite steps are therefore taken to reduce it by running the electrolyte at an elevated temperature and by the closest practicable disposition of the electrodes. There, with exactly parallel electrodes, the conditions are more nearly those of the accumulator. In the usual electro-plating tanks, however, very irregularly sized work is being handled, not allowing of any very exact disposition of the anodes to secure the minimum resistance. Generally anodes of large dimensions minimize resistance. Under ideal conditions similar increases in anode and cathode areas should proportionally reduce the resistance of the bath. Under more practical conditions this does not hold as the path of the current is not "rectangular," but follows a somewhat devious course owing to the large sectional area of the solution in comparison with that of the work being plated. It will thus be appreciated that where baths are being worked with the voltmeter alone, large increases in cathode areas will necessitate small increases in the bath voltage in order to maintain constant current densities. Poor contacts between the rods and suspended anodes and work are often responsible for appreciable resistances with consequent loss of power.

EXAMPLES

1. The equivalent conductance of N. $AgNO_3$ is 67·6. Calculate the resistance of 1 dm^3 of the solution.

Conductivity

= Equivalent conductance/Cubic centimetres per gramme-
equivalent

= 67·6/1 000 = 0·067 6 mho

Specific resistance = 1/0·067 6 = 14·8 Ω

Resistance of 1 dm^3 = 14·8 × 10/100 = 1·48 Ω

2. Normal copper sulphate has an equivalent conductance of 25·8 mho. Calculate the resistance of the solution in a conductivity cell with a cell constant (l/a) of 0·5.

Conductivity = 25·8/1 000 = 0·025 8 mho

Specific resistance = 1/0·025 8 = 38·8 Ω

Resistance in cell = 38·8 × 0·5 = 19·4 Ω

3. A decimetre cube of 0·1 N. copper sulphate carries a current of 0·2 A with a p.d. of 4·4 V with copper electrodes. Assuming no polarization, calculate the equivalent conductance of the solution.

Resistance of 1 dm^3 = E/I = 4·4/0·2 = 22 Ω

Specific resistance

= 22 × area/length = 22 × 100/10 = 220 Ω

Conductivity = 1/220 = 0·004 5 mho

Equivalent conductance

= conductivity × cubic centimetres per gramme-equivalent

= 0·004 5 × 10 000 (for an N/10 solution)

= 45 mho

4. Calculate the electrolytic resistance of the solution in a cell fitted with lead electrodes comprising 12 anodes and 11 cathodes equally spaced 1 cm apart and having an area of 1 ft^2. The solution is N . H_2SO_4 with an equivalent conductance of 198.

Conductivity of solution = 198/1 000 = 0·198 mho

Specific resistance = 1/0·198 = 5·05 Ω

Sectional area of solution (equal to the whole area of the cathodes) $= 2 \times 11 \times 12 \times 12 \times 6.45 \, \text{cm}^2$

while the length of the solution is 1 cm.

Total resistance $= (5.05 \times 1)/(22 \times 12 \times 12 \times 6.45)$

$= 1/4\,000 \, \Omega$ approx.

ELECTROLYTIC CONDUCTANCE (*contd.*)

Equivalent Conductance and Dilution. A question which naturally arises is : Are these values of equivalent conductance constant for other degrees of dilution? As an example, the specific resistance of 0.1 N . KCl has been carefully determined to be 89.28 Ω. Its conductivity is therefore

$$1/89.28 = 0.011\ 2 \text{ mho}$$

The gramme-equivalent is contained in $10\ 000$ cm^3 and the equivalent conductance thus becomes

$$0.011\ 2 \times 10\ 000 = 112 \text{ mho}$$

Compared with the figure of 98.2 for the normal solution of KCl there is an obvious increase in equivalent conductance. This increase is continued with further dilution and the phenomenon is common to all electrolytes.

This can readily be explained by the fact that electrolytic dissociation progresses with dilution.

$$KCl \rightleftharpoons K. + Cl^-$$

Dissociation is a reversible process, increasing with dilution with the formation of more conducting ions which again recombine to form non-conducting molecules with increasing concentration.

It will thus be seen that whereas conductivity decreases with dilution, equivalent conductance increases with dilution. This increase is shown for a number of electrolytes in Table XIII.

Maximum Equivalent Conductance. A survey of the figures in Table XIII at once shows the general increase of equivalent conductance with dilution. It will further show that the increments rapidly decrease, indicating that, sooner or later, a maximum value will be attained. These figures are plotted in the curves shown in Fig. 26. In this diagram it has been convenient to plot the equivalent conductances against the logarithm of the number of litres of solution containing 1 gramme-equivalent. Thus normal, decinormal, and centinormal solutions are represented by the distances 0, 1, and 2

TABLE XIII

EQUIVALENT CONDUCTANCE
Variation with Dilution ˙

Conc.	Litres per Gramme-equivalent	Equivalent Conductance					
		H_2SO_4	HCl	KCl	KOH	$CuSO_4$	$H . C_2H_3O_2$
N	1	198	301	98·2	184	25·8	1·32
0·1 N	10	225	351	112	213	45	4·6
0·01 N	100	308	370	122·4	228	72·2	14·3
0·001 N	1 000	361	377	127·3	234	101·6	41
0·000 1 N	10 000			129·1		113·3	
Infinite dilution		383	380	130·1	238·7	114	350
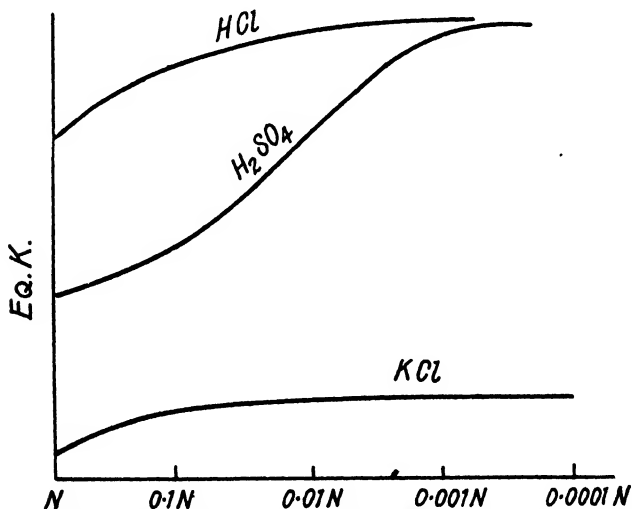
FIG. 26. MAXIMUM EQUIVALENT CONDUCTANCE AND DILUTION

respectively. There is a general flattening of the curve with increased dilution showing that we are nearing the point of maximum equivalent conductance.

It is impossible to obtain these maximum values directly by experiment, as the extremely weak solutions show such large specific resistances as to make their determination altogether unreliable. There are, however, alternative indirect methods

by which we are able to compute these maximum values. One of them involves a closer study of the freezing-points of these conducting solutions. These determinations can be made with great accuracy and they, too, show that, with increasing dilution, there is an increase in dissociation (see page 72). The relation between the depression of freezing-point and the equivalent conductance provides one method for the computation of the maximum values.

For example, a decinormal solution of potassium chloride gives a molecular depression of freezing-point of 3·46° C. That of non-dissociated substances is 1·86° C. (see page 70). The degree of dissociation of decinormal KCl is therefore—

$$\frac{3·46 - 1·86}{1·86} = \frac{1·6}{1·86} = 0·86$$

At this state of dissociation the molecular conductance is 112 (see Table XIII), this being the conductance when only 0·86 of the substance is dissociated. Complete dissociation should therefore give a correspondingly higher conductance of the order of—

$$\frac{112}{0·86} = 130$$

and the figure of 130·1 is accepted as the maximum equivalent conductance of potassium chloride, as the average arrived at by using the data from KCl solutions of different concentrations. While this method suffices for a large number of substances it is not applicable to others like acetic acid which, at moderate dilutions, are only slightly dissociated. Another method, viz. that of extrapolation (that is, computing beyond the range of experience as shown in the experimental part of the curve, in much the same way as absolute zero of temperature is obtained by continuing the curve relating the volume of a gas with its temperature), is, however, possible. In general, it may be said that any uniform curve may be represented by some mathematical expression with which, outside the experimental range of the curve, it is possible to compute with a fair degree of accuracy one dimension from the other. It is by this method that some of these maximum values of equivalent conductance have been obtained and generally agreed upon.

This scheme, however, is only possible in the cases in which dissociation has progressed to a considerable degree within the range of experiment.

Thus it is found that by plotting the equivalent conductance against the square root of the concentration a straight line results with strong electrolytes in dilute solution. Such a straight line can then be continued until it cuts the conductance scale at the point of infinite dilution. All that is necessary is that the values for these dilute solutions shall be obtained with some accuracy, as extrapolation from inaccurate data cannot be expected to lead to an accurate value for maximum conductance at infinite dilution. The following figures refer to the case of potassium hydroxide.

TABLE XIV

EQUIVALENT CONDUCTANCE OF POTASSIUM HYDROXIDE

Conc. (N)	Equivalent Conductance	$\sqrt{\text{Conc.}}$
0·001	234	0·031 6
0·005	230	0·071
0·02	225	0·14

The relevant graph is shown in Fig. 27, from which it will be seen that the maximum value thus deduced is in good relation with that obtained by more accurate means.

This, as will be seen, is not the case with acetic acid and similar weak electrolytes. The computation of the end of a long curve from only a relatively small portion of it at the beginning, is fraught with too much inaccuracy to be of any service. The maximum value for acetic acid therefore depends upon another line of exploration, and this can be more conveniently dealt with later (Chapter IX). For the present, it may be conceded that the figures assigned to the conductance of a number of electrolytes at infinite dilution are reasonably accurate, and other deductions based upon them can only be regarded as reliable in so far as these maximum equivalent conductance values are correct.

Some of these maximum values are indicated in Table XIII. It will be seen that they are not far in excess of those already

shown as within the range of measurement. These are values commonly accepted. They represent the conductance of the completely dissociated gramme-equivalent. This is a condition · which is theoretically never attainable, as the presence of ions carries some tendency to recombination resulting in the smallest amount of molecular substance in even the most
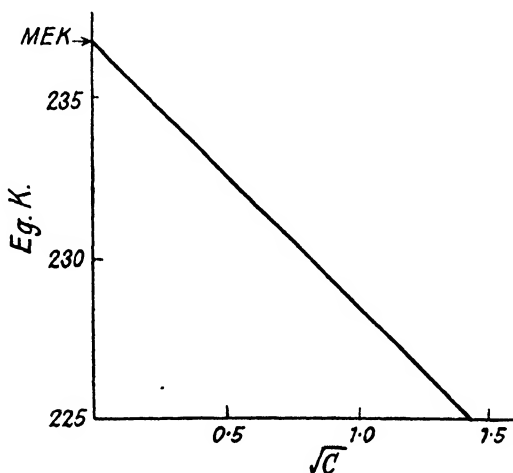
FIG. 27. EQUIVALENT CONDUCTANCE AND $\sqrt{\text{CONCENTRATION}}$ OF $\overline{\text{KOH}}$

dilute solutions. There is, however, a practical maximum attainable only with such extreme dilution. Such solutions are said to be infinitely dilute and the maximum equivalent conductance is therefore that at infinite dilution.

These values are of interest. In stronger solutions the lower values may in part be due to partial dissociation and also to the conductance values due to the individual ions. The maximum values, however, at once give some idea of the conductance which the ions contribute. All the acids have high values due to the hydrogen component. Potassium and sodium hydroxides show good values due to the OH ion. Neutral salts have relatively low values. The individual contributions of the ions, however, are not clearly perceptible from these maximum values which will require some analysis to reveal their origin. This matter will be proceeded with shortly, when we shall have some analysis of the conducting power of an electrolyte

in what are called the transport numbers of its ions (see page 118). A comparison of these values with the maximum equivalent conductances should throw some light on the problem.

Degree of Dissociation. A study of these equivalent conductances reveals the fact that dissociation progresses with dilution. Moreover, the conductance at any dilution is, possibly, a measure of the proportion of ions developed to the total possible by complete dissociation. In other words, we should have some good idea of the extent or degree of dissociation from the following expression—

$$\frac{\text{Equivalent conductance at given dilution}}{\text{Maximum equivalent conductance}}$$

These values can be calculated from the data set out in Table XIII. Thus normal potassium chloride has an equivalent conductance of 98·2 while that for complete dissociation is 130·1. Normal KCl appears, therefore, to be dissociated to the extent of

$$\frac{98 \cdot 2}{130 \cdot 1} = 0 \cdot 754,$$

while normal sulphuric acid has a similar value of $\frac{225}{383} = 0 \cdot 517$

These fractions are commonly referred to as the degree of dissociation and represented as α. This deduction at first seems reasonable. It may, however, later be criticized and for the present, therefore, a better term is that of conductance ratio.

This term preferably expresses a fact without attaching to it any interpretation. A number of these values is given in Table XV.

TABLE XV

CONDUCTANCE RATIO

Electrolyte	Concentration				
	N	0·1 N	0·01 N	0·001 N	0·000 1 N
H_2SO_4	0·517	0·588	0·804	0·942	
HCl	0·792	0·924	0·974	0·992	
KCl	0·754	0·861	0·941	0·978	0·992
KOH	0·771	0·892	0·955	· 0·980	
$CuSO_4$	0·225	0·395	0·633	0·891	0·984
$HC_2H_3O_2$	0·003 8	0·013	0·041	0·117	

These so-called degrees of dissociation may at first seem to be of more academic interest without any very practical application to the processes of electrodeposition. It will be realized, however, that the production of an electrodeposit finds its origin in the discharge of these metallic ions, and their concentration at the cathode may have some important bearing upon the nature of the deposit. Some generally recognized facts must here be taken into consideration. Silver and thallium, for example, are the only two univalent ions deposited from aqueous solutions of their mineral salts, and the deposits thus obtained are coarsely crystalline. Generally, too, deposits from the mineral salts are of much larger crystals than those of the complex salts such as the double cyanides. Lead deposited from the nitrate or acetate solution is very coarsely crystalline, and no satisfactory deposit can be produced from these solutions without the use of an addition agent. Again, the double cyanides give smoother deposits than mineral salts. This would appear to be due to the scarcity of metal ions. Hence it is that high metal ion concentration seems to favour the growth of existing crystals, while low metal ion concentration gives rise to nucleus formation with more numerous and smaller crystals, and hence a smoother deposit.

Again, there is a definite difference between crystal size in the case of nickel deposited from the single and double sulphate solutions, the latter, with complex ions, forming smoother deposits.

Effect of Temperature on Conductance Ratio. From the data given in Table XVI we have a further expression of the effect of temperature on conductance, and in this case on the equivalent conductances with their maximum values and therefore on the degree of dissociation (if such the ratio can be called) as calculated from the equivalent conductances. The marked increase in conductance with temperature is again noticed with that also of the maximum equivalent conductance. It will, however, be observed that there is no increase in the degree of dissociation with rise in temperature—rather the reverse. Increase in conductance with increased temperature is therefore due to increase in the speed of the individual ions and not due to any increase in their number. This increase in conductance emphasizes the need for temperature control in the determination of electrolytic resistance.

TABLE XVI

EFFECT OF TEMPERATURE ON EQUIVALENT CONDUCTANCE

	Conc. (N)	18° C.		100° C.	
		Equivalent Conductance	Conductance Ratio α	Equivalent Conductance	Conductance Ratio α
Potassium Chloride	0·0	130·1	1·0	414	1·0
	0·005	128·1	0·98		
	0·002	126·3	0·97	393	0·95
	0·01	122·4	0·94	377	0·91
	0·05	113·5	0·87	341	0·83
	0·1	112	0·86	336	0·81
Sodium Acetate	0·0	78·1	1·0	285	1·0
	0·000 5	76·0	0·97	275	0·96
	0·002	74·6	0·95	268	0·94
	0·01	71·2	0·91	253	0·89
	0·08	63·4	0·81	221	0·78

Conductance of Mixed Electrolytes. So far, we have been particularly concerned with single electrolytes. This is obviously the easier plan. Commercial electro-chemistry, however, frequently has occasion to resort to the use of solutions involving more than one electrolyte. In fact, few electro-depositing solutions are of a very simple type. In copper refining, sulphuric acid is added to copper sulphate to increase the conducting power of the solution, and this will provide an interesting case with which to explain the new · principle involved.

Normal sulphuric acid has a specific resistance of 5·05 Ω with an equivalent conductance of 198. Similarly, normal copper sulphate has a specific resistance of 38·8 Ω with an equivalent conductance of 25·8. Mixing these two electrolytes would appear to be similar to putting them, as it were, in parallel or adding their conductances. This is a matter which is subject to calculation, the results then being compared with those obtained by experiment.

Table XVII shows the relevant figures for a number of mixtures of the two compounds.

Follow out the method for a solution cont ining 50 g each

TABLE XVII

CONDUCTANCE OF MIXED ELECTROLYTES

Grammes $CuSO_4 . 5H_2O$ per Litre	Specific Resistance r	Conductivity k	H_2SO_4 (50 g/litre)		$k + k_1$	Specific Resistance of Mixture	
			r_1	k_1		Calculated	Found
0			4·8	0·208	0·208	4·8	4·8
50	65	0·015 4	4·8	0·208	0·223 4	4·47	4·9
100	45	0·022 2	4·8	0·208	0·230 2	4·34	5·1
150	29	0·034 4	4·8	0·208	0·242 4	4·07	5·3
200	24	0·041 7	4·8	0·208	0·249 7	4·00	5·5

of the two substances per litre. Add the reciprocals of their specific resistances thus—

$$\frac{1}{65} + \frac{1}{4 \cdot 8} = \frac{4 \cdot 8 + 65}{4 \cdot 8 \times 65} = \frac{69 \cdot 8}{312}$$

Inverting the value of the combined conductances we get—

$$\frac{312}{69 \cdot 8} = 4 \cdot 47 \ \Omega$$

as the *calculated* specific resistance of the mixture. According to the table, however, the value found by experiment is 4·9 Ω, and this apparent discrepancy persists throughout the table.

Some simple explanation should be forthcoming. Consider the two equations—

$$CuSO_4 \rightleftharpoons Cu.. + SO_4''$$
$$H_2SO_4 \rightleftharpoons 2H. + SO_4''$$
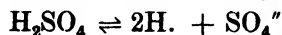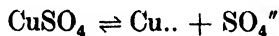
In the case of $CuSO_4$ the tendency of the ions to recombination is determined by the concentration of only the ions produced from $CuSO_4$. The addition of the acid, which is also dissociated, increases the concentration of the SO_4 ions, and therefore also the tendency of Cu.. and SO_4'' to recombination with the formation of a larger proportion of molecular copper sulphate. The same argument applies in the case of the dissociation of the acid and the subsequent addition of copper sulphate. Each substance thus suppresses the dissociation of the other, and a close survey of the data shows that the conductance of the

acid is actually depreciated by the addition of conducting copper sulphate. This is definitely shown in the table, in which it will be seen that the specific resistance of a 50 g/litre of sulphuric acid is successively increased by repeated additions of 50 g/litre of conducting copper sulphate, to the figures shown in the last column. In other words, there is a greater loss of conductance by the suppression of the dissociation of the acid and the disappearance of hydrogen ions than gain of conductance by the introduction of the conducting copper sulphate. Another striking case of mixed electrolytes is that of sodium acetate and acetic acid. Decinormal solutions are mixed, the acetic acid being only slightly ionized and the sodium acetate appreciably ionized, producing a good concentration of acetate ions. This increased concentration of acetate ions affects the recombination of the acetic acid ions to such an extent that in the mixture only about one-hundredth part of the previously ionized acid now remains in the ionized form. This is a general experience in the case of mixtures of electrolytes having a common ion. Further reference will be made to this in Chapter X dealing more specifically with chemical reactions.

Another example of the addition of two electrolytes with a common ion is that of the nickel plating solution for the treatment of zinc-base die castings. The nickel compound used is nickel sulphate to which appreciable quantities of other sulphates, for example, those of sodium or magnesium, are added. These have the effect of reducing the dissociation of the nickel sulphate, thus diminishing the concentration of the nickel ions and therefore inhibiting the "chemical" precipitation of nickel upon the more active zinc alloys, without reducing the total content of the nickel compound. With higher concentrations of nickel ions there is the marked tendency to the precipitation of nickel upon the metal to be plated with a corresponding solution of the zinc-base metal. With the application of the current, the deposit·of nickel would, under these latter conditions, be made on a dissolving and therefore loose surface, conditions which are far from ideal for the production of adhesive deposits.

Water Makes Sulphuric Acid Conductive. In this connection another question may be asked. It is usually stated that the addition of acid imparts conductance to water. Is this a correct

view of the matter? Water is a substance which is only very slightly dissociated. The extent of this dissociation will be dealt with later. Pure sulphuric acid is another insulator. The mixture of the two substances induces a large degree of dissociation of the acid with the production of a high concentration of hydrogen ions. This in turn will reduce the already small dissociation of the water, thereby reducing the already very slight conductance of the water, but at the same time imparting a considerable degree of conductance through the dissociation of the acid. It is merely a matter of recognizing the real principle involved when the usual form of statement is made. The fact is that the mixture of the two substances promotes the dissociation of the acid and therefore imparts conductance to it.

Conductance of Pure Water. So far we have disregarded any conductance which may be due to the water in which electrolytes have been dissolved. Where the conductance of the electrolyte is good, that of water is of little account; but where dealing with the low conductances involved with tenth-millinormal solutions, the conductance of water comes into greater prominence. By pure water, something better than ordinary distilled water is meant. Distilled water may be free from solids, but it will contain gases in solution some of which, like CO_2, form conducting compounds thus—

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons 2H. + CO_3''$$

The elimination of these gases involves distillation under reduced pressure. Subsequently the distillate must not be allowed to come into contact with any ordinary type of glass owing to the solubility of some of the silicates which are present. The condenser of the still is therefore usually of block* tin, the conductivity water then being preserved in high chemical resistance glass vessels away from exposure to the air.

The classic example of conductivity water was that prepared by Kohlrausch in 1894 by a succession of forty-two distillations under reduced pressures with all possible precautions against subsequent contaminations. This highly purified water was found to have a conductivity of 384×10^{-10} mho, that is, its specific resistance is $26\ 000\ 000\ \Omega$. At present

* Solid, or a substantially thick coating to function as solid.

we are not in a position to interpret what apparent degree of dissociation this conductivity indicates, but the matter will be referred to later.

For general laboratory purposes reasonably pure water is obtained in several distillations in highly resistant vessels of Jena* glass. During subsequent storage all corks should be covered with tin-foil.

For many years the dissociation of water was assumed to follow the simple course indicated in the following expression—

$$H_2O \rightleftharpoons H^+ + OH^-$$
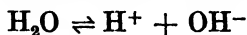
More recently, however, there is the growing conviction that the hydrogen ion is further combined with a molecule of water so that the equation should then be written—

$$2H_2O \rightleftharpoons OH_3^+ + OH^-$$

To this OH_3 ion the name hydroxonium has been given, but, while this possible hydration is not overlooked, the hydrogen ion is usually written in its more simple form.

Non-aqueous Solutions. While most of the work which has so far been treated has reference to aqueous solutions, it must be stated that these are not necessarily the most simple types. They are, however, in common use, hence their importance. They have the disadvantage of introducing some complexity in the formation of ion hydrates by the solvation† of the ions. This increases the difficulty of the elucidation of the problems and gives rise to somewhat discordant results. There are, however, many examples of electrolytes in non-aqueous solvents in which ionization still occurs but is not complicated by the formation of ion hydrates.

A study of these solutions has led to the enunciation of a number of laws which could hardly have been anticipated from a study of aqueous solutions. These laws, however, have little relevancy to the study of the subject from the point of view of electrodeposition and hence only a brief statement of them will be made.

Thus by a study of a large number of solutions in organic solvents in which the solute was tetra-ethyl-ammonium iodide $[N(C_2H_5)4I]$, Walden found that "the maximum equivalent

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* A highly chemically resistant type of glass.
† Combination with molecules of the solvent.

conductance of a salt is inversely proportional to the product of the square root of the molecular weight and the viscosity of the solvent," or

$$\text{Max. equivalent } K = \frac{\text{const.}}{\sqrt{M} \times v}$$

The examination of a large number of solutions served to give the value of the constant, which was of the order of 11·2, and these solutions included a few aqueous solutions in which, with the solute, there was little chance of hydration as, for example, in the rubidium salts.

Again, it was found that the degree of dissociation of a dissolved salt is practically constant for saturated solutions in any anhydrous solvent. This result was obtained by a study of the behaviour of tetra-ethyl-ammonium iodide in solvents such as methyl alcohol, glycol, acetone, ethyl alcohol, acetonitrile, etc.

These and other laws sum up the behaviour of non-aqueous solutions but the matter is one which need not be pursued, yet serves as a reminder that while electrolysis in industry is mainly concerned with aqueous mixtures, it is not impossible that important applications may accrue to non-aqueous solutions, in which case these investigations will merit greater attention. It may, in passing, be noted that attention is already being paid to the possibility of the electrodeposition of aluminium from solutions in organic liquids.

As an example, the work of Blue and Mathers* on the deposition of aluminium may be noted. The production of deposits of this metal from aqueous solutions is not to be expected unless some very unusual new properties, inhibiting the deposition of hydrogen, come into play. These at present are not known, and attention therefore must be given to the possibility of depositing this metal from organic solvents. These workers found that from a solution of the metal in a solvent comprising bromine, ethyl bromide and benzene, the metal appeared at the cathode at a current density of 8 A/ft² with an efficiency of 60 to 70 per cent.

As a variation on this method Keyes and Swann† were able to obtain deposits of aluminium from a mixture of aluminium

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* *Trans. Amer. Electro-chem. Soc.* (1934), Vol. LXV, p. 339; (1936) Vol. LXIX, p. 519.

† Bulletin 206, Engineering Experimental Station, University of Illinois.

bromide and tetra-ethyl-ammonium bromide at 100° C. With a current density of 40 A/ft² and with an aluminium anode they obtained an anode efficiency of practically 100 per cent, and found grey crystals of metal which proved to be aluminium at the cathode.

The method, however, did not prove very successful in the case of other metals, but the matter is one which justifies further investigation.

PROGRESS OF DISSOCIATION WITH DILUTION

Equilibrium in Chemical Changes. In the case of any reversible chemical change, the direction of the reaction and the extent to which it occurs are largely determined by the masses or concentrations of the original and resulting products. The hydrolysis of bismuth chloride as a familiar reaction in qualitative analysis may be taken.

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$
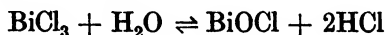
The reaction proceeds from left to right with the addition of water while the addition of acid reverses the reaction.

In order to allow any such reaction to proceed to completion it becomes necessary to remove one of the products. Obviously the addition of more water or bismuth chloride will lead to the formation of more bismuth oxychloride, while in the reverse direction the addition of more acid or oxychloride will result in the formation of more bismuth chloride.

This is an example of the well-known phenomenon of mass-action, and is quoted in this connection only as a reminder that the course of chemical reactions is dependent to some extent upon the quantities or concentrations of the reacting materials.

Progress of Dissociation with Dilution. It has now been seen that dissociation proceeds with dilution, and a general survey of the tables showing the degrees of dissociation at various dilutions seems to indicate that this progress is orderly in each case. There are no obvious fluctuations in the increases of dissociation. The progress seems steady in any one electrolyte though varying from that of the others. A question which arises is whether it is possible that this progress shows any uniformity in all cases. Is it possible to deduce a simple formula expressive of the progress of dissociation which will cover many or even all electrolytes? In other words, is there a law of dilution?

In the following expression—

$$NaCl \rightleftharpoons Na. + Cl^-$$

is recorded the reversibility of the process of dissociation with change of concentration. The matter can, however, be dealt with more quantitatively. The simple equation represents a condition of equilibrium between these opposing tendencies, dissociation of the molecules on the one hand and the recombination of the ions on the other. These tendencies will depend to some extent upon the concentrations of the components of the mixture. If more salt is added, more ions will be formed. The tendency to dissociation will be proportional to the concentration of the molecular material.

On the other hand, where two ions are concerned their tendency to recombination will be proportional to the product of their concentrations. Then—

Let α represent the "degree" of dissociation so that $1 - \alpha$ represents the undissociated salt. These relative quantities of materials are contained in the same volume so that their concentrations will be as follows—

$$NaCl \rightleftharpoons Na. + Cl^-$$

$$\frac{1-\alpha}{v} \qquad \frac{\alpha}{v} \qquad \frac{\alpha}{v}$$
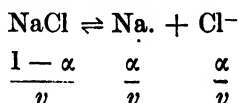
where v is the volume of the solution conveniently expressed as litres. The opposite tendencies of ionization and recombination will then be as follows—

$$NaCl \rightleftharpoons Na. + Cl^-$$

$$k\left(\frac{1-\alpha}{v}\right) = k'\left(\frac{\alpha}{v} \times \frac{\alpha}{v}\right) = k'\frac{\alpha^2}{v^2}$$
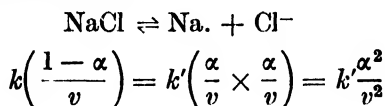
where k and k' are constants.

We then deduce the following equation—

$$\frac{k}{k'} = \frac{\alpha^2 v}{v^2(1-\alpha)} = \frac{\alpha^2}{(1-\alpha)v}$$

The factor k/k' can now be replaced by a single constant K which expresses the ratio of the tendency to dissociation of the molecular material, to that of the tendency to recombination of the ions. It is called the Dissociation or Ionization Constant. It is small for weak electrolytes and larger for strong electrolytes, and it may be constant for all dilutions of a single electrolyte.

The Case of Weak Electrolytes. The matter can be tested by reference to the data in the following table (XVIII) for acetic acid.

TABLE XVIII

DISSOCIATION CONSTANT OF ACETIC ACID AT 18° C.

v	Conductance	α	K
2·02	1·94	0·005 54	1·51 × 10⁻⁵
15·9	5·26	0·015	1·43 ,,
1 500	46·6	0·133	1·44 ,,
3 010	64·8	0·185	1·34 ,,
7 480	95·1	0·270	1·33 ,,
∞	350*		Average 1·41 × 10⁻⁵

As an example of one calculation—

$$K = \frac{\alpha^2}{v(1-\alpha)}$$

$$K = \frac{0\cdot015 \times 0\cdot015}{15\cdot9 \times 0\cdot985} = 0\cdot000\ 014\ 3$$

Having in mind the origin of these figures and that any error in the "degree" of dissociation is magnified in the square of this quantity and further reflected in the undissociated fraction, and also the wide range of dilution, it will have to be agreed that the value for K comes out with a remarkable degree of constancy. For acetic acid, a weak acid, the value is small, expressive of the slight degree of dissociation. With an electrolyte which dissociates more freely the value of K is greater. Take, for example, the case of formic acid, the data for which are found in Table XIX.

TABLE XIX

FORMIC ACID (H . COOH)

v	Equivalent Conductance	α	K
8	15·2	0·041	0·000 22
32	29·3	0·079	0·000 212
128	55·5	0·150	0·000 207
512	102·1	0·276	0·000 205
1024	134·7	0·364	0·000 202
∞	370		(Av.) 0·000 209

* It should be noted that this value has yet to be obtained by a process to be determined later.

Formic acid is a somewhat stronger acid than acetic acid.

As an example of an alkali the case of ammonium hydroxide may be taken. (Table XX.)

TABLE XX

AMMONIUM HYDROXIDE (NH_4OH)

v Litres per Gramme-molecule	Gramme-molecules per Litre	α	Ionic Conc.	Molecular NH_4OH	K
1	1·000	0·004 7	0·004 7	1·000 −0·004 7	0·000 023
8	0·125	0·013 5	0·001 7	0·125 −0·001 7	0·000 023
64	0·015 9	0·037 6	0·000 6	0·015 9−0·000 6	0·000 023
256	0·003 9	0·075 4	0·000 3	0·003 9−0·000 3	0·000 023

Ostwald's Law of Dilution. In each of these, as in many other, examples there is a remarkable constancy in the calculated values of the dissociation or ionization constant.

The cases of these weak electrolytes definitely show that the progress of dilution is not in any sense haphazard, but is of sufficient uniformity to be regarded as following a law, and this uniform behaviour on dilution is known as Ostwald's law of dilution, embodied in the following expression—

$$\text{Ionization constant, } K = \frac{\alpha^2}{(1-\alpha)v}$$

where α = degree of ionization and

v = number of litres containing 1 gramme-equivalent of the solute.

It will be observed that the numerical value of K will be dependent upon the units chosen. For the expression, however, degree of dissociation or ionization is usually expressed as a fraction and the volume as litres containing 1 gramme-equivalent of the substance. Incidentally, in the examples considered the equivalent and molecular quantities are the same.

At a higher temperature the figures vary appreciably. Those given in Table XXI apply for acetic acid at 25° C.

There is, it will be observed, a considerable increase in the conductance figures and also that for the maximum equivalent conductance, and some care must be exercised to differentiate

between the figures obtained at different temperatures, otherwise unexplainable discrepancies will appear.

<div align="center">TABLE XXI</div>
<div align="center">DISSOCIATION CONSTANT OF ACETIC ACID AT 25° C.</div>

Conc. (N)	Equivalent Conductance	α	K
0·01	16·2	0·042	0·000 018 4
0·005	22·8	0·059	0·000 018 5
0·002	35·2	0·090 6	0·000 018 0
0·001	48·7	0·125	0·000 017 8
0·000 5	64·5	0·166	0·000 016 7
0·000 2	104	0·268	0·000 019 4
∞	388		(Av.) 0·000 018 1

The following list of dissociation constants will be of interest—

<div align="center">TABLE XXII</div>

Acetic acid	. . . . .	1·4	$\times\ 10^{-5}$
Formic acid	. . . . .	20·9	,,
Propionic acid	. . . .	1·4	,,
Monochloracetic acid	. . . .	155	,,
Carbonic acid	. . . .	0·030 4	,,
Hydrogen sulphide	. . . .	0·005 7	,,
Hydrocyanic acid	. . . .	0·000 13	,,

Some of these figures are indicative of the very low ionization of substances well recognized as weak acids.

From these dissociation constants it becomes possible to calculate the degree of dissociation at given dilutions. Thus—

$$K = \frac{\alpha^2}{v(1-\alpha)}$$

hence

$$\alpha^2 = Kv(1-\alpha)$$

For very weak acids α is small and $1-\alpha$ is therefore practically unity. Hence—

$$\alpha^2 = Kv \text{ and } \alpha = \sqrt{(Kv)}$$

This expression can now be tried out on the data available for acetic acid and given on page 109.

There is in Table XXIII good agreement which, however, disappears with decreasing concentration.

TABLE XXIII

DISSOCIATION OF ACETIC ACID, CALCULATED AND FOUND

v (litres)	α	
	Experimentally	Calculated from K
2·02	0·005 54	0·005 33
15·9	0·015	0·015
1 500	0·133	0·145
3 010	0·185	0·205

Strength of Acids. This review of the process of electrolytic dissociation leads to a clearer conception of what is usually called the strength of acids. Normally, sulphuric acid is looked upon as being a very strong acid, having in mind its physical properties, such as weight and oiliness, but mainly for its chemical properties in the decomposition of chlorides, nitrates, and many other groups of compounds liberating acids, which are thus regarded as weaker. When the acid acts on sodium chloride in accordance with the following equation—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$
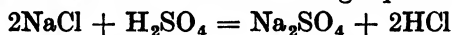
it must be remembered that the hydrochloric acid, being volatile, is removed from the sphere of the chemical action. If, however, sulphuric acid is added to a relatively weak solution of salt, only a part of the chloride is converted to sulphate : while, on the other hand, if hydrochloric acid is added to a solution of sodium sulphate, a larger part of the latter salt is converted into chloride. As the acidic properties are due to hydrogen ions, a better measure of acid strength would be the concentration of hydrogen ions existing in the acid solution. Table XXIV, on page 110, shows four well-known acids, in the order of their strength, based on this reasonable conception.

For the weaker acids the dissociation constant provides a good guide, and Table XXII, on page 108, serves to place them in a good order. From this it is interesting to see the effect of the substitution of chlorine in acetic acid yielding monochlor-acetic acid.

This conception is confirmed by other data : for example, the heat developed in neutralization, to which reference will later be made.

TABLE XXIV

STRENGTH OF ACIDS

Acid	Degree of Dissociation	
	N. Solution	0·001 N. Solution
HNO$_3$	0·82	0·98
HCl	0·792	0·992
H$_2$SO$_4$	0·517	0·942
H . C$_2$H$_3$O$_2$	0·003 8	0·117

The Case of Strong Electrolytes. Two examples of strong electrolytes will now be taken. The first (Table XXV) is that of KCl for which it may be taken that we have very reliable data, and this is embodied in the conductance at different dilutions. From the degree of dissociation the ionization "constant" has been calculated by the usual process.

TABLE XXV

POTASSIUM CHLORIDE

Conc.	Equivalent Conductance	α	K
N	98·2	0·755	2·32
0·1 N	112	0·861	0·53
0·01 N	122·4	0·941	0·15
0·001 N	127·3	0·978	0·043
∞	130·1		

There seems to be little constancy in this value of K. Take next the case of copper sulphate (Table XXVI).

This again shows no sign of a constant value for what we are calling the dissociation constant. Exactly the same result occurs in the case of many electrolytes which are largely dissociated at moderate dilutions, but that it does not occur with weak electrolytes has been evidenced.

We here meet a problem with strong electrolytes which does not occur with weak electrolytes, and an adequate answer to the difficulty is not easily forthcoming. As far as the study has advanced, the results have proved so entirely satisfactory that

TABLE XXVI

COPPER SULPHATE

Conc.	Equivalent Conductance	α	K
N	25·8	0·226	0·066
0·1 N	45	0·395	0·025 8
0·01 N	72·2	0·633	0·010 9
0·001 N	101·6	0·891	0·007 3
∞	114		

there can be no doubt as to the general truth of the suggestion of electrolytic dissociation. Here, however, is a problem which, though difficult, need not throw doubt upon the well-founded conception of the constitution of electrolytes, but which may be regarded as calling for more information before formulating a more detailed conception of the phenomena involved.

Towards the elucidation of the problem other formulae for deriving a dissociation constant have been suggested. One, by Rudolphi, is as follows—

$$K = \frac{\alpha}{(1-\alpha)\sqrt{v}}$$

The results obtained with this formula are shown for copper sulphate, silver nitrate, and potassium chloride in the following Tables (XXVII–XXIX)—

TABLE XXVII

COPPER SULPHATE
(Rudolphi's Formula)

Conc.	Equivalent Conductance	α	K
N	25·8	0·226	0·292
0·1 N	45	0·395	0·210
0·01 N	72·2	0·633	0·172
0·001 N	101·6	0·891	0·258
∞	114		

It must be agreed that these values show a greater degree of constancy though, with the exception of silver nitrate, the variations are far greater than those with Ostwald's law in the case of weak electrolytes.

TABLE XXVIII

SILVER NITRATE

(Rudolphi's Formula)

v Litres per gramme-molecule	α	$\sqrt{v}$	K
16	0·828	4	1·20
32	0·875	5·65	1·24
64	0·899	8	1·11
128	0·926	11·31	1·10
256	0·951	16	1·21
512	0·962	22·6	1·12

TABLE XXIX

POTASSIUM CHLORIDE

(Rudolphi's Formula)

v Litres per gramme-equivalent	α	$\sqrt{v}$	K
1	0·755	1	3·08
10	0·861	3·16	1·96
100	0·941	10	1·60
1 000	0·978	31·6	1·41

However constant may be the values of K derived from Rudolphi's formula, there is to be noted the fact that the expression itself is one which is not easily interpretable. While α and $1 - \alpha$ are readily appreciated quantities, $\sqrt{v}$ is not so understandable.

It will be appreciated that these formulae should express definite physical ideas and not be mere arithmetical or algebraical expressions without any possible relation to physical properties. Yet it is also possible that such definite harmonies may embody physical ideas not previously recognized to have immediate application to the problem.

Again, Vant Hoff proposed as an alternative the following expression—

$$K = \frac{\alpha^3}{(1 - \alpha)^2 v}$$

Applied on the values for silver nitrate we get—

TABLE XXX
SILVER NITRATE
(Vant Hoff's Formula)

v (Litres)	α	K
16	0·828	1·2
32	0·875	1·3
64	0·899	1·14
128	0·926	1·1
256	0·951	1·3
512	0·962	1·2

Here again a degree of uniformity is attainable by the use of the expression proposed by Vant Hoff, but the problem is not one of mere arithmetic. Rather is the matter one of the expression of well-recognized phenomena in terms which are capable of being stated with exactitude and physical meaning. These later formulae fail to fulfil these requirements and therefore cannot be regarded seriously as any solution of the difficulty.

Another and very successful formula for the conductance of strong electrolytes was suggested by Kohlrausch as follows—

$$1 \to \alpha \propto \sqrt{C} \text{ where } 1 - \alpha \text{ is small}$$

Tried out on potassium chloride we have the following figures—

TABLE XXXI
KOHLRAUSCH FORMULA WITH KCl

v	α	$1-\alpha$	$\sqrt{C} = \dfrac{1}{\sqrt{v}}$	$\dfrac{1-\alpha}{\sqrt{C}}$
200	0·961	0·039	0·070	0·55
100	0·943	0·057	0·100	0·57
50	0·922	0·078	0·141	0·55
20	0·888	0·112	0·223	0·50
10	0·861	0·139	0·310	0·43

Good agreement must be admitted where, as suggested, $1 - \alpha$ is small, with obvious deviations in which this factor increases, and it might be possible that some further evidence

may be forthcoming which will justify the application of this factor of the square root of the concentration in the explanation of the behaviour of strong electrolytes.

Seemingly the problem must be left for the present in the hope that further data will be forthcoming from an extended investigation of electro-chemical phenomena which will assist in clarifying a problem which, at present, is not readily understandable.

Arguments For and Against Electrolytic Dissociation. At this stage it might be well to consider the evidences which have been adduced for the theory of electrolytic dissociation as brought forward by Arrhenius and the arguments which have been set against it. In its inception the theory met with the sternest opposition.

1. It was argued that it was impossible to conceive the existence of sodium ions in aqueous solutions in view of the known extreme reaction of this element with water. Similarly, too, a chloride solution shows no evidence of either green colour or the usual bleaching action. In reply it was pointed out that these elements in the atomic or molecular form must be very different from the ionic form, in which their electrical properties, which make them susceptible to migration under the influence of an applied p.d., largely determine their behaviour.

More recently, however, research has shown that this separation of the ions of, for example, sodium chloride is to be traced even in the solid before it dissolves. X-ray examination of crystals reveals the interesting evidence that, in the smallest groups which go to make the cubical crystal of salt, we are dealing not with molecules of NaCl, but a cubical spacing of sodium and chlorine atoms. This form of disposition of the constituents of the molecules is called a space lattice. That for salt has the form of a cube, which sets the shape of the larger crystal. In this lattice for salt, both sodium and chlorine atoms are disconnected from each other and occupy easily determinable positions, so that there are individual sodium and chlorine atoms both at the corners and other symmetrical positions of the cubic lattice. This, now being a well-recognized fact—and this and similar evidence has quite revolutionized our conception of the ultimate structure of matter—at least

prepares us for the readier reception of their separation in aqueous solutions in the form of charged ions.

2. Many of the most stable substances, such, for example, as the alkali chlorides, are the most amenable to dissociation. This appeared to be inconsistent, and it was therefore suggested that the unique properties acquired by these salts in aqueous solution were probably due to the formation of complexes with solvent molecules rather than to any simple separation of their constituent parts. In further reply it may be stated that there is abundance of evidence to indicate the association of solvent molecules with the charged ions formed by electrolytic dissociation, so that both phenomena may, and do, contribute to the observed results.

3. If the molecules are undissociated in solution and electrolysis is the separation of their components by the agency of electrical energy, then it would appear that there should be no current in an electrolyte with a p.d. less than that required to effect this decomposition of the molecule. The evidence available goes to show that the smallest p.d.'s suffice to produce some current in an electrolyte, and this at least indicates some type of partial separation before the application of the p.d. For the maintenance of the separation, however, a definite minimum p.d., varying with the electrolyte, becomes necessary.

4. The instantaneity of the production of an electric current in an electrolyte with the application of a p.d. evidences the existence of electrical particles throughout the solution prior to the application of the p.d. With completely undissociated materials time would be involved in effecting the necessary separation of the parts of the molecules throughout the chain of molecules between the two electrodes.

5. If ionization results in the production of free or detached ions, then it should be possible to effect some sort of separation of these electrically-charged particles by physical methods other than that of the application of a p.d. Attempts have been made to confirm this. In one case an electrolyte producing a heavy ion, viz. iodine from iodides, was centrifuged, when the heavier iodine ion was found in excess at one end of the centrifuged tube with the lighter ions at the other. Similar small amounts of separation have also been effected by the application of a large electrostatic charge at the end of a tube containing an

electrolyte. It must, however, be remembered that even though the ions may be separated their electrical charges are considerable and prevent that degree of separation which would give rise to appreciable accumulations of the different ions with, at the same time, the accumulation of the opposite electrical charges in considerable quantity.

6. Reference may also be made to the fact that many chemical substances, ordinarily very reactive in aqueous solutions, fail altogether to exhibit the same properties when dissolved in other solvents. A number of examples may be cited. A solution of dry hydrochloric acid gas in toluene, kept dry by the addition of calcium chloride, reveals little or no conductance. It is equally unresponsive to its usual chemical reactions, such, for example, as dissolving metals or attacking marble. From this it would appear that its usual properties must be attributed to the ions formed by dissociation in aqueous solution.

Again, many organic compounds appear to contain radicals common with those of electrolytes. Caustic soda and ethyl alcohol both contain the hydroxyl group, but alcohol reveals no alkaline properties because in water it does not dissociate, and it is the hydroxyl ion which is responsible for the usual alkaline properties.

In much the same way many salts, which in solution react and give coloured products, fail to do so when intimately ground together in the dry state. Here it might be argued that such grinding, however fine, does not bring the material into anything like molecular subdivision and hence no chemical reaction, but from experience with so many other reactions it is far more probable that the reason lies in the fact that in the dry state the materials are molecular, while in the presence of moisture reactive ions are formed, as many chemical reactions between salts which take place in aqueous solutions are not possible when these substances are dissolved together in organic solvents.

7. Reviewing the work of the last few chapters, the observed facts both on the physical and electro-chemical sides have been wonderfully consistent with the theory. This harmony has yet to be made even more apparent, and, as has been seen, has given remarkably consistent quantitative results, the most prominent of which has been the law of dilution as applied to

weak electrolytes. It may be safely anticipated that the ob-
served discrepancies of strong electrolytes will yield to further
treatment, which, however, may necessitate some modification
of the simple theory so far propounded.

It may thus be concisely stated that, although the Arrhenius
theory may call for some modification, no case has yet been
made out for its abandonment.

Nor can the discussion of the mechanism of electrolytic
conductance be left without some reference to difficulties not
usually explained. It has been noted that water with its high
degree of dissociating power is characterized by a high dielectric
constant of the order of 80. Liquid HCN, however, has a value
of 95 for this property, but solutions in this liquid are relatively
poor conductors. One of the most simple cases of electrolysis
is that, as pointed out by Faraday, of fused silver chloride
with silver electrodes. Here there is no third substance as
water to complicate the process. Water is a unique liquid in
several of its properties. It exists in a polymerized form of
di- and tri-molecules associated with which may be the unusually
high latent heat of evaporation with its profound influence
on the economy of many things natural. It is, moreover, by
no means uniform in its behaviour towards many chemical
substances. It provides almost the only solvent for common
salt, and also for cane sugar. Soap solutions in it conduct
electricity but show no marked increase in boiling-point or
depression of freezing-point, while in alcoholic solution these
physical expectations are realized without, on the other hand,
appreciable conductance. Obviously there is much yet to be
learned in relation to this subject of the conductance and
constitution of electrolytes.

TRANSPORT NUMBERS

Introduction. In electrolytic conduction there is the definite idea of the motion of two opposite streams of oppositely charged ions, the total effect constituting current. It would be a matter of interest and importance to know more of this orderly motion or migration of the ions. If ionic speed is involved it should be possible to express it in terms of centimetres per second. As a start it might be easier to determine relative rates of migration of ions.

Relative Rates of Migration of Ions. For the most part ions are colourless and their motion is therefore not obvious. With some coloured ions it is possible not only to observe their motion, but also make an approximate determination of it. In Fig. 28 a glass tube having an "N" shape is partly filled with copper sulphate solution and partly with sulphuric acid, the liquids being added and adjusted to give a sharp boundary at the point A. With the production of current there will be motion of the copper ions towards the cathode, and the blue wave front will be seen to advance. The process is slow, but the experiment can be arranged and conducted in a manner which admits of an approximate computation of the speed of the copper ions. Other coloured ions, for example that of permanganate compounds (MnO_4'), can be similarly dealt with. Further, colourless ions can be followed by colour changes which they may effect, for example, the decoloration of slightly alkaline phenolphthalein by an advancing boundary of hydrogen ions. This is commonly known as the Moving Boundary method of measuring ionic speeds. More accurate methods are required, and these, introduced by Hittorf over eighty years ago, involve the determination of the changes of composition of the anolyte or catholyte accompanying electrolysis.

FIG. 28. IONIC MIGRATION

Hittorf's Method. Imagine a cell (Fig. 29) divided into two compartments by some convenient porous partition, A and C being the anolyte and catholyte respectively. Assume each of these compartments to contain 20 gramme-equivalents of silver (2 160 g) as silver nitrate. The anode and cathode are of silver. The determination of the silver in these solutions is a matter of simple chemical analysis. A current is generated sufficient to effect the deposition of 10 gramme-equivalents of silver, that is, one-half of the quantity contained in the cathode compartment. (Actually this current will be $26.8 \times 10 = 268$ Ah.)
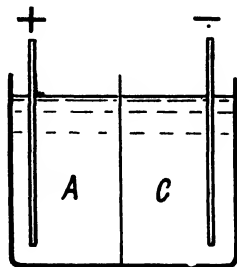
In the absence of ionic migration the silver content of the catholyte will have been reduced to 10 gramme-equivalents, that of the anolyte having been increased by anodic solution by a similar amount, and the original 40 gramme-equivalents will be distributed as 30 gramme-equivalents in the anode compartment and 10 gramme-equivalents in the cathode section.

Fig. 29. Ionic Migration

Chemical analysis, however, reveals the fact that there are only 25.3 gramme-equivalents of silver in the anolyte, while there are 14.7 gramme-equivalents in the catholyte. Hence during the deposition of 10 gramme-equivalents of silver, 4.7 gramme-equivalents of silver have migrated from the anolyte to the catholyte. Similarly, 5.3 gramme-equivalents of NO_3 ions have migrated towards the anode. The different quantities of migrating ions are at once a measure of the current for which they are responsible, and thus in silver nitrate 0.53 of the current is concerned with the migration of the anion while 0.47 of the current is accounted for by the transportation of the silver ion towards the cathode. We need not at this stage concern ourselves with any changes at the electrodes other than those of simply the solution of the metal from the anode and its deposition on the cathode.

A similar experiment may be made with copper sulphate. Put 10 gramme-equivalents of the salt (and therefore of copper) into each compartment. This time develop sufficient current to deposit 8 gramme-equivalents of copper. Without migration

the copper content of the catholyte will have been reduced to 2 gramme-equivalents, while that of the anode compartment will have increased to 18 gramme-equivalents. But migration has taken place, and its extent is revealed by the analysis, which shows that the cathode compartment contains 5 gramme-equivalents of copper and the anolyte 15 gramme-equivalents. Hence during the deposition of 8 gramme-equivalents of copper, 3 gramme-equivalents of copper ions have migrated towards the cathode representing 0·375 of the current towards the cathode, while the remaining 0·625 was concerned with the migration of the sulphate ion towards the anode.

Hittorf's Apparatus. For the accurate determination of transport numbers a much more refined type of apparatus and its skilful handling is necessary. That used by Hittorf, who, in 1853-9, did the pioneering work, is depicted in Fig. 30. In a modified form, three tubes are used arranged for the simple withdrawal of the anolyte and catholyte after the required electrolysis, the solution in the middle tube remaining constant in composition throughout the experiment. The solution in an example is silver nitrate. Silver is dissolved from a convenient anode and deposited upon a silver wire cathode. The compositions of the two solutions can be determined both before and after electrolysis, the coulombs passed through being determined by a copper coulometer in the circuit. Alternatively, the weight of silver deposited may be taken as a measure of the coulombs passed. The following may be taken as typical data from such an experiment—

FIG. 30. HITTORF'S MIGRATION APPARATUS

Electrolyte :—Silver nitrate

Coulombs passed equivalent to 0·047 g Cu.
Catholyte contained· 1·315 g Ag before expt.
     ,,   ,,   1·231   ,,   after expt.
           Loss = 0·084 g.

$$\text{Silver deposited} = \frac{0 \cdot 047 \times 108}{31 \cdot 8} = 0 \cdot 160 \text{ g.}$$

Hence silver migrated to the extent of—

$$0 \cdot 160 - 0 \cdot 084 = 0 \cdot 076 \text{ g,}$$

from which—

$$\frac{0 \cdot 076}{0 \cdot 160} = 0 \cdot 47$$

is the share of the current concerned with the transport of the silver ion, the remaining $0 \cdot 53$ being carried by the NO_3 ion.

Transport Numbers. These shares of the total current carried by the individual ions are called Transference or Transport numbers, and a number of accepted values are given in Table XXXII.

In electro-chemical symbols

$$v = \text{velocity of anions}$$
$$u = \text{velocity of cations}$$

Hence. $v/(u + v) =$ share of current carried by anions
and $u/(u + v) =$ share of current carried by cations
Hence, T.N. of cation $= u/(u + v)$
and T.N. of anion $= v/(u + v)$

TABLE XXXII
TRANSFERENCE OR TRANSPORT NUMBERS

Electrolyte	Cation	Anion
NaCl	0·396	0·604
KCl	0·496	0·504
NH_4Cl	0·492	0·508
$AgNO_3$	0·471	0·529
$MgSO_4$	0·381	0·619
$CdCl_2$	0·430	0·570
Na_2SO_4	0·390	0·610
K_2SO_4	0·492	0·508
$CuSO_4$	0·375	0·625
$CdSO_4$	0·384	0·616
$BaCl_2$	0·447	0·553
H_2SO_4	0·822	0·178
HCl	0·833	0·167
HNO_3	0·841	0·159
KBr	0·495	0·505
NaOH	0·190	0·810
LiCl	0·328	0·672

These figures lead to simple conclusions, some of an important practical character. In the first place metal ions do not migrate as fast as they are deposited. Continuous deposition, therefore, calls for some method of keeping the cathode surface well supplied with these ions ready for deposition. Hence the usual methods of circulation or stirring. Secondly, salts tend to accumulate around the anode and sometimes, in the absence of methods to ensure uniformity of the solution, crystallize out on the anode. Thirdly, the large transference number of the hydrogen ion suggests its comparatively great speed.

Relative Ionic Speeds. It must, however, be pointed out that these transport numbers provide no direct comparison between the speeds of, say, the potassium and sodium ions. The fractions are concerned with only the individual pairs of ions. When the speed of Cl^- is represented as $0 \cdot 604$ then that of Na. is $0 \cdot 396$, while that of potassium is represented as $0 \cdot 496$ only when that of Cl^- is taken as $0 \cdot 504$.

A simple calculation will serve to put these ions into some comparative order. Taking the most rapid ion, viz. H, as having a speed of 100, that of Cl becomes $0 \cdot 167 \times 100/0 \cdot 833 = 20$, while with a relative speed of 20 for Cl, that of Na becomes $0 \cdot 396 \times 20/0 \cdot 604 = 13 \cdot 1$. Other similar values can be worked out by the systematic comparison of pairs of ions with a common ion.

Such results are shown in Table XXXIII. They show the

TABLE XXXIII

RELATIVE RATES OF IONIC MIGRATION

Cations			Anions		
H	.	. 100	OH	.	. 55·6
Cs	.	. 20·7	SO$_4$	.	. 21·7
Rb	.	. 20·5	Cl	.	. 20
K	.	. 19·6	Br	.	. 20
NH$_4$	.	. 19·3	NO$_3$	.	. 18·9
Ba	.	. 16·1	C$_2$H$_3$O$_2$	.	. 11·8
Cd	.	. 15·1			
Ag	.	. 14·9			
Mg	.	. 13·3			
Na	.	. 13·1			
Cu	.	. 13			
Li	.	. 9·8			

relatively high speed of the hydrogen ion and thus to a large extent explain the good conductance of the acids, and also that of the hydroxyl ion which accounts to a large extent for the excellent conductance of the strong alkalis.

The figures in the table, however, have no absolute value. They are purely comparative and will have to be transferred sooner or later to a more absolute scale.

Conditions Influencing Transport Numbers. It might be asked whether these fractions are affected by possible changes in the electrolytic conditions. The effect of temperature is illustrated by the results shown in Table XXXIV, there being a general tendency towards the equalization of the values. There must be some reason for this, which will soon come to light.

TABLE XXXIV

EFFECT OF TEMPERATURE ON TRANSPORT NUMBER

Electrolyte	Cation Transport Number			
	0° C.	18° C.	30° C.	96° C.
NaCl . . .	0·387	0·396	0·404	0·442
KCl . . .	0·493	0·496	0·498	
AgNO$_3$ . .	0·461	0·471	0·481	

Secondly, the current density appears to have no effect on these transport numbers, this being deduced from the comparative figures shown in Table XXXV.

TABLE XXXV

EFFECT OF CURRENT DENSITY ON TRANSPORT NUMBER

Current Density	113	420	958
Transport Number	0·291	0·285	0·289

Apparently, therefore, increased current density results from the general increase in the rate of migration. In other words, with a small current the whole of the ions in the system are in slow motion. The effect of increasing the current is not to increase the number of ions in action, but generally to accelerate their motion.

There appears, however, to be a noticeable difference in the transport number of some of the ions with varying degrees of dilution. The relevant results for the silver ion in silver nitrate solutions are shown in Table XXXVI. For the time being we shall not inquire further into some possible explanation as, when this is attempted, we may also be able to account for the somewhat anomalous figures for the relative rates of migration of the alkali metal ions shown in Table XXXVII.

TABLE XXXVI

EFFECT OF DILUTION ON TRANSPORT NUMBER

Wt. of Water Dissolving 1 Part by Wt. of $AgNO_3$	Transport Number of Ag. Ion
2·48	0·532
5·18	0·505
14·5	0·475
49·44	0·474
104·6	0·474
247·3	0·476

TABLE XXXVII

RELATIVE SPEEDS OF ALKALI IONS

	Li	Na	K	Rb	Cs
Ionic mass.	7	23	39	85	133
Relative speed	9·8	13·1	19·6	20·5	20·7

This progressive change is in accordance with the expectation from Mendeleef's law.

It may, however, be remarked in passing that the mobility of the heavy caesium ion in comparison with the light lithium ions is surprising, and some explanation of this should be forthcoming as the study of this phenomenon develops.

Effect of Hydration. Another factor influencing the rate of migration of ions is the fact that, as will be seen later, they are for the most part not entirely free, but more usually associated with a number of water molecules. This is called hydration. Water molecules have therefore to be dragged

along with the moving ion, and this extra mass of moving material must slow down the rate of migration. If an ion is not associated with water molecules, its rate of migration is unimpaired. Hydration therefore calls for some method of determining the degree and concomitant slowing down of the migration process. This is a matter which must be borne in mind with a view to elucidation as the study of hydration proceeds.

Abnormal Results. Again there would appear to be a number of abnormalities in these results which call for explanation. For example, the transport numbers of the anion in cadmium iodide solutions are—

Normality of solution	0·01	0·05	0·1	0·5	1	2
Transport Number of anion	0·56	0·64	0·71	1	1·12	1·22

Obviously, the anion in a number of these cases cannot be transporting more than the total current. The answer to the difficulty is supplied by the fact that in determining the transport number the chemical determination was that of the iodine in the anolyte. This becomes excessive owing to the formation of a complex ion of the type of $I . CdI_2^-$, so that CdI_2 is, in the form of this complex ion, being transferred to the anolyte. A similar anomaly would have been observed had the analysis been concerned with the determination of cadmium in the catholyte. Such complex ions provide interesting problems for those interested in electrodeposition, in which many double cyanides find extended use.

The case of copper potassium cyanide may be taken by way of illustration. In the simple form of cell shown in Fig. 29 assume that 10 gramme-equivalents of copper are contained in each compartment, subsequently "passing" current sufficient to deposit 5 gramme-equivalents of copper. Without ionic migration, the anolyte will increase its copper content to 15 gramme-equivalents and the catholyte become reduced to 5 gramme-equivalents. Analysis, however, shows that the anolyte contains more than this amount, while the catholyte content falls short of that anticipated with no migration.

Obviously, therefore, copper has migrated towards the anode in the form of a complex ion, while in all processes of electrodeposition it is required to move toward the cathode. Dissociation takes the course indicated thus—

$$CuK_2(CN)_3 \rightleftharpoons K. + CuK(CN)_3^-$$
$$CuK(CN)_3^- \rightleftharpoons K. + Cu(CN)_2^- + CN^-$$

if the formula $CuCN . 2KCN$ is taken for the double cyanide compound, and this is common to the similar double cyanides of other metals. In continued deposition, some stirring becomes very essential, though easily assured.

Determination of Formulae of Double Cyanides. These double cyanides are numerous and of considerable importance in electrodeposition, providing stable compounds which are available for the deposition of their metals on those more negative. Their chemical composition follows no fixed rule. Potassium ferrocyanide and ferricyanide with formulae $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$, or $Fe(CN)_2 . 4KCN$ and $Fe(CN)_3 . 3KCN$ respectively, provide familiar examples. Those of copper are less definite, there being a number of these complex double cyanides according to the method of preparation. The formula most usually ascribed to the compound is $CuCN . 2KCN$. Methods for definitely fixing these formulae comprise—

1. Re-crystallization without change of composition.
2. Conductivity variations with titration.
3. Potentiometric measurements with titration.

Re-crystallization may be termed a purely chemical method following the lines usually adopted in the purification of a salt. As an example of the conductivity method the composition of silver potassium cyanide has been determined to be $AgCN . KCN$ in the following manner.* Approximately decinormal potassium cyanide solution was diluted with several amounts of water and titrated with decinormal silver nitrate, the specific resistance being determined from time to time during the titration following the usual course of acid and alkali conductiometric titrations. (See page 137.) The results are shown in Fig. 31, in which the persistent quantity of 5·2 ml and 10·7 ml of silver nitrate represent the formation of the

* *Trans. Amer. Electro-chem. Soc.*, Vol. LXXII, p. 473.

double and single cyanides respectively according to the following equations—

$$2KCN + AgNO_3 = AgK(CN)_2 + KNO_3$$
$$AgK(CN)_2 + AgNO_3 = 2AgCN + KNO_3$$
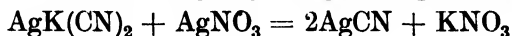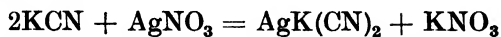
The decrease in resistance after the 10·7 point represents the added quantities of conducting silver nitrate. Strictly speaking,
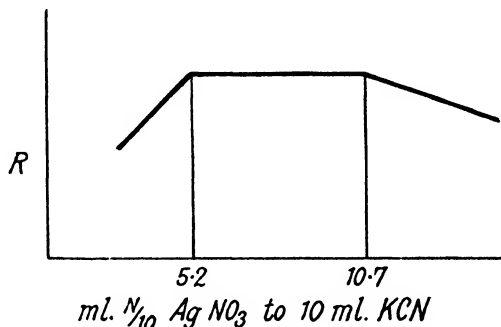
FIG. 31. ADDITION OF SILVER NITRATE TO POTASSIUM CYANIDE: RESISTANCE CHANGES

the 10·7 point observed should be $2 \times 5·2 = 10·4$ ml., but it was observed that though at the 5·2 stage there was some slight opalescence, due to the first formation of the single cyanide which increased with further additions of silver nitrate, there was no appreciable flocculation and precipitation of the single cyanide until this excess of 0·3 ml. of silver nitrate had been added. The research is being extended to other double cyanides and will doubtless clear away some of the uncertainty regarding the exact composition of these compounds. Nevertheless, while the composition of the copper compound may be $CuK_2(CN)_3$ many of the simple reactions of this compound are commonly explained by the formula $CuK(CN)_2$.

Combining Transport Numbers and Maximum Equivalent Conductances. We have now two important properties of electrolytes. The maximum equivalent conductance represents the conductance supplied by a gramme-equivalent of the substance when completely dissociated. This is a definite quantity for each individual electrolyte. This conductance, however,

is what is called an additive property. It has two components, these being the contributions of the anions and cations, the relative values of which are expressed in the transport numbers.

These quantities can now be brought together. Take the case of sodium chloride. the maximum equivalent conductance of which is 109·1. From our knowledge of transport numbers, we gather that 0·604 of the current is due to the anion and 0·396 due to the cation. The individual shares are therefore—

$$\text{Anion (Cl) } 0·604 \times 109·1 = 65·9$$
$$\text{Cation (Na) } 0·396 \times 109·1 = 43·2$$

These results carry the interpretation that if we could put 35·5 g of chlorine ions between our standard electrodes 1 cm apart and apply a p.d. of 1 V, the developed current would be 65·9 A. If, then, we add 23 g of sodium ions without the production of any molecular salt, the current will be increased by 43·2 A, giving a total of 109·1 A for the 58·5 g of completely dissociated sodium chloride.

The question arises: Are these values specific to the ions? Is the same value forthcoming for chlorine from data taken with, say, potassium chloride? For KCl the relevant data are: Maximum equivalent conductance = 130·1, and transport numbers are for K = 0·496 and Cl = 0·504. None of these figures appears to coincide with those for sodium chloride. Put them through the same operation, thus—

$$\text{Anion (Cl) } 0·504 \times 130·1 = 65·6$$
$$\text{Cation (K) } 0·496 \times 130·1 = 64·5$$

The value for chlorine agrees in both cases, and this agreement persists whatever chloride is taken.

Specific Ionic Mobilities. Again from a succession of sodium compounds we invariably obtain the number 43 for sodium, and from potassium compounds the value is consistently of the order of 64·6. These definite contributions of these ions to the maximum equivalent conductances of electrolytes are called the Specific Ionic Mobilities. Others are obtained in a similar manner and are brought together in Table XXXVIII.

From these figures we deduce that each of the ions acts in developing current quite independently of its accompanying ion. They enjoy a measure of independence which is called

TABLE XXXVIII
SPECIFIC IONIC MOBILITIES

Electrolyte	Anion	Cation	Maximum Equivalent Conductance
H_2O . . .	174	315	489
H_2SO_4 . . .	68	315	383
HCl . . .	65·5	315	380·5
HNO_3 . . .	61	315	376
$HC_2H_3O_2$ . .	35	315	350
KCl . . .	65·5	64·6	130·1
NaCl . . .	65·5	43·6	109·1
KOH . . .	174	64·6	238·6
$CuSO_4$ . . .	68	46	114
$AgNO_3$ . . .	61	54	115

the Freedom of the Ions, a freedom which enables them to exhibit individual characteristics though not allowing them to exist without the company of an equivalent quantity of an opposite ion.

In case the student is tempted to work out others it should be pointed out that the values in Table XXXVIII represent the averages of numerous experimental results from different workers and some slight variations are to be anticipated in data derived from different sources, having in mind, too, the nature of the experiments from which these results arise.

Dissociation of Pure Water. After all due care in the preparation of pure water the conductivity has been determined to have a value of 384×10^{-10} mho.

This represents a specific resistance of $26\,000\,000\;\Omega$. From the specific ionic mobilities of hydrogen and hydroxyl (315 and 174 respectively) we get, by addition, the maximum equivalent conductance of water, so that 18 g of completely ionized water give a conductance of 489 mho. The quantity of dissociated water per cubic centimetre is therefore $384 \times 10^{-10}/489$ gramme-molecules. Invert this figure and divide by 1 000, and we have the number of litres of water which contain a molecular weight of dissociated water. The figure is of the order of 12 700 000. This represents an appreciable conductance when compared with some of the very dilute solutions which the electro-chemist is sometimes called upon to handle.

For most purposes, however, we do not go far wrong in regarding water as an insulator.

For so slight a degree of dissociation as that shown by water only the first of two possible stages can be regarded as having been reached. The reaction is therefore expressed as follows—

$$H_2O \rightleftharpoons H. + OH^-$$

Maximum Equivalent Conductance of Weak Electrolytes. It has already been pointed out that in the case of weak or feebly dissociated electrolytes there is some difficulty in the computation of the maximum equivalent conductance. Acetic acid (see page 93) is a case in point. The figure can, however, now be arrived at by the following method. The specific ionic mobilities of the two ions are separately determinable from other compounds exhibiting much more marked dissociation. Potassium acetate dissociates freely and the specific ionic mobility of the $C_2H_3O_2$ ion is therefore readily obtained. That of the hydrogen ion is also obtained from the strong acids. The addition of these two values $35 + 315 = 350$ gives the maximum equivalent conductance for acetic acid, a figure which has already been used in the discussion of the law of dilution.

Other cases of weak electrolytes are similarly dealt with.

Absolute Velocity of Ions. From the first it has been indicated that sooner or later we must come to the expression of ionic mobility on an absolute scale, that is, in terms of centimetres per second or similar units. With the specific ionic mobilities settled we are able to go a stage further in this quest. For this purpose consider one centimetre cube of N . HCl between standard electrodes with a p.d. of 1 V. Assume that the acid is wholly dissociated. The figure for dissociation of this concentration of the acid is of the order of 0·79. The assumption does not, however, invalidate the argument as we are really concerned with a solution which is normal with respect to ions and not to total mass of the acid, and this is easily attained by taking somewhat stronger acid.

The maximum equivalent conductance of this acid is $315 + 66 = 381$, and with a p.d. of 1 V a current of 0·381 A will be generated in this centimetre cube of this ionically normal acid. Of this current, 0·315 A will be concerned with the migration of hydrogen ions, which occur in the centimetre

cube to the extent of 0·001 gramme-equivalents : and 0·066 A with the transference of the anion Cl⁻, which occurs to the same equivalent strength.

By the time sufficient coulombs have passed to account for the deposition of this 0·001 gramme-equivalents of hydrogen, those ions first in proximity to the anode will have migrated to the cathode, that is, they will have traversed a distance of 1 cm. To deposit 0·001 gramme-equivalents of hydrogen, we require 96 540/1 000 = 96·54 C. or A sec, and as the current associated with the migration of the hydrogen ions is 0·315 A, the time required for the migration of hydrogen ions through 1 cm will be 96·54/0·315 = 306 sec, corresponding to 1/306 = 0·003 26 cm/sec. This rate of migration, however, is generated with a p.d. of 1 V across a length of 1 cm and is increased proportionately with increase of p.d. The fall of potential per centimetre length is called the Potential Gradient, and thus it is usual to express the absolute rate of migration in terms of centimetre per second, per volt per centimetre, or, more briefly, cm/sec/volt/cm.

Having obtained the value for the hydrogen ion, all others can be readily calculated from the relative rates of migration as expressed in the values known as specific ionic mobilities as shown in Table XXXIX.

TABLE XXXIX

ABSOLUTE VELOCITIES OF IONS

cm/sec/volt/cm.

Cations				Anions			
H .	.	.	0·003 26	OH	.	.	0·001 8
Cu .	.	.	0·000 476	Cl .	.	.	0·000 681
Na .	.	.	0·000 451	SO₄	.	.	0·000 703
K .	.	.	0·000 668	NO₃	.	.	0·000 631
Ag .	.	.	0·000 56	C₂H₃O₂	.	.	0·000 356

From these figures it will be seen how exceedingly slow is this rate of migration. Take, for example, the copper ion. Its rate of migration is 0·000 476 cm/sec with a potential gradient of 1 V.

Imagine a copper sulphate solution with copper electrodes 10 cm apart and a p.d. of 1 V across them. The value of the

current does not concern us, this depending upon the area of the electrodes and the concentration of the electrolyte. Copper ions are formed at the anode. They migrate and are subsequently deposited at the cathode. What time is involved in their migration from the anode to the cathode? The distance is 10 cm and the potential gradient is therefore 0·1 V.

The time required is therefore—

$$\frac{10}{0\cdot000\ 476 \times 0\cdot1 \times 3\ 600} = 58\cdot3 \text{ hr.}$$

In other words, copper ions formed at the anode will, under these conditions, arrive at the cathode over 58 hr later if only

ionic migration comes into play. This well illustrates the need for some type of stirring where continued deposition is involved, and fortunately this requisite is readily supplied.

Incidentally, too, it may be noted that our expression of current has been reduced to very simple terms. It
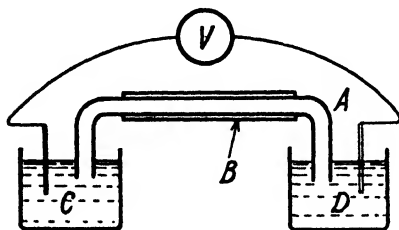
FIG. 32. SPEED OF IONS:
LODGE'S METHOD

was originally pointed out that current is a factor embracing the number of ions and their rates of migration. The number and therefore the mass of the ions is concerned with the strength of the solution and the degree of dissociation at that concentration, while the rate of migration combines the two fundamental units of length and time.

Moving Boundary Methods. The foregoing is a method of computation of ionic migration against which nothing can be urged. It might, however, be interesting if these results could be made more obvious by actual measurements even if the latter were only approximate.

Several methods have been devised, one of which, due to Sir Oliver Lodge,* may be briefly described. In Fig. 32 *A* is an inverted flat U-tube. It is filled with a solution of sodium chloride containing the merest trace of alkali and phenolphthalein. Into this solution in the course of preparation is added

---

* *British Association Report* 389 (1886).

sufficient gelatine to give it rigidity when cold, so that the tube can be inverted while still retaining its contents. The gelatine merely provides a fairly rigid yet very porous structure in which the electrolyte is retained.

Beakers C and D into which the tube is inverted contain dilute sulphuric acid with small platinum electrodes. Without the application of any p.d. the acid and therefore hydrogen ions diffuse into the tube neutralizing the trace of alkali, thus removing the violet colour of the phenolphthalein. This is allowed to progress until the colour is being removed from the horizontal portion of the tube in which, by a suitable scale B, its progress can be measured.

By the application of a p.d. across the electrodes ionic migration is developed, thus increasing the rate at which the phenolphthalein is decolorized from the anode and towards the cathode. This increased rate is definitely due to hydrogen ion migration. It can be approximately measured, and some computation of the potential gradient made, from the voltmeter reading taken during the experiment.

The following values found by this method are recorded together with those deduced by the principle which has been derived from the specific ionic mobilities. These experimental

TABLE XL

ABSOLUTE VELOCITIES OF IONS (LODGE)

Ion	Absolute Velocity (cm/sec/volt/cm.)	
	Found	Calculated
Barium . .	0·000 12	0·000 57
Strontium . .	0·000 15	0·000 56
Chlorine . .	0·000 14	0·000 68
Bromine . .	0·000 14	0·000 70
Hydrogen . .	0·002 60	0·003 20

results only show a fair degree of accuracy owing to the very difficult circumstances attaching to the maintenance of a sharp boundary and to the measurements, especially that of the potential gradient.

A further experimental method designed and carried out by

Whetham* is indicated in Fig. 33. Two electrolytes having a common ion and practically equal conductances were chosen, one having a coloured ion. The selected electrolytes were potassium carbonate and potassium dichromate, a sharp junction of the two liquids being obtained. The movement of the coloured dichromate ion towards the anode under controlled and
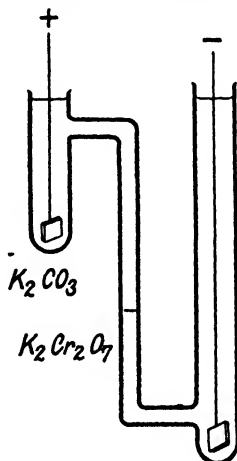
FIG. 33. SPEED OF IONS: WHETHAM'S METHOD

definitely known electrical conditions was thus observed and the results obtained were more satisfactory than those by the previous method.

Whetham's results are embodied in Table XLI.

TABLE XLI

ABSOLUTE VELOCITIES OF IONS (WHETHAM)

Ion	Absolute Velocity (cm/sec/volt/cm.)	
	Found	Calculated
Copper . .	0·000 29	0·000 47
Chlorine . .	0·000 58	0·000 68
Cr_2O_7 . . .	0·000 47	0·000 47
Calcium . .	0·000 35	0·000 53
Silver . . .	0·000 49	0·000 56
SO_4 . . .	0·000 45	0·000 70

* *Trans. Royal Society*, 184A 337 (1893), 186A 507 (1895).

Again, a review of the calculation involved in the computation of the absolute rate of migration of the hydrogen ion (page 131) reveals the fact that this figure is obtained as follows—

$$\frac{\text{Current per volt transporting the ion per square centimetre}}{\text{Coulombs required to remove ions from the cubic centimetre}}$$

$$= 0{\cdot}315/96{\cdot}54 \text{ A,}$$

and multiplying numerator and denominator each by 1 000 we have—

$$\frac{315}{96\,540} = \frac{\text{Specific ionic mobility of the ion}}{\text{Faraday}}$$

so that generally

$$\frac{\text{Absolute velocity of ions}}{\text{(cm/sec/volt/cm.)}} = \frac{\text{Specific ionic mobility}}{\text{Faraday}}$$

APPLICATIONS TO GENERAL CHEMICAL PRACTICE

Introduction. The applications of the theory of solutions are obviously of considerable importance in the study of many chemical reactions in which, for the greater part, we are intimately concerned with the use of substances in the form of aqueous solutions. The theory so far developed shows that, for example, a dilute solution of hydrochloric acid is something more than a mere mixture of water and acid molecules. The fact that a large proportion of the acid is dissociated and that there is, therefore, a definite concentration of hydrogen ions and chlorions, must be taken into account in considering the course of many chemical reactions including those related to qualitative and quantitative analysis in which concentrations exert a profound influence.

Neutralization of Acids and Alkalis. The simple question: "Why are the acids acid?" finds its answer in the common presence of hydrogen ions. Acidity, common to all these substances, can hardly be accounted for by the presence of dissimilar ions such as NO_3, SO_4, Cl, etc., as these also are present in solutions of the neutral salts of the respective acids. Similarly, the alkalis are alkaline by reason of the common ion OH. Now it is well recognized that the neutralization of equivalent quantities of many acids and alkalis is attended by the same heat evolution, which might not be easily accounted for if we are dealing with molecular materials without much apparent harmony in their composition. The equation —

$$NaOH + HCl = NaCl + H_2O$$
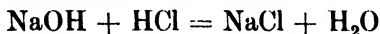
assumes a different aspect when written in terms of the ionic theory thus—

$$Na. + OH^- + H. + Cl^- \rightarrow Na. + Cl^- + H_2O$$
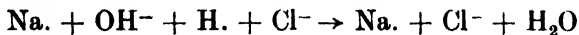
This form expresses the fact that neutralization is concerned with the combination of hydrogen and OH ions with the formation of non-dissociated water, the sodium and chlorine ions remaining unaffected by the reaction.

Reduced to its more simple terms the neutralization becomes—

$$H. + OH^- \rightleftharpoons H_2O$$

from acids   from alkalis   undissociated water molecules
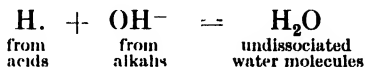
The similar process with a common heat evolution thus finds adequate explanation (page 158).

Neutralization by Electrical Resistance Method. The point of completion of some chemical reactions in solution may be accurately ascertained by an electrical method which is based upon ionic speed changes. Such a method is useful in the case of neutralization in which indicators are unsuitable owing perhaps to a masking of the colour by existing coloured compounds such as dyestuffs.

By maintaining a fairly uniform concentration the formation and disappearance of certain ions may be rendered evident by taking repeated measurements of the electrical resistance of a certain volume of the solution during the course of the titration. The introduction of a swift ion, like hydrogen, for example, causes a rapid fall in resistance, while the replacement of a fast ion by one with a lesser degree of mobility is accompanied by a corresponding increase in resistance.

Take, for example, the reaction—

$$NaOH + HCl \rightleftharpoons NaCl + H_2O$$

The alkali solution originally contains the Na. and OH^- ions. Addition of HCl causes the replacement of the moderately fast OH^- (Specific ionic mobility = 174) with the much slower Cl ion (Specific ionic mobility = 65), with an increase of resistance. With the first excess of HCl there will be the introduction of the rapidly moving H ion (Specific ionic mobility = 315) with a marked decrease in resistance, which is further rapidly decreased by the presence of more HCl. With successive additions of HCl, therefore, to an alkaline solution there will first be an increase in resistance, followed immediately after neutralization by a rapid decrease.

These changes of resistance can now be plotted against the known additions of acid, and by continuing the two branches of the curve the point of intersection will indicate the exact addition of acid to effect neutralization.

Typical curves are given in Fig. 34. Curve *A* represents the

increase of resistance by the addition of acid to alkali, while curve B shows the effect of excess of acid. The point of inter-section C marks the point of neutralization by the amount of alkali represented at N.

The conditions are, however, different with a weak acid like acetic acid. Here the resistance of the acid is large owing to its small degree of dissociation. The addition of sodium hydroxide to it involves the formation of sodium acetate with a large degree of dissociation. Relatively few hydrogen and acetic ions (from the acetic acid) are replaced by many more sodium and acetic ions, thus reducing the resistance (XY). This continues until the point of neutralization (Y) is reached by the addition of alkali indicated at M, after which the further addition of alkali will involve the introduction of rapidly moving OH ions with a marked reduction of resistance. This change is indicated in curve YZ of Fig. 34, where resistance is plotted against frequent additions of alkali.

ACB   Acid to Alkali

XYZ   Alkali to HĀ

FIG. 34. NEUTRALIZATION BY CONDUCTANCE

Amphoteric Electrolytes. A number of chemical compounds is known which exhibit acidic or basic properties according to the chemical "atmosphere" in which they are placed. Arsenious oxide, for example, dissolves in hydrochloric acid, giving arsenious chloride of the usual metallic salt class.

$$As_2O_3 + 6HCl = 2AsCl_3 + 3H_2O$$
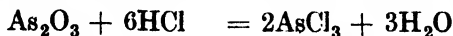
In sodium hydroxide it also dissolves, giving sodium arsenite, thereby exhibiting acidic properties.

$$As_2O_3 + 6NaOH = 2Na_3AsO_3 + 3H_2O$$
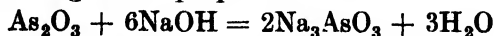
Some electrolytes behave similarly. Aluminium hydroxide, though only very slightly soluble, ionizes in two ways, thus—

(1) $Al(OH)_3 \rightleftharpoons Al... + 3OH^-$

and   (2) $Al(OH)_3 \rightleftharpoons H^+ + AlO(OH)_2^-$
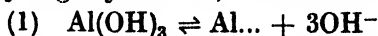
In the presence of hydrogen ions, dissociation proceeds according to equation (1) while in an alkaline atmosphere, that is in the presence of OH ions, dissociation follows the course of equation (2). To such electrolytes the terms amphoteric or ampholyte are also applied. Many other substances behave similarly. While acetic acid definitely ionizes as follows—

$$C_2H_4O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$
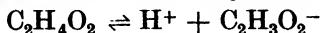
the introduction of an amino group, as, for example, in aminoacetic acid or glycocoll ($CH_2 . NH_2 . COOH$), imparts amphoteric properties so that ionization takes two courses as follows—

(1) $NH_2 . CH_2 . COOH + H_2O \rightleftharpoons NH_3 . CH_2 . COOH. + OH^-$

(2) $NH_2 . CH_2 . COOH \rightleftharpoons NH_2 . CH_2 . COO^- + H$
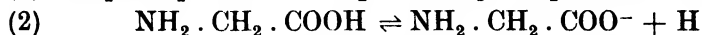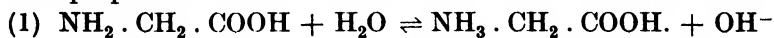
The course of ionization depends upon the "atmosphere." Under acidic conditions dissociation proceeds according to equation (1), the hydroxyl ions being removed by the hydrogen ions from the acid. Under alkaline conditions the second type of dissociation takes place, the hydrogen ions being removed by the hydroxyl ions of the alkali. Chemically, too, this compound combines with an acid forming an acid salt and forms also with sodium hydroxide a sodium salt by replacement of the carboxylic hydrogen by that metal.

Similar conditions hold also for zinc, which, in the so-called acid solutions, forms a zinc ion $Zn^{..}$, while in alkaline solutions —and these are largely used in electrodeposition—the zinc exists in the form of a complex ion ZnO_2''. Tin acts in the same manner, forming tin ions $Sn^{..}$ in "acid" solutions and stannite SnO_2'', or stannate SnO_3'' ions, in alkaline solutions, largely used in the electrodeposition of the metal.

Replacement of One Metal by Another. Take the case of zinc put into copper sulphate. The usual form of equation is—

$$Zn + CuSO_4 = ZnSO_4 + Cu$$
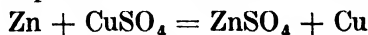
The similar reaction with the chloride is—

$$\dot{Zn} + CuCl_2 = ZnCl_2 + Cu$$
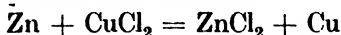
Again, as with other examples of zinc with copper salts, there is a common heat evolution. This finds adequate explanation when any one of these reactions is expressed in a form which introduces ionized materials. Then—

$$Zn + Cu.. + SO_4^{--} = Zn.. + SO_4^{--} + Cu$$
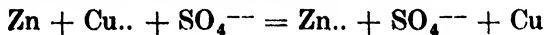
the so-called acidic radical cancelling out from both sides of the equation in all cases. This reaction will demand closer investigation when considering the electro-chemistry of the Daniell cell. Reduced to simple terms we have—

$$Zn + Cu.. = Zn.. + Cu$$
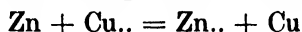
Many other cases follow on similar lines.

The avoidance of this simple immersion deposition is essential to the production of adhesive deposits. Simple immersion deposition is accompanied by the superficial solution of the more negative metal being plated. Subsequent deposits, therefore, are made on a loose foundation, a condition most likely to lead to stripping. This trouble is avoided by reducing the concentration of the positive metal ions either by converting them into complex ions, as in the cases of all cyanide solutions, or by the large addition of a conducting salt with a common ion, as in the addition of magnesium sulphate to nickel solutions required for the deposition of the metal on zinc or its alloys.

Mixtures of Substances Without Precipitation. A solution of sodium chloride is added to one of potassium nitrate. Whatever products there may be are soluble in water. There is therefore no precipitation, yet evaporation of the mixed solution shows the presence of all four possible salts in proportions determined by the relative quantities of the two original substances. Chemical action has taken place but there is no external evidence of it in the form of heat evolution. Written chemically, the reaction is—

$$NaCl + KNO_3 \rightleftharpoons KCl + NaNO_3$$
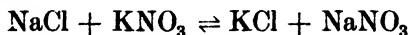
the reaction being reversible. Written from the ionic point of view the reaction becomes—

$$Na. + Cl^- + K. + NO_3^- \rightleftharpoons K. + Cl^- + Na. + NO_3^-$$
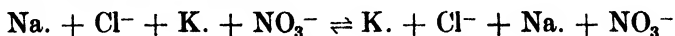
This, however, would only be a true statement if both solutions were at infinite dilution. Under ordinary conditions of dilution some part of the two original salts would not be dissociated, while the ions formed by this partial dissociation would combine to a certain extent forming molecules of the two other products. Heat absorptions, on the one hand, are exactly balanced by heat formations on the other.

Some Analytical Examples. Qualitative analysis is to some extent concerned with the identification of basic and acidic radicals in solids or solutions. There are, for example, well-recognized tests for "copper," as it is usually called. These include the displacement of copper by iron or zinc, the precipitation of copper sulphide in acid solutions with sulphuretted hydrogen, and the production of the blue colour with an excess of ammonia. These tests, however, are not productive of results when applied to a copper solution in the form of a double cyanide. From such a solution iron does not precipitate copper, in fact solutions of this type are kept and heated in iron tanks in the usual electrodeposition processes. Nor does sulphuretted hydrogen give a black precipitate of copper sulphide from the cyanide solution, hence the separation from cadmium in Group II, while ammonia is also indifferent. The explanation of these apparent anomalies is found in the fact that the double cyanide solution does not contain any appreciable quantity of copper ions, while the tests which we usually apply for, as we say, copper are more strictly tests for cupric ions. Few analytical text-books are written from this standpoint, though the fact is not lost sight of by their authors.

Many well-known chemical facts at once receive adequate explanation from this suggestion of electrolytic dissociation. The colour of solutions is a case in point. Solutions of copper nitrate and sulphate are blue with, however, somewhat different shades of that colour. That of copper chloride is definitely green. In all cases dilution yields a common blue colour due to the common copper ion. In the solid dehydrated form, copper chloride is yellow. In strong solutions this, combined with the blue colour due to the first formed copper ions, yields the green, which with dilution passes to the blue characteristic of the copper ion. Thus —

$$CuCl_2 \rightleftharpoons Cu.. + 2Cl^-$$
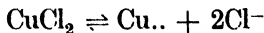
The persistent yellow colour of soluble chromates is due to the CrO_4^{--} ion; that of the soluble dichromates to the $Cr_2O_7^-$ ion, while that of the alkaline permanganates must be ascribed to the persistent MnO_4^- ion. In fact there is abundant evidence that in the crystalline form many compounds have already begun this process of dissociation with the water of crystallization.

Oxidations and Reductions. It will first be appreciated that the oxidation of ferrous to ferric salts involves the increase in the active valency of the iron ion. Ferrous ions are divalent while those of ferric are trivalent, and the conversion of ferrous chloride to ferric chloride with, say, chlorine is usually expressed as follows—

$$2FeCl_2 + Cl_2 = 2FeCl_3$$

This again is not a reaction between molecules. The chlorine which is taken up in the reaction first assumes the ionic form in which it also occurs in the dissociated ferric compound. Its assumption of the negatively charged ionic form involves the liberation of an equal and opposite positive charge which increases that of the ferrous ion to that of the ferric thus—

$$FeCl_2 \rightarrow Fe.. + 2Cl^-$$
$$Cl_2 \rightarrow 2Cl^- + 2\bigcirc$$

Adding these reactions we get—

$$2Fe.. + 4Cl^- + 2Cl^- + 2\bigcirc = 2Fe... + 6Cl^-$$
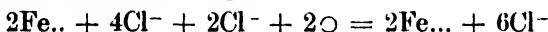
Other oxidizing reagents can be brought into line with this simple case.

Turning now to the reduction of ferric to ferrous iron it will be remembered that this is not brought about by merely bubbling the gas hydrogen through the ferric solution. Acidification of the solution followed by the addition of zinc readily effects the reduction due, as we ordinarily say, to the production of nascent or atomic hydrogen. What we are really concerned with is the production of zinc ions at the expense of the ferric ions thus—

$$2Fe... + Zn = Zn.. + 2Fe..$$

the ferrous and zinc ions combining to some extent with chlorine ions to form molecular chlorides, the total reaction being then written chemically—

$$2FeCl_3 + Zn = 2FeCl_2 + ZnCl_2$$
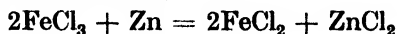
Solubility of Relatively Insoluble Substances. While many substances are so slightly soluble in water as to be regarded as practically insoluble, insolubility in the absolute sense is not admitted. Barium sulphate and silver chloride, for example, are usually regarded as insoluble substances, and this is admitted

in the precipitation of these substances in the quantitative estimations of sulphates and chlorides. They, however, do possess a measurable degree of solubility. That for silver chloride amounts to only 1·5 parts per million or 1·5 mg/litre.

This is obviously far too small an amount to be estimated by the process of saturating water and evaporating a measured volume to dryness. This would involve the evaporation of 1 litre of solution to recover 1·5 mg for weighing. A much more reliable method involves the estimation of the electrical conductivity of the saturated solution. By methods which have previously been described, the specific resistance of this solution is of the order of 800 000 Ω.

At this extreme dilution it may be reasonably assumed that the substance is completely dissociated. The specific ionic mobilities of Ag and Cl are 54 and 65·5 respectively. The maximum equivalent conductance of silver chloride is therefore the sum of these two quantities, viz., 119·5. It will suffice to call this 120, meaning that 143·5 gm of completely dissociated silver chloride give rise to a conductance of 120.

Now the conductance of 1 cm³ of the saturated AgCl solution is 1/800 000 mho. Hence—

120 mho are produced by 143·5 g of ionized AgCl

$$1/800\ 000\ \text{mho is produced by } \frac{143\cdot5}{120} \times \frac{1}{800\ 000} \text{ g AgCl}$$

$$\text{equivalent to } \frac{143\cdot5 \times 1\ 000 \times 1\ 000}{120 \times 800\ 000} = 1\cdot5 \text{ mg/litre}$$

In the case of calcium sulphate the saturated solution has a specific resistance of 295 Ω. The specific ionic mobilities of calcium and SO_4 are 46 and 68 respectively, giving a maximum equivalent conductance of 114 for calcium sulphate. On the basis of the similar calculation we have—

$$CaSO_4 \text{ per litre} = \frac{136 \times 1\ 000}{2 \times 114 \times 295} = 2 \text{ g.}$$

Here the maximum equivalent conductance is for $\frac{1}{2}CaSO_4$, hence the 2 in the denominator.

Solubility Product. In approaching this topic, reference may be made to the fact that many solids are soluble in liquids

which are immiscible. For example, iodine dissolves in water and also, but much more freely, in ether. If iodine is shaken up with a mixture of ether and water insufficient to dissolve the whole of the solid, that is, to ensure saturation in both of the solvents, there is a definite proportionality between the quantities of the iodine dissolved in the two liquids. This ratio can readily be determined in this and many similar cases. This ratio is called the "partition coefficient." As another example, acetic acid dissolves in water and in ether, being more soluble in water than in ether, the relative proportions or "partition coefficient" being as 1·9·: 1·0. Moreover, this ratio is practically the same as that of the solubilities in the two liquids separately, and, still further, it has been definitely shown that it does not alter even when the two liquids solvents in contact with each other are not saturated.

This matter can now be brought down to the more interesting examples of substances which are usually regarded as insoluble, but which, it will be realized, are as a matter of fact very slightly soluble. Take, for example, the case of silver chloride, of which a saturated solution stands in contact with the solid. There is then a constant ratio between the concentration of the silver chloride in the solution and the solid. In the case of the solid the concentration is 100 per cent, and this makes the concentration of the dissolved silver chloride constant.

At this extreme dilution it may be assumed that the silver chloride is completely dissociated, giving a similar ionic concentration for each of the ions. The product of these ionic concentrations is known as the "solubility product." That for silver chloride is obtained in the following manner, the concentrations being expressed in terms of gramme-molecules or gramme-ions per litre. The solubility of silver chloride is 1·5 mg/litre or 0·001 5 g/litre. Expressed in terms of gramme-molecules, the solubility becomes $0·001\ 5/143·5 = 1·05 \times 10^{-5}$. Completely dissociated, the ions have the same concentration, and the solubility product (S) for silver chloride is therefore—

$$S = 1·05 \times 10^{-5} \times 1·05 \times 10^{-5} = 1·1 \times 10^{-10}$$

It is well recognized that these solubility products are constant for individual substances. It follows that if the concentration of either ion is increased by the addition of another

substance yielding either ion, this ionic product which cannot increase will be kept constant by the precipitation of some of the substance.

In the following equation assume both substances have been added together in exactly equivalent quantities.

$$AgNO_3 + NaCl = AgCl + NaNO_3$$
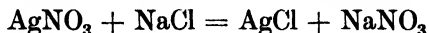
The precipitation of silver chloride is incomplete by the amount (though only very slight) which remains in solution and which is completely dissociated. The addition of an excess of silver nitrate increases the silver ion concentration and with it the product of the ionic concentrations of silver and chlorine. This at once leads to the precipitation of a further small amount of silver chloride, which substance is therefore more completely precipitated in the presence of an excess of silver nitrate than with its exactly theoretical amount.

An excess of sodium chloride might therefore be expected to exert a similar effect. This, however, is not the case, as here a complex ion of the type $AgCl_2^-$ is formed, leading to the re-solution of some of the precipitated silver chloride, and hence a less complete quantitative recovery.

TABLE XLII

SOLUBILITY PRODUCTS

Substance	Solubility (g/litre)	Solubility Product
AgCl . .	0·001 5	$1·1 \times 10^{-10}$
Ag_2CrO_4 .	0·025	$1·7 \times 10^{-12}$
$CaSO_4$ . .	2	$2·3 \times 10^{-4}$
$CaCrO_4$ . .	$5·6 \times 10^{-3}$	$1·9 \times 10^{-9}$
HgCl . .	$1·05 \times 10^{8}$	2×10^{-21}
$PbSO_4$ . .	0·041	$2·3 \times 10^{8}$
$BaSO_4$ . .	$2·3 \times 10^{-3}$	$1·2 \times 10^{10}$
$BaCrO_4$ . .	$3·8 \times 10^{3}$	$2·3 \times 10^{-10}$

These solubility products are, in many cases, determinable by comparatively simple analysis. That for potassium bromate, for example, is obtained by making a saturated solution of the substance, cooling to 20° C., taking out a measured quantity, mixing with an excess of potassium iodide and, after acidifying with sulphuric acid, titrating with N/10 sodium thiosulphate.

A further volume of the solution is taken and a known amount of potassium bromide is added. After shaking and standing, the bromate is redetermined, and from the decreased bromate concentration and the known increased potassium ion concentration a constant product is obtained.

Applications in Qualitative Analysis. Many curious variations in the solubilities of the sulphides of the metals give rise to methods of their separation. A number of well-known metallic sulphides are precipitated in fairly strong acid solution and are therefore thrown down by passing H_2S after the removal of silver, lead and mercurous with excess of hydrochloric acid. Others, such, for example, as those of nickel, cobalt, manganese and zinc, are partially precipitated in originally neutral solutions and completely thrown down in alkaline solutions. The conception of solubility product provides an adequate answer for these differences of behaviour. The following values for solubility products are interesting in this connection: HgS, 4×10^{-54}; CuS, 8×10^{-45}; CdS, 5×10^{-29}; ZnS, 1×10^{-20} and MnS, $1\cdot4 \times 10^{-15}$. The passage of H_2S into solutions of these metallic salts will lead to the precipitation of the sulphides, when the product of the concentration of the two ions exceeds the solubility product. Of the two ions greater variation is practically possible with the gas rather than with the metallic salt. As a weak acid the dissociation of H_2S—

$$H_2S \rightleftharpoons 2H. + S''$$
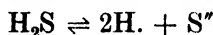
is variable with the concentration of hydrogen ions due to the amount of acid present. In the presence of acid the sulphur ion concentration is lowered with the result that the metal ion concentration is increased, and with it a less complete precipitation of the metallic sulphide. In a neutral zinc sulphate solution the passage of H_2S only effects partial precipitation of the zinc sulphide, owing to the acid set free. A more complete precipitation is obvious by the addition of water, which reduces hydrogen ion concentration and therefore increases the sulphur ion concentration and with it a reduction of the metal ion concentration. A more complete result is obtained by the addition of sodium acetate, the "buffering" effect of which is referred to in Chapter XVI.

These solubility products, together with the formation of

many complex ions, are responsible for many reactions advantageously employed in both qualitative and quantitative analysis.

Solubility Product of Water. In the case of water the ionic concentration is 0.8×10^{-7} gramme-molecules per litre, and the ions are in equilibrium with the liquid. The usual expression for the relation of these concentrations therefore holds as follows—

$$\frac{(H) \times (OH)}{(H_2O)} = K$$

The concentration of the water liquid, however, is constant, being of the order of $1\,000/18 = 55$ gramme-molecules per litre.

Hence $$(H) \times (OH) = K$$

and the ionic product, that is the product of the concentrations of the ions, is therefore $(0.8 \times 10^{-7})^2 = 0.64 \times 10^{-14}$. This figure varies with temperature as shown in Table XLIII.

TABLE XLIII
IONIZATION OF WATER

Temperature (C.)	$K \times 10^{14}$
10	0·3
20	0·69
30	1·48
40	3·02
60	9·33
80	23·4
100	51·3

Thus the very limited dissociation of water is appreciably increased with an increase of temperature.

Water Testing. In one form of water-testing apparatus some attempt is made to determine the relative qualities of solids in well waters drawn from the same source. Imagine such a water to contain a number of impurities always in the same proportions. A sample is carefully analysed and the conductance of the water determined. From time to time the conductance of the water is redetermined in an apparatus specially designed for easy and comparative measurements. Assuming,

then, that the impurities are constant in nature and also in relative proportions, the electrical conductance becomes a rough measure of the amount of solids present.

The principle of the method will readily be followed as also will be the limitations of its applicability.

Acidity and Alkalinity of " Salts." Simple chemical notions teach that salts are neutral compounds while experience soon shows this to be not exactly true.

Ferric chloride, for example, is strongly acid. The reason is this : Ferric chloride is partially hydrolyzed in water, the ferric hydroxide remaining dissolved in the excess of chloride or assuming the colloidal form.

$$FeCl_3 + 3H_2O = Fe(OH)_3 + 3HCl$$
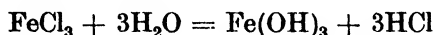
In any case, it is only very slightly ionized. On the other hand the equivalent quantity of hydrochloric acid set free is almost completely ionized, and thus there is a preponderance of hydrogen ions with resulting acidity. The phosphates of sodium provide another interesting example. Trisodium phosphate should apparently be a neutral compound. A litmus test shows it to be strongly alkaline. Assume a small degree of hydrolysis thus—

$$Na_3PO_4 + 3H_2O = 3NaOH + H_3PO_4$$
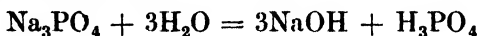
Viewed as chemical compounds the alkali and acid are formed in exactly equivalent quantities and this therefore does not account for the alkalinity. Caustic soda, however, dissociates far more than phosphoric acid, and thus we have an excess of OH ions and therefore alkalinity.

In the same way disodium hydrogen phosphate should be an acid phosphate and give an acid reaction. Hydrolysis yields—

$$Na_2HPO_4 + 2H_2O = 2NaOH + H_3PO_4$$
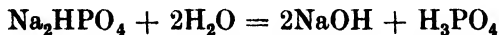
Here the acid is molecularly in excess of the alkali, but the greater ionization of the latter compound more than counter-balances that of the relatively larger quantity of the acid, thus giving a slightly alkaline solution.

THERMO-CHEMISTRY

Introduction. If chemistry is defined as a study of the properties of substances as they are mainly dependent upon composition, and also the changes of properties with change of composition brought about by mutual interaction, it is also concerned with a number of phenomena attendant upon chemical change. One of the most important is that of heat evolution and absorption. Thermal change invariably accompanies chemical change. In fact in the absence of thermal change it may almost be said that there is the absence of chemical change. The study of these thermal changes is called Thermo-chemistry.

To the elementary student the following equations—

$$C + O_2 = CO_2$$
and
$$2H_2 + O_2 = 2H_2O$$
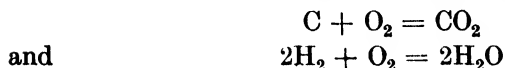
may appear as adequate representations of the complete combustion of carbon and hydrogen. The masses of the substances reacting and produced are in agreement with the general law that no matter is either created or destroyed. Thermo-chemistry, however, takes into account another factor. If we could have a balance which weighed both matter and energy it would then be very obvious that 44 g of carbonic acid gas weighed very much less than 12 g of carbon and 32 g of oxygen. The difference represents the energy in the original components which does not persist in the product. The energy is usually manifested in the form of heat developed during the combustion process.

Forms and Transformation of Energy. Defining energy as the power of doing work, we are at once able to measure the energy set free or absorbed during chemical change. Every substance or system of substances contains energy differing in amount and ease of liberation and utilization. This sum total of inherent energy is called the "intrinsic energy," and the intrinsic energy of two systems of substances capable of intercation will differ by the amounts absorbed or evolved during the reaction. The whole of this energy is not made manifest

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during the course of the reaction, and the term "free energy" may be applied to that portion which is liberated, and "bound energy" to that portion not made manifest. In these latter days of scientific discovery we are told of the enormous stores of energy locked up within the atom, and which have been so devastatingly released in recent warfare, and have now assumed international importance, and are now being further investigated as a source of energy to replace rapidly dwindling supplies of the more common forms of fuel. We are here more concerned with the free energy.

Of the common forms of energy, mechanical energy is seen in the production of motion against resistance. Such energy is usually transmitted by means of ropes, belts, pulleys, and shafts. Electrical energy is transmitted through conductors, and is capable through suitable media of conversion into the mechanical form. Heat, which is molecular motion, is transmitted by conduction, convection and radiation, while chemical energy is that latent form resident in chemical substances and set free during chemical change.

These several forms are mutually transformable. Mechanical to electrical takes place in the dynamo, and the reverse process in the electric motor. Electrical energy is converted into heat in all forms of resistance by what are commonly called the I^2R losses, expressing the fact that the heat developed is proportional to the product of the square of the current and the resistance, and the reverse process takes place in the thermocouple and thermopile. Joule's quantitative experiment is based on this principle, upon which he determined that a British Thermal Unit (heat required to raise the temperature of 1 lb of water through 1° F.) was equivalent to 778 ft.-lb, and the joule (volt-ampere-second) equivalent to 0·239 g.cal. The calorie (gramme-calorie) is the amount of heat required to raise the temperature of 1 g of water through 1° C., or, more accurately, one-hundredth of the heat required to raise the temperature of 1 g of water from 0° C. to 100° C. There are no special units of chemical energy, it not being expressed until it has undergone transformation into heat, when calories provide a convenient unit. Chemical energy is transformed into electrical energy in the usual forms of voltaic cell, the reverse process taking place when electrical energy is utilized

in the production of chemical materials. Some of these trans-
formations can be carried out quantitatively, while this is
not possible with others. It would be difficult to get any exact
relationship of mechanical and electrical energy by means of
a dynamo or motor owing to unavoidable losses, but this
important comparison can be effected by transforming each of
these forms of energy separately into heat and comparing the
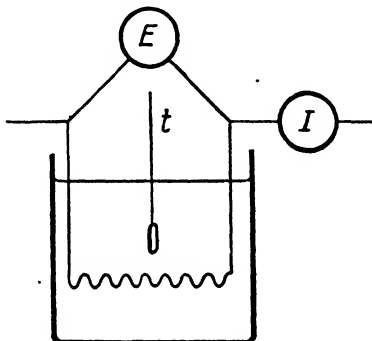
FIG. 35. CALORIMETER

quantities developed. It was by this means that a careful re-
lationship was obtained and by which we learn that a horse-
power is equivalent to 746 W.

For example, the quantitative transformation of electrical
energy to heat is obtained by methods of dissipating the heat
produced by electrical energy into a medium in which it can
be quantitatively absorbed and measured. A simple type of
calorimeter for this purpose is shown in Fig. 35 in which cur-
rent is passed through a coil of high resistance wire immersed
in water. Simple electrical measurements and temperatures give
the required details. Some element of design in the propor-
tioning of the quantity of water used and the energy input is
obviously required, together with adequate arrangements for
the prevention of the escape of heat during the experiment.
Note, too, must also be taken of the amount of heat absorbed
by the apparatus itself, a figure which, expressed in terms of a
change of temperature of 1° C., is called the water equivalent
of the calorimeter. These details, however, are not our immedi-
ate concern. The experiment is one which is capable of being

carried out with the greatest accuracy, and upon it depends our exact knowledge of the relationship of these two forms of energy. The following typical, though approximate, figures for an experiment may be taken as an illustration—

Mass of water, 2 000 g. Initial Temperature, 15° C. Final Temperature, 22·5° C. Current, 20 A. P.D., 10 V. Time, 5 min. For the sake of simplicity omit the amount of heat absorbed by the calorimeter vessel. Then the heat transferred to the water is the product of the mass of water and the increase in temperature. Hence—

Calories transferred to the water
$$= 2\ 000 \times (22 \cdot 5 - 15) = 15\ 000.$$

Further, the electrical energy measured as joules is the product of the volts, amperes, and seconds. Hence—

$$\text{Joules} = 10 \times 20 \times (5 \times 60) = 60\ 000$$
$$60\ 000\ \text{J} = 15\ 000\ \text{g.cal.}$$
$$1\ \text{J} = 0 \cdot 25\ \text{g.cal.}$$

These are approximate figures. The more exact figure is 0·238 8 or 0·239, which is frequently taken as 0·24.

$$\text{Now}\qquad 1\ \text{h.p.} = 33\ 000\ \text{ft.-lb/min.}$$
$$= \quad 550\ \text{ft.-lb/sec.}$$
$$778\ \text{ft.-lb} = 1\ \text{B.Th.U.}$$
$$= 454 \times \tfrac{5}{9} = 252\ \text{g.cal.}$$
$$1\ \text{ft.-lb} = 252/778 = 0 \cdot 324\ \text{g.cal.}$$

Hence
$$1\ \text{J} = 0 \cdot 238\ 8/0 \cdot 324 = 0 \cdot 737\ 2\ \text{ft.-lb.}$$
$$1\ \text{h.p.} = 550/0 \cdot 737\ 2 = 746\ \text{J/sec.}$$
$$= 746\ \text{W.}$$

These are relationships generally useful in calculations of the energy set free and required during the course of chemical changes.

Thermo-chemical Values. A very large number of figures representing thermal changes accompanying chemical change are available in the appropriate literature. Many have been determined directly in suitable calorimeters in which the chemical changes between exact quantities of substances have been effected in such a manner that the developed heat is

transferred to water and there estimated. The following may be taken as typical of a number of interesting and important cases, gramme-equation quantities being referred to—

$$C + O_2 = CO_2 + 96\ 960 \text{ g.cal.}$$

$$2H_2 + O_2 = 2H_2O + 136\ 800 \text{ g.cal.}$$

$$H_2 + Cl_2 = 2HCl + 44\ 000 \text{ g.cal.}$$

$$2Al + 3O = Al_2O_3 + 391\ 500 \text{ g.cal.}$$
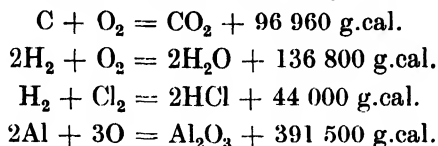
These are examples in which there are heat evolutions. Such reactions are said to be "exothermic."

Where the chemical change is accompanied by an absorption of heat, as for example in the production of calcium carbide—

$$CaO + 3C = CaC_2 + CO - 108\ 000 \text{ g.cal.}$$
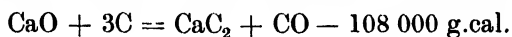
the reaction is said to be "endothermic." Obviously the reversal of an exothermic change must be endothermic, and thus—

$$2H_2O = 2H_2 + O_2 - 136\ 800 \text{ g.cal.}$$
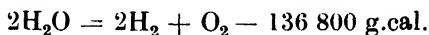
Further examples are given in Table XLIV ·in which the values more conveniently refer to chemically equivalent quantities and are therefore more easily comparable.

TABLE XLIV

THERMO-CHEMICAL DATA

Element	Calories per Gramme-equivalent			
	With Oxygen	With Chlorine	With Fluorine	With Sulphur
Magnesium . .	72 900	75 500	105 000	39 800
Aluminium . .	65 250	53 360	92 000	20 730
Calcium . .	65 450	84 900	108 000	46 000
Silicon . .	55 000			
Potassium . .	50 000	105 600	110 000	51 850
Sodium . .	49 900	97 700	109 700	44 100
Zinc . .	42 700	50 000	69 000	20 660
Hydrogen . .	34 200	22 000	37 600	
Iron . .	31 850	41 000	63 000	12 800
Carbon to CO_2 .	24 240			
Carbon to CO	14 500			
Lead . .	25 150	41 380		10 200
Copper . .	18 580	32 870	44 000	10 150

A few examples of the application of these figures may now be given. The reduction of copper oxide by hydrogen may be written thus—

$$CuO + H_2 = H_2O + Cu$$
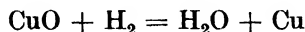
18 580 g.cal. represent the energy required to separate the copper and oxygen and 34 200 g.cal. are then forthcoming by the combination of hydrogen and oxygen. There is thus an excess of heat of $34\,200 - 18\,580 = 15\,620$ g.cal. per gramme-equivalent. The reaction is exothermic and, once started, proceeds with the evolution of energy. It is well known that after preliminary warming up, a mass of copper oxide becomes self-glowing on passing hydrogen over it.

Again it may be asked: What are the possibilities of the reduction of alumina with carbon? The thermo-chemical equation will be—

$$Al_2O_3 + 3C = 2Al + 3CO$$
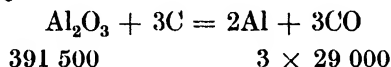
$$391\,500 \qquad\qquad 3 \times 29\,000$$

The reaction involves the absorption of—

$$(391\,500 - 3 \times 29\,000) = 304\,500 \text{ g.cal.}$$

per 54 g aluminium and is thus very endothermic. From this it may be assumed that there will be the greatest difficulty in effecting the reduction. While it can be effected on the small scale by the application of electrical heating which is very local and intense, the reduction is not practicable on any scale owing also to the formation of aluminium carbide, otherwise such might be the method of extracting aluminium from alumina. As is well known, the metal is extracted electrolytically, this providing a much more convenient method of applying the necessary energy.

Law of Constant Heat Summation. It can now be noted that some reactions may be carried out in more stages than one. Thus—

$$C + O_2 = CO_2 + 96\,960 \text{ g.cal.}$$

and also $\qquad C + O = CO + 29\,000$ g.cal.

and $\qquad\qquad CO + O = CO_2 + 67\,960$ g.cal.
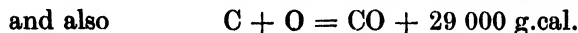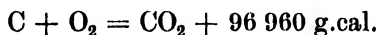
Whether carried out in one or two stages the total energy set free in the conversion of 12 g of carbon to CO_2 is the

same. The law of constant heat summation as stated by Hess is that : "The heat production of a chemical change is dependent upon the original substances and final products and independent of the intermediate stages through which the products are formed."

An interesting point in the combustion of carbon is the fact that the first stage is attended by the production of far less heat than the second stage. We might or might not be justified in calling these equal stages of oxidation, but it appears obvious that the smaller heat evolution of the first stage is due to the fact that solid carbon is being converted into a gaseous product, while in the second stage there is no change of state, without assuming that the difference in the two heat productions exactly represents the latent heat of evaporation of the solid carbon.

This law of constant heat summation is at once of service in the estimation of the thermal changes which would attend reactions which cannot directly be carried out. Thus it is required to know the heat of formation of anhydrous zinc sulphate which cannot be made directly from its elements. By a slightly circuitous route we have the following data—-

$$Zn \to ZnO = 85\ 400 \text{ g.cal.}$$
$$S \to SO_3 = 103\ 000 \text{ ,,}$$
$$SO_3 \to H_2SO_4Aq = 41\ 500 \text{ ,,}$$
$$ZnO \text{ in } H_2SO_4Aq = 26\ 000 \text{ ,,}$$
$$\overline{255\ 900} \text{ ,,}$$
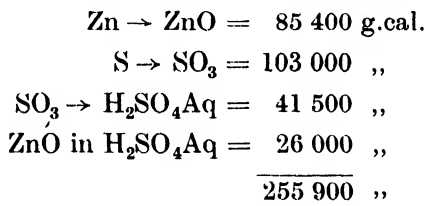
The addition of these positive values gives a total of 255 900 g.cal., representing the formation of a *solution* of 161 g.cal. $ZnSO_4$ from its elements.

The last stage of the process, viz., the actual solution of the zinc sulphate, can now be got directly. The figure is of the order of 19 000 g.cal., and this value is now deducted from the above gross value, leaving the figure of $255\ 000 - 19\ 000 = 236\ 000$ g.cal., representing the heat of formation of anhydrous zinc sulphate from its elements. Another example may also be given. It is, for instance, required to determine the heat of formation of hydrogen iodide (HI). The compound is not formed by direct combination. Its value is of a negative

character. The value may be deduced from those attaching to the displacement of iodine from potassium iodide by chlorine. The stages are as follows—

$$KI \cdot Aq = KOH + HI \cdot Aq \qquad - 13\ 660 \text{ g.cal.}$$

$$HI \cdot Aq = HI + Aq \qquad - 19\ 200 \text{ ,,}$$

$$HI = H + I \qquad x \text{ ,,}$$

$$H + Cl = HCl \qquad + 22\ 000 \text{ ,,}$$

$$HCl + Aq = HClAq \qquad + 17\ 300 \text{ ,,}$$

$$HCl \cdot Aq + KOHAq = KClAq \qquad + 13\ 740 \text{ ,,}$$

$$\text{Total} \qquad \overline{20\ 180} + x \text{ g.cal.}$$

But

$$Cl + KI\ Aq = KClAq + I \qquad + 26\ 210 \text{ g.cal.}$$
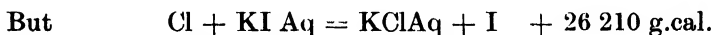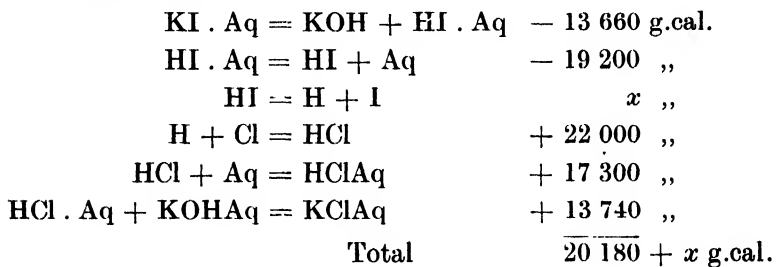
$$20\ 180 + x = + 26\ 210$$

$$x = \qquad 26\ 210 - 20\ 180$$

$$= \qquad 6\ 030$$

$$\therefore H + I = HI - 6\ 030 \text{ g.cal.}$$

Heats of Dilution. Again, the state of dilution affects the heat evolution. This is instanced in the accompanying data embodied in Tables XLV and XLVI, showing the thermal changes by the addition of sulphuric acid and sodium chloride respectively into increasingly larger quantities of water. The figures for salt are those anticipated. Those for sulphuric acid carry the significance that prior to the use of H_2SO_4 in a reaction some energy must be expended in extracting the acid from its

TABLE XLV

HEATS OF DILUTION OF SULPHURIC ACID

Dilution			Calories Evolved
H_2SO_4	H_2O	.	6 380
H_2SO_4	$2\ H_2O$	.	9 420
H_2SO_4	$3\ H_2O$	.	11 140
H_2SO_4	$20\ H_2O$	.	16 260
H_2SO_4	$200\ H_2O$	.	17 060
H_2SO_4	$800\ H_2O$	.	17 640
H_2SO_4	$1\ 600\ H_2O$	.	17 860

solution, this energy being greater with the dilute than with the stronger acid. This point has an important bearing on the chemistry and electro-chemistry of the lead accumulator, to which reference is made in the following chapter.

<div align="center">TABLE XLVI</div>
<div align="center">HEATS OF SOLUTION OF SODIUM CHLORIDE</div>

Solution	Thermal Change
NaCl + 9·2 mol. H$_2$O	— 410 g.cal.
,, + 14·3 ,, ,,	— 560 ,,
,, + 33·3 ,, ,,	— 840 ,,
,, + 100 ,, ,,	— 1 030 ,,
,, + 325 ,, ,,	— 1 070 ,,

Increasing dilution gives no further thermal change. In considering salt solutions, therefore, it is convenient to express them as NaCl . Aq, indicating a state of dilution which has given rise to maximum heat of solution.

Effect of State. Again, the heat of combustion of hydrogen depends upon the physical state of the product, there being a larger evolution of heat when the product is in the solid form than in the liquid state, and in the liquid state than in the gaseous state. This is obviously due to the latent heats of water and steam. '

The relevant figures are as follows—

H$_2$ + O = H$_2$O (ice at 0° C.) 69 800 g.cal.

H$_2$ + O = H$_2$O (liquid at 0° C.) 68 400 g.cal.

H$_2$ + O = H$_2$O (gas at 100° C. and 760 mm Hg.) 56 900 g.cal.
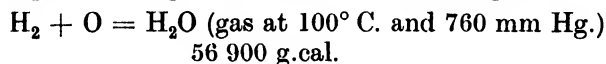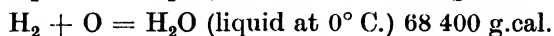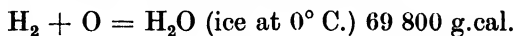
Thus 68 400 − 56 900 = 11 500 = 18 × (537 + 100).

Again, the heat of combustion of carbon is dependent upon the physical state or allotropic form of the element. This is illustrated by the following figures—

Charcoal	.	.	96 960 g.cal. per 12 g.
Diamond	.	.	94 430 ,, ,, ,,
Graphite	.	.	94 260 ,, ,, ,,

These and similar considerations must therefore be allowed for in the very varied conditions accompanying chemical change.

Numerous examples are obtainable from relevant sources and a large amount of data is available. For the present, however, only such figures will be given as required in the development of the theme.

Thermo-chemical Laws. From a mass of data it is natural that a number of well-defined laws should emerge. The enumeration of some of these will be of interest.

1. Chemical reactions tend to the formation of the greatest heat evolution. For example, at one stage in the displacement of copper from the sulphate by means of zinc, there must be the choice for the formation of zinc sulphate or the re-formation of copper sulphate. Zinc sulphate has the largest heat formation and the thermo-chemical equation is—

$$Zn + CuSO_4 . Aq = ZnSO_4 . Aq + Cu + 50\ 150\ g.cal$$
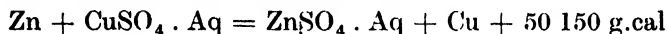
In the displacement of one metal by another the heat evolution is independent of the acidic radical. This is readily explained in the light of electrolytic dissociation when the reaction becomes—

$$Zn + Cu.. + SO_4^{--} = Zn.. + SO_4^{--} + Cu.$$
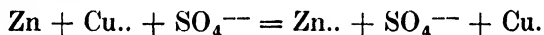
Written in this form there is expressed the fact that the acidic radical plays no part in the change.

2. Neutralization of acid and alkali is a change accompanied usually by a constant heat evolution.

$$NaOH + HCl = NaCl + H_2O + 13\ 700\ g.cal.$$

$$KOH + HNO_3 = KNO_3 + H_2O + 13\ 700\ g.cal.$$
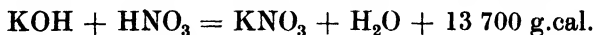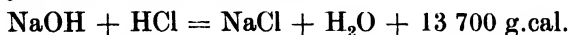
More strictly the formulae in these equations should be followed by the expression Aq, to indicate that they represent solutions of these substances in excess of water and not the solid compounds.

In the light of the usual conception of dissociation the former of these reactions becomes—

$$Na. + OH^- + H. + Cl^- = Na. + Cl^- + H_2O$$
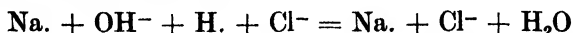
from which it appears that the neutralization process is consistently concerned with the combination of the hydrogen and

hydroxyl ions to form water molecules which are, as has already been seen (page 129), dissociated only to the slightest degree.

Incidentally, it may be of interest to add values for other examples of neutralization. Some are—

$$NaOH + HF \rightarrow 16\ 400 \text{ g.cal.}$$
$$NaOH + HCN \rightarrow 2\ 800 \quad ,,$$
$$NH_4OH + HCl \rightarrow 12\ 270 \quad ,,$$
$$NH_4OH + HCN \rightarrow 1\ 300 \quad ,,$$
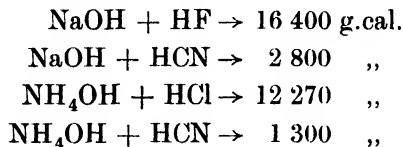
From these values it is apparent that there are deviations from the general figure of 13 700 in the cases of either weak bases or weak acids. Generally the heat equivalent of about 13 700 g.cal. obtains in the cases in which the acids and alkalis are very largely dissociated. With the weaker electrolytes, however, another factor, that of the heats of dissociation, enters the equation and to some extent accounts for the deviations from the heat evolutions in the cases of largely dissociated substances.

This deviation in the case of weak acids is due to the fact that they are only feebly dissociated. Neutralization is therefore a two-stage process: (1) that of ionization, followed, or accompanied, by (2) neutralization. Thus—

$$\text{(1) } HCN \rightarrow H. + CN^-$$
$$\text{(2) Neutralization}$$

Now

$$NaOH \text{ Aq.} + HCN \cdot \text{Aq.} = NaCN \cdot \text{Aq.} + H_2O + 2\ 800 \text{ g.cal.}$$
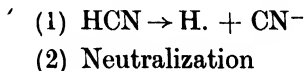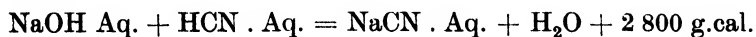
If we regard neutralization as producing a constant amount of heat, viz., 13 700 g.cal., then—

$$13\ 700 - 2\ 800 = 10\ 900 \text{ g.cal.}$$

is evidently the amount of heat absorbed in the dissociation of a gramme-molecule of HCN. This is known as the heat of ionization and is, in this case, − 10 900 g.cal. On the other hand, the neutralization of sodium hydroxide and hydrofluoric acid yields an excess of heat over the usual 13·700 g.cal. The acid (strictly H_2F_2) is much less dissociated than HCl, relative values for decinormal solutions being 15 and 92 per cent. The

excess heat is due to the ionization of H_2F_2 in two stages, thus—

$$H_2F_2 \rightarrow HF_2^- + H.$$
$$HF_2^- \rightarrow 2F^- + H.$$
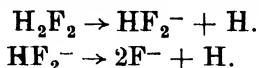
this dissociation being attended by the evolution of heat.

3. *Thermo-neutrality of Salts which Mix without Precipitation.* It is well known that many mixtures of salts may be made which are not accompanied by the precipitation of new compounds. A mixture of potassium chloride and sodium nitrate, for example, yields, in addition to these compounds, crystals of potassium nitrate and sodium chloride. In the ordinary acceptance of the term chemical action has taken place, but there is no heat evolution. Unexpressed thermal changes have balanced each other.

4. *Heat Evolution and Work Done.* Again, the heat evolution of a chemical change is a measure of the work done or energy evolved, and therefore a measure of the work which must be done in order to restore the system to its original form. By this law we are enabled to calculate the thermal or energy efficiencies of operations where a larger amount of energy is put into the system than was originally set free. Examples of this principle will follow when electrolytic decompositions are considered.

If, for example, the extraction of aluminium is a matter of decomposing the oxide without making any use of the heat of evolution of the carbon monoxide formed as shown in the following equation—

$$Al_2O_3 + 3C = 2Al + 3CO$$
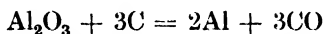
then it is obvious that the minimum electrical energy required for the liberation of 54 g of the metal will be—

$$6 \times 65\,250 = 391\,500 \text{ g.cal.}$$

or its equivalent, as the formula weight represents 6 gramme-equivalents. This figure can now be converted into kilowatt-hours per ton by the following simple calculation, in which each of the factors concerned will be readily recognized and appreciated—

Kilowatt-hours per ton Al

$$= \frac{391\,500 \times 4 \cdot 2 \times 454 \times 2\,240}{54 \times 3\,600 \times 1\,000} = 8\,600$$

If the usual consumption of electrical energy in the commercial process is set at 25 000 kWh this represents an energy efficiency of—

$$\frac{8\ 600 \times 100}{25\ 000} = 34 \cdot 4 \text{ per cent}$$

Another interesting case which may be referred to is that of the thermit mixture, which is powerfully exothermic. Taking the case of the reduction of oxide of iron for the production of small quantities of the liquid metal for welding purposes, the following equation may be taken to approximately represent the reaction—

$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe$$

$6 \times 31\ 850$	$6 \times 65\ 250$
191 100	391 500
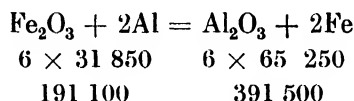
the figures being taken from Table XLIV, thus showing the reaction to be exothermic to the extent of

$$391\ 500 - 191\ 100 = 200\ 400 \text{ g.cal.}$$

for the gramme-equation quantities. This enormous amount of heat is first liberated in the limited mass of products, and from their relative masses and specific heats some computation of the highest temperature attainable may be deduced. While there must be a rapid loss from so exalted a temperature there is, nevertheless, a sufficient amount of heat produced to allow of the addition of a fair amount of iron and alloys to give a welding mixture with the desired properties.

One other case may be referred to. When zinc dissolves in acid, evolving hydrogen, work is done when the gas expands against atmospheric pressure and at any given temperature. Thus—

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

A gramme-molecule of gas is expressed, and $PV = RT$ $= 2T$ g.cal., where T is the absolute temperature. At $16°$ C. and N.P. the energy absorbed in this formation of gas is $2(273 + 16) = 578$ g.cal.

Strength of Acids. It will have been seen that the heats of strong acids and alkalis are practically constant, while those in the cases of the weaker compounds are markedly less. Even the strong acids have their appreciable differences, and

these can be made a basis for the comparison of acid strengths with results comparable with, though perhaps not with exact quantitative harmony, the results obtained by their degrees of dissociation. For this test, imagine an equivalent of an alkali to be added to a mixture of equivalents of two acids, one strong and the other weak. Their individual heats of neutralization are known. The insufficient quantity of alkali neutralizes these acids in the proportion of their degrees of dissociation. In an example, let

H = observed heat of neutralization of the mixture,

h = heat of neutralization of the stronger acid A,

h_1 = heat of neutralization of the weaker acid B:

and x = the fraction of alkali combining with the stronger acid.

Then,
$$H = xh + (1 - x)h_1$$
$$= x(h - h_1) + h_1,$$

from which
$$x = (H - h_1)/(h - h_1).$$

Hence strength of A : strength of B :: x : $1 - x$.

Deductions from Thermo-chemical Data. Again, a very large number of deductions can safely be made from the values of heat thermal changes accompanying chemical change. A few may be indicated.

1. The most stable compounds are those in the formation of which there has been the greatest heat evolution, and their reduction by elements with lower heat evolutions cannot be anticipated.

Generally speaking, fluorides are more stable than chlorides, and these in turn are more stable than oxides. Illustrative of this may be cited the fact that aluminium is extracted electrolytically from a fused mixture of the fluorides of aluminium, calcium and sodium containing dissolved alumina, the electrical conditions being controlled to effect the preferential decomposition of the oxide.

2. Metals giving compounds of high heat formation are

those which normally might be expected to corrode readily. This will be readily seen by a glance at the Table XLIV, though other factors will be the nature and adhesion of thin films of corrosion products in virtue of which, for example, aluminium preserves its lustre longer than might be anticipated from its position in the thermo-chemical list, on account of the production of a thin, continuous, adherent and insoluble coating of the oxide which has been the cause of so much trouble in the early attempts at welding, soldering, and electro-plating of the metal.

3. Metals, the formation of the salts of which is attended by considerable heat evolutions, are not to be expected to occur free in nature, while those at the lower end of the list are frequently found in the uncombined form. Similarly metals at the head of the table involve considerable energy expenditure in the chemical part of their extraction, while conversely those at the bottom of the table require much less, although there may be a large amount of work necessary in the handling of their raw materials. It will be appreciated, for example, that from the compounds of the noble metals the mere application of heat suffices to liberate the metal, while in the case of some compounds the action of light effects some type of decomposition which constitutes a first stage in the process of the reduction which takes place in the development of the photographic image.

4. Taking a broad view of the thermo-chemical properties of the metals and their compounds, and having in mind the thought that in its earlier history the earth was once at an elevated temperature at which no chemical compounds could possibly exist, we may be able to arrange the compounds which occur in nature in some sort of order in which they were formed, and among the first to be formed would be those of the extremely active metals like the alkali and alkaline earth metals with the most active non-metals as, for example, fluorine.

5. An elaboration of this list would also indicate the possibilities of the replacement of metals by others, those usually active replacing those usually less active. Such information will be of use in the selection of electrolytes for the purposes of deposition of the metals upon others, and here it is well known that there are limitations in the choice and that, for

example, copper cannot be successfully deposited from the sulphate solution upon such more active metals as iron and zinc.

6. While we might be tempted at first to call this the thermo-chemical order of the elements or possibly the metals, later investigations will show that a much more reliable order will be forthcoming from a study of the potentials developed by these metals when standing in solutions of their salts. This order is then known as the electro-chemical series. That deduced from a study of the thermo-chemistry of the metallic compounds follows the same order but with less precision. The fact that many of the properties are dependent more on the ions than on the molecules, and ionization occurs to such vastly different extents and even along different lines, necessitates a rather careful discrimination in placing them in any definite order of activity.

THERMO-CHEMISTRY (*contd.*)

Introduction. The thermo-chemistry of a number of chemical changes which can be alternatively achieved electrolytically, or which, in their progress, give rise to the liberation of electrical energy, can now receive closer attention.

It might seem that, if some chemical changes can be accompanied with electrical changes, there should be reasonable expectation of many others exhibiting similar phenomena. If, for example, zinc reacts with a copper sulphate solution in the apparatus known as the Daniell cell with the evolution of energy approximately expressed by the well-known voltage of 1·09, there might be some chance of realizing the chemical activity of the combustion of carbon with the production of its equivalent amount of energy in the electrical form, and thus realize the ideal of the long-looked-for carbon cell. This is a subject which has claimed considerable attention and to which brief reference will later be made. For the moment, however, it must suffice to point out that electrolytic changes take place through the medium of ions, and these must first exist in a suitable medium. Some more simple problems may first be considered.

The Daniell Cell. When zinc is put into copper sulphate solution there is an observed evolution of heat. The experiment done casually may not seem to indicate this, but the calorimeter can be called into service and the reaction carried out quantitatively. Thermo-chemically it is expressed thus—

$$Zn + CuSO_4 \cdot Aq = ZnSO_4 \cdot Aq + Cu + 50\ 150 \text{ g.cal.}$$
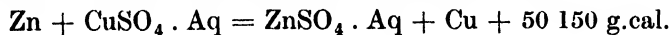
The figure is fairly definite and well accepted. The same reaction, moreover, can be carried out in the Daniell cell. Assume this to have gone on until 65 g of zinc have been dissolved in the one compartment of the cell, other substances being affected in their equivalent quantities, including the deposition of copper to the extent of 63·6 g in the other compartment.

In the absence of any local action at the zinc, that is, when

coulombs have been developed equivalent to the amount of zinc dissolved, then, according to Faraday's law, there will have been the production of $2 \times 96\,540 = 193\,080$ C. The energy production of the reaction can be stated in two forms as follows—

<div align="center">

Electrical
Energy   Heat
($E \times I \times t$ joules)   (calories)

</div>

The product $I \times t$ represents the coulombs and the addition of the factor 0·24 brings the joules to calories. The quantities then become—

$$E \times 2 \times 96\,540 \times 0·24 = 50\,150$$

from which $E = \dfrac{50\,150}{2 \times 96\,540 \times 0·24} = 1·083$ V

The expression may be viewed more generally by the recognition that $50\,150/2$ represents the heat evolution in calories per gramme-equivalent, while the product of $96\,540$ and $0·24$, both of these figures being constant and approximate only, may be taken as $23\,100$.

The general expression then becomes—

$$E = \frac{\text{calories per gramme-equivalent}}{23\,100}$$

and this very simple formula, originally due to Thomson, is applicable for the calculation of the approximate e.m.f.'s developed by, or required in, electro-chemical reactions. For the moment it must be admitted that it does not take into account every possible factor, as it is well known that the e.m.f. of a Daniell cell, for example, is slightly dependent upon the concentrations of the electrolytes and also upon the temperature of the cell, but the expression will constitute an introduction to a more detailed study of these influences later.

E.M.F. Required to Effect Chemical Decomposition. The two following equations express reactions of considerable interest—

$$\text{Cu} + \text{O} = \text{CuO} + 37\,160 \text{ g.cal.}$$

$$\text{CuO} + \text{H}_2\text{SO}_4 \,.\, \text{Aq} = \text{CuSO}_4 \,.\, \text{Aq} + \text{H}_2\text{O} + 18\,800 \text{ g.cal.}$$
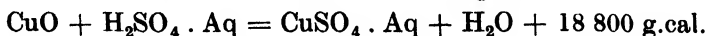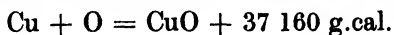
Copper is readily oxidized to CuO with the heat evolution indicated. The oxide dissolves in dilute sulphuric acid, giving

an aqueous solution of copper sulphate. Expressing the two reactions together we have—

$$Cu + O + H_2SO_4 \,.\, Aq = CuSO_4 \,.\, Aq$$
$$+ \; H_2O \; (37\;160 + 18\;800 = 55\;960 \text{ g.cal.})$$
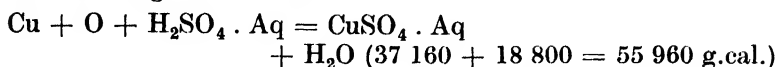
When copper sulphate solution is electrolyzed with an insoluble anode, the reverse reaction takes place thus—

$$CuSO_4 \,.\, Aq + H_2O = Cu + O + H_2SO_4 \,.\, Aq - 55\;960 \text{ g.cal.}$$
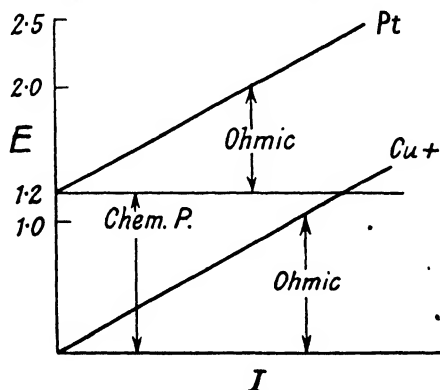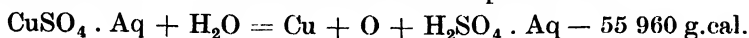
FIG. 36. E/I CURVES WITH CHEMICAL DECOMPOSITION

This action is endothermic, that is, if carried out electrolytically will involve a minimum consumption of electrical energy equivalent to 55 960 g.cal. The equation expresses definite quantities of substances, in this case 2 grammeequivalents. The energy requirement per gramme-equivalent is therefore 55 960/2 = 27 980 g.cal, and this divided by 23 100 at once gives 1·21 V as the e.m.f. required to effect the decomposition of copper sulphate solution with an insoluble anode.

This result finds its general confirmation by taking a number of p.d. and current readings during the course of such an experiment. Fig. 36 shows the results obtained with both a copper (or soluble) anode and a platinum (or insoluble) anode. For this purpose we will select platinum, as with some other insoluble anodes, lead for example, secondary effects such as the peroxidation of the metal would introduce complications. With the copper anode the curve finds its origin at the zero, while the curve with the insoluble anode definitely gives a

reading indicating that a minimum e.m.f. of 1·21 V is required to produce a maintained current. The following figures (Table XLVII) are those derived from such an experiment.

<div align="center">

TABLE XLVII

SOLUBLE AND INSOLUBLE ANODES

</div>

Copper Anode			Platinum Anode				
E (V)	I (A)	$R = \dfrac{E}{I}$ (Ω)	E	I	$\dfrac{E}{I}$	$E \qquad e$	$R = \dfrac{E - e}{I}$
0·8	1·0	0·80	2·15	1·0	2·15	0·9	0·940
1·15	1·5	0·76	2·45	1·5	1·63	1·2	0·820
1·5	2·0	0·75	2·80	2·0	1·40	1·55	0·795
1·9	2·5	0·76	3·25	2·5	1·30	2·0	0·816
2·3	3·0	0·77	3·65	3·0	1·22	2·4	0·813
3·1	4·0	0·77	4·35	4·0	1·09	3·1	0·785

These figures are approximate only, being intended to illustrate one type of polarization, viz. that due to chemical decomposition and therefore called chemical polarization. In the same experiment it would be difficult to entirely eliminate concentration polarization, but in this case it will not be prominent and has therefore been omitted. From the figures and diagram it is apparent that for the production of any current or current density an increased e.m.f. is required with the insoluble anode over that required by the soluble copper anode. This difference is constant. While readings with very small currents might not be made with ease, the "curves" (straight lines in each case—Ohm's law being a proportional law) can be extrapolated, in the case of the copper anode to the zero point of both current and e.m.f., and with platinum to the figure of 1·21 V, this being a minimum below which little or no current is produced and above which current is now produced proportionally with the added e.m.f.

Later it will be necessary to add a note of refinement to these curves when other factors of a minor character have to be considered (see page 204).

In much the same way many other electro-chemical reactions

can be dealt with, giving, apparently, a good agreement between the thermo-chemical data with that obtained electrochemically. To take another case, that of the lead accumulator, we have the generally accepted values for the different compounds inserted in the equation representing the sum of the chemical changes taking place during discharge—

$$PbO_2 + Pb + 2H_2SO_4 = 2PbSO_4 + 2H_2O$$
$$62\ 400 \qquad 2(192\ 000) \quad 2(216\ 000) + 2(68\ 400)$$
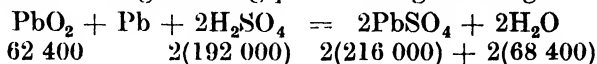
This makes the reaction exothermic to the extent of 122 400 g.cal. per gramme-equation (= 2 gramme-equivalents) quantities. with an equivalent e.m.f. developed of—

$$\frac{122\ 400}{2 \times 23\ 100} = 2\cdot66\ V$$

The unusually high figure is accounted for by the fact that the thermo-chemical value for sulphuric acid is that of the anhydrous compound. In the accumulator, however, we are dealing with a relatively dilute solution, and an amount of energy equivalent to the heat of hydration is required to first extract the acid from its dilute solution. This is of the order of 18 000 g.cal. per gramme-molecule. The total heat evolution is therefore 122 400 − 2(18 000) = 86 400 g.cal. corresponding to a calculated e.m.f. of 86 400/(2 × 23 100) = 1·87 V, a more usual figure.

It is of course well known that the e.m.f. of the accumulator is a function of the acid concentration, for which approximate empirical formulae have been devised. Illustrative, too, of the phenomenon is the fact that with two accumulators put "back to back," the one with the weaker acid will be charged at the expense of that made up with the stronger acid until, theoretically, the acid content of both is the same.

. For the decomposition of aqueous zinc sulphate solution as is usual in the electrolytic extraction of the metal, the chemical action is—

$$ZnSO_4 \cdot Aq + H_2O = Zn + O + H_2SO_4 \cdot Aq$$
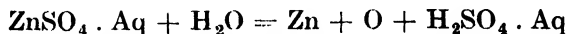
From the thermo-chemical data given on page 153, it appears that—

$$Zn + O = ZnO + 84\ 500\ g.cal.$$

and

$$ZnO + H_2SO_4 \cdot Aq = ZnSO_4 \cdot Aq + H_2O + 26\ 000\ g.cal.$$
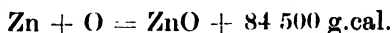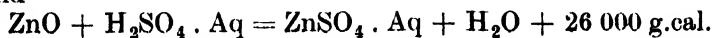
The production of aqueous zinc sulphate solution from zinc, oxygen, and aqueous sulphuric acid is attended by the evolution of 84 500 + 26 000 = 111 000 g.cal for 2 gramme-equivalents, requiring an e.m.f. of 111 000/(2 + 23 000) = 2·4 V, apart from other minor factors which may influence this figure, particularly the over-voltage of the oxygen at the per-oxidized lead anode, to which reference is made on page 215.

Upon the basis of this simple and approximate principle it becomes possible to calculate the e.m.f. required for the electrolytic decomposition of numerous compounds using the simple formula—

$$\text{E.M.F.} = \frac{\text{Heat evolution (calories per gramme-equivalent)}}{23\ 100}.$$

A number of such values are given in Table XLVIII.

TABLE XLVIII

CALCULATED MINIMUM E.M.F.'S FOR DECOMPOSITION OF COMPOUNDS

	Oxides	Chlorides	Fluorides
Magnesium	3·17	3·28	4·58
Aluminium	2·83	2·32	4·00
Calcium .	2·85	3·69	4·70
Potassium	2·17	4·60	4·80
Sodium .	2·17	4·24	4·78
Zinc	1·86	2·17	3·00
Hydrogen .	1·44	0·96	1·63
Copper	0·81	1·43	1·92

From these values it is readily appreciated that in such a mixture as the "melt" of an aluminium furnace, for example, only one of the constituents may be decomposed with a controlled e.m.f. This "melt" usually contains the fluorides of aluminium, calcium and sodium constituting the solvent, in which the chemically purified alumina is dissolved. The extraction of the aluminium is, in the main, due to this preferential decomposition of the oxide of aluminium, the loss being made good periodically by the addition of further quantities of pure alumina.

Total and Free Energy. This interesting subject has been

taken thus far to illustrate an important, though only approximate, principle, and it now becomes necessary to examine the problem with greater detail to observe not only slight deviations but in some cases striking disagreements, and hence to necessitate a more exact theoretical conception of the problem involved. Revert to the case of the Daniell cell. The thermo-chemistry of the chemical reaction is definitely obtained by calorimetric methods. The figure is 25 075 g.cal. per gramme-equivalent. Now the e.m.f. produced by the cell is separately and very exactly determinable, and is 1·096 V, which figure is converted into its heat equivalent by multiplying by 23 100, and thus becomes 25 320 g.cal. This figure is definitely in excess of that obtained thermo-chemically. More energy is evolved in the electrical form than is accounted for by the chemical reaction. The difference is small, but it is there. The Daniell cell has the power of extracting heat from its surroundings and converting it into electrical energy. The cell cools in operation.

Take next the lead storage cell. With acid of the strength of $H_2SO_4 : 20H_2O$ and at 17° C. the accurately measured e.m.f. is 2·01 V, while the thermo-chemical value is 87 200 g.cal. per gramme-equation quantities. The thermal equivalent of the observed e.m.f. is therefore—

$$2·01 \times 2 \times 23\ 100 = 92.860 \text{ g.cal.}$$

This is again in excess of the chemically observed value, and again the accumulator takes up heat from its surroundings and converts it into electrical energy. In other words the cell cools during discharge. This cooling effect is not bound to be observed on account of the heat formed by the electrical resistance of the solution, but it is definitely proved by the principles outlined and applied. A still more striking case is that of the Clark cell, a usual type of "standard" cell used in potentiometry (page 182). Its essential constituents are zinc, mercurous sulphate and mercury, the chemical change involved being—

$$Zn + Hg_2SO_4 = ZnSO_4 + 2Hg + 81\ 320 \text{ g.cal.}$$
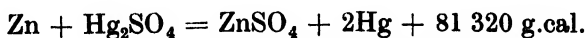
The e.m.f. of the cell is 1·429 V corresponding to a heat value of $1·429 \times 2 \times 23\ 100 = 66\ 320$ g.cal. Here the electrical output of energy is far less than is anticipated. The remainder

of the chemical energy is evolved as heat, warming up the cell in action and at the same time varying its e.m.f. It is well understood that the cell is used for such purposes as potentiometric work which do not involve the production of current.

From this last example, as with others, it becomes obvious that the whole of the energy of a chemical reaction is not necessarily convertible into the electrical form. We should distinguish between the total energy available and that converted into other and externally usable form. The terms total and free energy are sufficiently explicit. Represent these by the symbols U and E respectively and their difference, that is, the energy not converted into the electrical form, by q. We have the simple relation—

$$U = E + q$$

If q has a positive value then the cell warms while with a negative value the cell cools, heat being extracted from the surroundings and converted into electrical energy. It will be well to call this "reversible heat" and it will be recognized that this is proportional to the current produced. In cases in which q has a negative value it may be counteracted by heat developed through the ohmic resistance of the electrolyte and which heat, as is well known, is proportional to the square of the current.

Voltaic Cells. The subject of voltaic cells calls for some consideration in a treatise on electro-chemistry. It was with the advent of the nineteenth century that electric current was first generated from a combination of metals and those liquids which afterwards came to be called electrolytes. In the earliest form or *Wollaston cell* the combination consisted of plates of zinc and copper immersed in a solution of sulphuric acid. In this and all other cells fundamental principles are independent of the shape or size of the component parts.

FIG. 37. SIMPLE CELL

They depend entirely upon the chemical, and in a small measure the physical, characteristics of the chemical substances of which they are constructed. This simple cell is depicted in Fig. 37, which shows the direction of the current generated in the conventional manner. In course of action zinc ionizes, displacing hydrogen ions which are discharged at the
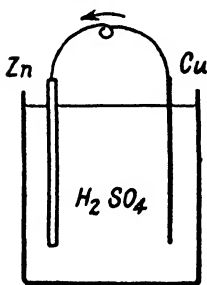
copper plate. This is the action with pure zinc. If, however, impure zinc is used, hydrogen is also liberated at the zinc plate. This represents solution of zinc without the production of an equivalent amount of electricity. More strictly we should say that small electrical currents are set up between the zinc and the impurities exposed on its surface. These numerous small currents are dissipated as heat in the solution near to the zinc, and do not contribute to the main current which is available for use externally. The phenomenon is called "local action." With impure zinc the difficulty is overcome by the amalgamation of the zinc which then acts as a pure metal. This beneficial action must later be accounted for (see page 212). The chemical action is represented thus—

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$
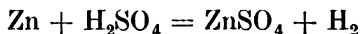
For many years this simple type of voltaic cell was the only one available. It was set up in various forms of which the so-called "voltaic pile" was an illustration. In it zinc and copper plates were separated by cloth discs soaked with the acid. This amounted to putting a large number of small cells in series, thereby increasing the voltage proportionally with the number of couples used.

The action of the simple cell, however, suffers seriously from a considerable defect. Its effectiveness falls off owing mainly to the formation on the copper plate of a thin film of adherent hydrogen which offers considerable resistance to the passage of the current. Another supposed defect was called polarization, and was assumed to be in the form of a tendency of the deposited hydrogen to pass back into solution and so develop a reverse e.m.f. This tendency was commonly shown by substituting a platinum plate for the zinc, when a definite current was to be observed. But this tendency is not necessarily there when the zinc plate is in use. For any reversal of the current to take place there would needs be the solution of the hydrogen film from the copper plate and the concomitant deposition of zinc from the solution on to the zinc plate. A more careful investigation proves that this is lacking. What is observed with the substitution of the platinum plate is that a new form of "gas cell" is set up between the deposited hydrogen on the copper plate and the oxygen of the air which is occluded in the

surface of the platinum. Its duration will be determined more by the amount of oxygen carried on the platinum plate than by the much more abundant hydrogen on the copper plate.

After a more careful definition of the term polarization and some idea of its operations have been given, it may be of interest to turn back to this example of the simple cell to see more clearly that the term has little or no application in this connection.

For a time this was the only method of obtaining what had come to be called "voltaic electricity," but it constituted a new tool in the hands of science through which numerous possibilities were soon to be realized. The definite aim at the improvement in the cell always had, as its objective. either the removal of the hydrogen film by mechanical or chemical methods or, alternatively, the deposition of other substances in place of hydrogen without its inherent defect.

Smee Cell. In this development the copper plate was substituted by one of platinized silver. A film of platinum was obtained on the silver plate by treatment with a solution of a platinum salt. This film is microscopically rough, thus effecting the removal of the small hydrogen bubbles and the diminution of its evil effects. This form of cell was largely used for many years in electrodeposition, especially in electrotyping, but has, of course, with the advent of the dynamo, long ceased to be a practical source of current.
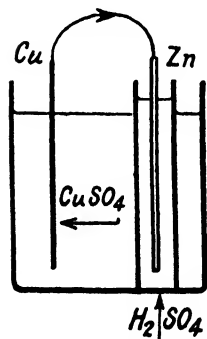
FIG. 38. DANIELL CELL

Daniell Cell. This type was introduced in 1836 and has the advantage of the deposition of copper in place of hydrogen. In its original form it was composed of a zinc plate immersed in dilute sulphuric acid into which also was placed a porous pot containing copper sulphate containing a piece of copper. Again, the form and shape are of little importance in a study of its principle. A very common form of the cell is shown in Fig. 38, in which a copper vessel, preferably round, contains copper sulphate solution in which is placed a porous pot containing sulphuric acid in which was immersed a rod of amalgamated zinc.

In any case the simple chemical action is represented by the following equations—

$$Zn + H_2SO_4 = ZnSO_4 + 2H$$
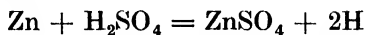
The hydrogen is not liberated as such but, passing in the ionic form into the copper sulphate, preferentially deposits copper thus—

$$2H + CuSO_4 = H_2SO_4 + Cu$$
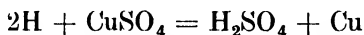
The changes in the composition of the solutions can readily be seen from these reactions, and they especially indicate the need for the maintenance of an adequate supply of copper sulphate near to the copper plate or pot. In the absence of copper sulphate the cell degenerates into a simple cell with its pronounced ill-effects.

With the use of amalgamated zinc steady currents can be produced over long periods. Such a cell develops an e.m.f. of 1·09 V.

Closer investigation shows that the operation of the cell is almost independent of the liquid in contact with the zinc. For example, the acid may be replaced by zinc sulphate which, even with its somewhat higher resistance, is steady in its action over long periods. On the copper side, the sulphate may be replaced by other solutions containing copper ions such as copper nitrate, chloride or acetate.

These variations of construction with different solutions might reasonably have been deduced from an elementary knowledge of chemical reactions taking place between ions rather than between molecules.

Zinc metal and copper ions thus appear to be the essential components, and the two essential reactions are—

(1) the passage of the metal zinc into the ionic form, and

(2) the passage of copper ions into the metallic form.

It will later be necessary to consider these actions in an endeavour to trace the origin of the e.m.f. developed.

Other Cells. Many other types of cells were in due course developed. The *Grove* cell introduced a platinum plate in strong nitric acid in place of the copper and its salt in the Daniell cell. In this case the ionic hydrogen effected the reduction of the acid as follows—

$$2H + 2HNO_3 = 2H_2O + 2NO_2$$
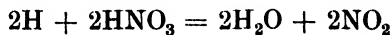
Nitrogen peroxide, a brown gas, is evolved, some dissolving in the acid forming a greenish blue solution. This is obviously a case in which the essential materials, zinc and nitric acid, could not be allowed to come into direct contact, otherwise a vigorous chemical action on the zinc would considerably depreciate the efficiency of the cell. *Bunsen* produced a cheaper form by the substitution of a block or rod of gas carbon in place of the platinum. This cell was at one time largely used
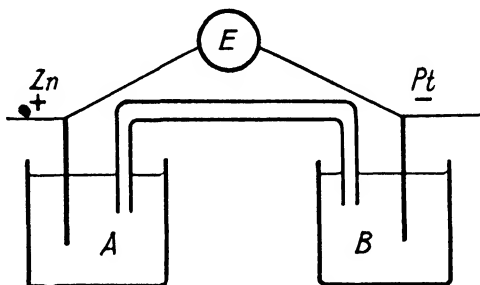
Fig. 39. ACTION AT A DISTANCE

for many examples of electrodeposition even after the advent of the dynamo.

In the "bichromate" cell, potassium dichromate ($K_2Cr_2O_7$) provides the oxidizing agent. The dichromate, however, can be introduced into the acid in contact with the zinc, thus eliminating the use of a porous pot. The special chemical action is as follows—

$$3Zn + 3H_2SO_4 = 3ZnSO_4 + 6H$$

$$6H + \underset{\text{(red)}}{K_2Cr_2O_7} + 5H_2SO_4 = \underset{\text{(green)}}{Cr_2(SO_4)_3} + 2KHSO_4 + 7H_2O$$
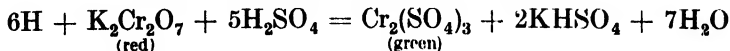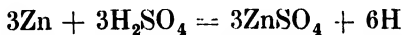
This action is evidenced by the change of colour from the red dichromate to the green chromium sulphate. In the *Leclanché* cell a carbon rod is surrounded by manganese dioxide as the "depolarizer." This solid oxidizing agent, however, acts more slowly than one in solution. Hence the use of this cell for intermittent work in, for example, electric bell circuits.

Many other types of cells have been introduced. These, however, will suffice to demonstrate the fundamental principles.

Action at a Distance. In connection with the constitution of voltaic cells the following problem may appropriately be considered. In Fig. 39 two beakers A and B are filled with a solution of potassium sulphate and connected together by an inverted U-tube containing the same solution. A contains a zinc plate and the plate in B is of platinum. Across the two plates is some form of current indicator or voltmeter. There is no indication of e.m.f. or current. For zinc to dissolve in A, that is to form zinc ions, there must be the replacement of an equivalent quantity of some ion at the plate in B. Hydrogen or copper would provide suitable replaceable ions, and this involves adding sulphuric acid or copper sulphate into the potassium sulphate solution, not, however, in A with the zinc but in B away from the zinc. Put in A, the acid or copper sulphate would yield hydrogen or copper, but without the production of electrical energy, the zinc dissolving by what is usually regarded as a purely chemical process with the liberation of its energy in the form of heat. This solution is what is commonly called "local action," that is, the solution of zinc without the conversion of its chemical energy into the available electrical form. Put into B, the acid or copper sulphate provides hydrogen or copper ions which can now pass out at the platinum plate with the production of an e.m.f. or, in other words, an equivalent amount of electrical energy. After the same manner, the nitric acid in the Grove or Bunsen cell is separated from the zinc, as also is the copper sulphate in the Daniell cell. In most voltaic cells using zinc as the soluble metal there is this separation of the reacting materials, so that the electrical effects are the result of the formation and replacement of ions at the opposite electrodes. Hydrogen evolved at the zinc plate represents wasteful solution of the zinc without equivalent production of electrical energy, while zinc dissolving with the replacement of ions at the opposite electrode represents the ionization of zinc with the production of electrical energy which is the aim of the usual type of voltaic cell.

The Problem of the Fuel Cell. The relatively low efficiency of the process of transforming the latent energy of many natural fuels, coal for example, into electrical energy has been a problem which has attracted a vast amount of attention in the world of engineering. Twenty years or so ago we were

mourning the very low efficiencies which ruled in the power stations supplying the electrical energy for general lighting and industrial work. This efficiency was of the order of 10 per cent, and even lower in many cases. In process of time larger power stations combining every modern improvement in design and operation, including that of higher superheat of the steam, preheated air supply, utilizing heat from the flue gases, more efficient condensing systems with the return of a larger proportion of the heat of the waste steam to the incoming water, have succeeded in raising this figure to somewhere of the order of 25 per cent with very little prospect of increasing it beyond 30 per cent. The advances so far made have resulted in a welcome reduction of the consumption of fuel per unit of energy available for distribution, but the use of water and steam as the medium for this transformation of energy, definitely limits the efficiency figure by reason of the latent heat of the steam, so much of which is unrecoverable and passes away in the cooling water.

Small wonder, then, that attention has been turned to the possibility of the more direct conversion of the energy of coal into the electrical form.

If we may once again revert to the case of the Daniell cell we have here an example of the combustion of a substance, zinc, which bears some analogy to coal in such a manner that its latent energy is almost completely converted into the electrical form. The mere admixture of zinc and copper sulphate may, however, result, as has been referred to on page 165, in the production of heat, and definite arrangements are required in order to effect a quantitative transformation of the energy of zinc into electrical energy.

Similarly, many attempts, some of them very crude both in design and operation, have been made to achieve this desirable end with coal. Space does not permit, nor does the occasion require, any rehearsal of these abortive attempts, but it was obviously altogether too crude an idea to suggest the possibility of the direct conversion of the energy of coal into the electrical form by making lumps of coal "anodes" in an iron tank which served as the cathode, and which contained electrolytes of fused salts with the introduction of oxygen or air to effect the combustion of the coal. These and similar attempts were made

without any recognition of the fact that in all examples of voltaic cells previously considered the active materials are in the ionic form. Moreover, the recorded results were for the most part altogether out of harmony with what might have been expected, and in many cases exceeded the theoretical possibilities, regardless of the external heat applied to keep the materials in the molten form.

Passing from these early cells employing solid fuel, others using gaseous fuels were tried out. Carbon, for example, can be converted—with the loss of about 30 per cent of its total energy—into carbon monoxide. This is soluble in a number of reagents, including cuprous chloride, in which contact with oxygen can be effected, bringing about its conversion to carbon dioxide. Hydrogen again is possible of electrolytic oxidation with the development of electrical energy, but the gas has first to be obtained by the use of some natural fuel. A more indirect method of working is that of the electrolytic oxidation of a metal electrode and the cyclical re-extraction of the metal from the product of oxidation. Zinc, for example, could be oxidized by the use of some fused electrolyte into which air is continuously introduced with the subsequent recovery of the metal by solid fuel. The thermal extraction of zinc from its oxide, however, is one of the least efficient of these metallurgical extractions, and therefore a less basic and more easily recoverable metal is to be preferred. For this purpose tin has been suggested and experimented with, with some success.

In each and all of these attempts, however, the problems of polarization arise, together with that of the volume of the cell in relation to energy output. The problem is one which seems to have merited some attention* from those qualified to discern the possibilities and to avoid the initial difficulties, and while some success has attended the early stages of the more scientific investigation of the problem, there still seems to be a long distance to travel before the goal of an efficient fuel cell is attained.

* Evans and Rideal: *Trans. Faraday Soc. 17.* 466, 1925 6.

ELECTRODE POTENTIALS

Comparison of E.M.F.'s. Potentiometry. In Fig. 40 AB represents a high resistance wire of uniform cross-section and therefore of uniform resistance. It may conveniently be of the order of 100 cm long and mounted over a metre scale. Across it a p.d., such as that obtained from a single accumulator D, is applied through a key K, producing a small current in the wire along which there is, on account of the uniform resistance, a uni-

Fɪɢ. 40. Pᴏᴛᴇɴᴛɪᴏᴍᴇᴛᴇʀ
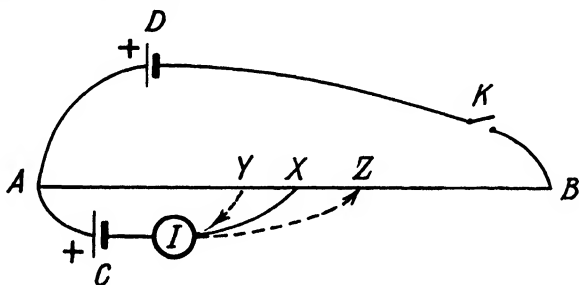
form fall of potential. The p.d. across one length of, say, 10 cm will be the same as that across any other portion of 10 cm.

Another cell C is now connected as shown with its positive terminal joined with the positive terminal of the accumulator at the end point of the wire A. From the other electrode attach some type of sensitive current indicator I, a galvanometer for example, with a loose end, which is now moved along the potentiometer wire until a point is found at which, with contact, no current is observed in the galvanometer and hence in the second circuit. Call this point X. The fall of potential along AX is a measure of the e.m.f. of the cell C. At a point Y, so that AY is less than AX, current in the direction indicated will be seen in the second circuit, while at another point Z, so that AZ is greater than AX, current will be observed in the second circuit in the opposite direction.

AX thus becomes a measure of the e.m.f. of the cell. By

the arrangement shown, however, we have no idea of the exact fall of potential along the whole of the wire, and therefore also of the part AX. To meet this need a similar circuit introducing a standard cell with a definite and known e.m.f. is separately applied to the potentiometer wire.

This method of comparing e.m.f.'s and, where some standard of e.m.f. is available, for determining absolute values is termed potentiometry. It has a very large application in both electrical and electro-chemical work. In the simple type represented in Fig. 40, and comprising a straight length of wire, there is the need for absolute uniformity in the section of the wire, so that the fall of potential shall be uniform. Moreover, the wire needs calibration or standardization, and this is done with a standard cell. Thus, after applying a standard cell, the wire could be calibrated in terms of fall of potential, but this quantity is more conveniently expressed in terms of length.

More accurate types of potentiometer make use of the wire in a spiral form with much more accurate methods of making the contacts in finding the neutral point. Wire and sliding contacts are then suitably mounted on a box and the indicator conveniently arranged with substantial terminals for making the contacts with the external part of the system. Again, however, we are more concerned with the results obtained by the accurate application of the principles of potentiometry than the more practical details of the process. There may be occasions for the determination of the e.m.f.'s of cells in which, not only the magnitude, but also its direction are unknown. In any case, the e.m.f. of the accumulator or other source of p.d. must exceed that to be measured. At first it is impossible to guarantee that the cell is connected up in the right manner, but this is soon revealed by the deflections on the instrument. If, as must be the case, the fall of potential along the wire is greater than that to be measured, then deflections of the instrument needle all in one direction, without any indication of a neutral point, show that the unknown cell is incorrectly connected. Reversal of the connections will then secure the required neutral point.

Further, when very small differences of potential are to be measured the neutral point will be found near to the end of the potentiometer wire so that one measurement is very small and

the other large. Small errors on this small measurement are then magnified to a point of inadmissible inaccuracy. The difficulty is surmounted by introducing into the circuit a standard cell, which considerably augments the small p.d. to be measured. This brings the neutral point nearer the middle of the scale, within the range of accurate measurement on the wire, with increased accuracy in the result.

Standard Cells. These are voltaic cells set up in convenient form and with standard materials to give definite e.m.f.'s under given conditions, especially that of temperature. Two examples may be mentioned.
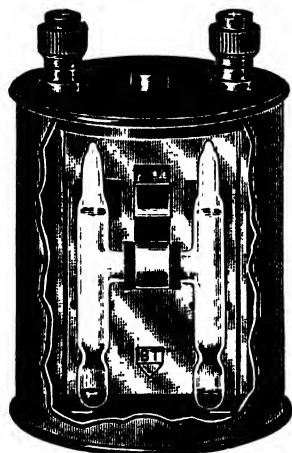
FIG. 41. WESTON STANDARD CELL

1. The Weston cell comprises a cadmium or cadmium amalgam electrode in a saturated solution of cadmium sulphate, and a mercury electrode in a saturated solution of mercurous sulphate. Fig. 41 shows the combination, and also its appearance in a form in which it is usually set up, and which is capable of ordinary use without fear of breakage or detraction from its accurate e.m.f. standard. At 18° C. the generally accepted value of the Weston cell is 1·016 V.

2. The Clark cell comprises a zinc electrode in a saturated solution of its sulphate, and again with a mercury electrode in a solution of mercurous sulphate. Its e.m.f. at 15° C. is 1·429 V. Both of these cells have temperature coefficients,* which must be applied in examples of more accurate work. That of the Clark cell is considerable, and only very small currents for very short times can be allowed in its use as a standard cell (see page 171). That of the Weston cell is, however, very small and, for many purposes, negligible.

Essential to the use of these standard cells are the requirements that their composition must remain unchanged, and the addition of crystals of the two electrolyte substances is usually

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* Temperature coefficient = fractional change of e.m.f. per degree C.

made in order to guarantee the saturation of the electrolyte in contact with the electrodes.

In use, the cells only give current, and that very small, for the very brief periods involved in making contact with the potentiometer wire. As has been pointed out, the Clark cell in particular must not be allowed to produce appreciable current on account of its high temperature coefficient and, therefore, abnormal heating effect.

In making a potentiometer test assume the use of a Weston standard cell with its reading on the potentiometer wire of 55 cm, while that of the cell under test, for example, a Daniell cell, to be 59·3 cm.

Hence
$$\frac{E \text{ of Daniell cell}}{E \text{ of Weston cell}} = \frac{59·3}{55·0}$$

Hence e.m.f. of Daniell cell $= \frac{59·3}{55·0} \times 1·016 = 1·095$ V

Much more elaborate forms of apparatus may be and are used. Accuracy in determinations involves many avenues of care, but we are here more concerned with the principle of the method employed and the results obtained, rather than a detailed discussion of the steps taken to ensure the greatest accuracy.

Such, then, is the potentiometric method of (1) comparing e.m.f.'s of cells and (2) measuring e.m.f.'s if a standard cell is available. At the point when the final reading is taken no current is passing. We thus get the full e.m.f. on open circuit, while any voltmeter reading, however high the resistance of the instrument, will give a somewhat and unknown lower reading owing to the passage of the current, however small this may be.

Analysis of E.M.F. Revert again to the Daniell cell. It develops approximately 1·09 V with the variations which have been already indicated, these being concerned with the concentration of the electrolytes, the temperature, and the reversible heat.

It must now be recognized that there must be some origin of this e.m.f. It must somewhere have one or more sources which should be traced. If more than one source, the magnitudes of the several sources should be determinable.

In the Daniell cell there appear to be three boundaries at which differences of potential might occur. These are: (1)

the zinc plate, (2) the copper plate, and (3) the junction of the two solutions. There might also be small thermo-electric e.m.f.'s set up with varying temperature at the contacts between the plates and the connecting wires, but these are small and will be omitted as not constituting a part of the electro-chemical system. Again, for the moment, the possibility of a small p.d. at the contact of the two liquids will be omitted, and attention confined to what are obviously the two most important points, the contacts of the plates with their respective electrolytes. What are the possibilities here and how can they be explored?

This conclusion that these are the two positions that count in the problem is reached by simplifying the usual chemical equation—

$$Zn + CuSO_4 = ZnSO_4 + Cu$$
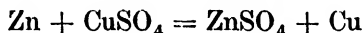
Written ionically, the equation becomes—

$$Zn + Cu.. + SO_4'' = Zn.. + SO_4'' + Cu$$
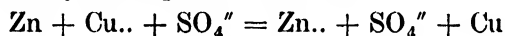
and the two components of the reaction are—

(a) the conversion of metallic into ionic zinc, and (b) the conversion of ionic copper into the metallic form.

Electrolytic Solution Pressure. During the reaction zinc "dissolves," that is, produces ions. This might give rise to a p.d. If the electrolyte is zinc sulphate there is already an "atmosphere" of zinc ions in the solution. Attribute to the zinc some tendency to "evaporate" off into the ionic form. This conception is due to Nernst. Call this its "electrolytic solution pressure." Again, attribute to the zinc ions already in solution a "vapour pressure." This has been called osmotic pressure, not altogether a good term, as the phenomena of osmosis are confined to the reactions taking place at a semi-permeable diaphragm. The term ionic pressure will be clear if not an exactly true expression. Denote the electrolytic solution pressure by P and the ionic pressure as p.

Three cases then arise—

1. If $P > p$, metal will tend to pass into the ionic form, and as the ions are positively charged the metal plate will become negatively charged. As will be subsequently seen, zinc behaves in this manner and the p.d. between the metal and the solution of some specified ionic strength should be determinable.

2. If $P < p$, ions will tend to pass from the solution forming neutral metal, the metal plate thus becoming positively charged. As will be seen later, this phenomenon occurs with copper in a solution of copper sulphate.

3. If $P = p$, then there will be no p.d. between the plate and electrolyte, a condition which may not happen casually with any ordinary metal, but which can certainly be realized under controlled conditions.

The case is somewhat, but not exactly, comparable with that of the solution of a salt. Salt passes into water, there ionizing and forming sodium and chlorine ions. The process of solution continues until the osmotic pressure of the ions and molecules attains that of the tendency of the solid molecules to pass into solution. A condition of equilibrium is reached with excess of the solid representing saturation. The formation of sodium ions which are positively charged is accompanied by the formation of an equivalent number of negatively charged chlorine ions, and there is thus an electrical equilibrium.

Fig. 42.
ELECTRICAL
DOUBLE LAYER

If, however, a metal stands in a solution of one of its salts, that is, in a solution of its own ions, the metal may tend to pass into solution with the formation of new ions which are positively charged. There is, however, no accompanying production of negative ions, and negative charges are therefore accumulated on the metal electrode. Only an exceedingly small amount of this ionic material, far below analytical quantities, will thus pass into solution, as this leads to the accumulation of positive charges in the film of electrolyte in contact with the metal plate and negative charges on the metal electrode. This so-called "double layer" provides the measurable difference of potential without any appreciable passage of the metal into solution (Fig. 42). Conversely other metals may tend to pass from the ionic into the molecular or solid form, and if this occurs, even to the slightest degree, there will be the accumulation of positive charges on the metal with a layer of negative charges on the film of electrolyte adjacent to it.

Before proceeding with this matter quantitatively it will

become necessary to adopt some methods of measurement and standards of expression. For the moment, however, it will be appreciated that the e.m.f. of the Daniell cell is possibly the sum of these two reactions at the zinc and copper plates.

Electrode Potentials. This term is used to signify the difference of potential between a metal and the solution in which it stands. Two of these electrode potentials, or "single" potentials as they are sometimes called, contribute to the e.m.f. of the Daniell cell, and also to all other examples of electrochemical cells. It is required to determine these individual electrode potentials.

A glance at the problem will at once indicate that the value of any single potential is not to be obtained by a mere study of the e.m.f.'s of cells. All voltaic cells comprise two of these electrodes, and no amount of variety in their combinations will serve to give the exact value of a single one.

It will be recalled that in the measurement of e.m.f. some type of standard cell of definite and known e.m.f. is required. Unknown e.m.f.'s can be compared with those of the standard cells and thus determined.

Measurement of Single Potentials. Coming now to the measurement of electrode potentials, we are concerned with a single metal in, for example, a solution of one of its salts. It is now customary to call these single electrodes by the expressive term of "half-cells," as any electro-chemical cell comprises two such electrodes. It will be obvious that for this purpose we shall require something in the nature of a standard electrode, one which can preferably be made up easily and with accuracy and of which the value is definitely known.

Standard Electrodes. There are several standard electrodes in common use, each with its own particular value. In contrast with standard cells, standard electrodes are usually made up from time to time by the experimenter. The glass parts are purchasable, but the actual chemical materials are usually introduced just prior to any series of experiments. Essential to accurate work, therefore, is the ready realization of standard conditions in the materials used and their application. This point will be obvious in the brief descriptions of the standard half-cells which follow.

Calomel Electrode or Half-cell. The constitution of this

electrode is shown in Fig. 43. Mercury, with which electrical contact is established by means of a platinum wire sealed in a glass tube, stands in contact with a solution of mercurous chloride (calomel) in a potassium chloride solution. Mercurous chloride is, in any case, only very slightly soluble, and the introduction of some of the solid in the recently precipitated and washed form serves to maintain saturation and hence constant concentration of mercurous ions. To bring this electrode in contact with any other electrode of a different constitution requires a metallic contact with the mercury through the glass tube, which contains a small quantity of mercury into which the connecting copper wire dips. On the solution side contact is established with any other convenient liquid by gently blowing the solution to fill the side limb. The electrode is easily set up, and to ensure constant concentration of the mercurous ions a standard solution of potassium chloride is necessary. This is usually of normal strength. The electrode thus constituted is known as the "normal calomel electrode." In

FIG. 43. CALOMEL ELECTRODE

this system there is the inherent tendency for the mercurous ions to precipitate themselves on to the mercury electrode, thus giving it a positive charge. In this respect it behaves like copper.
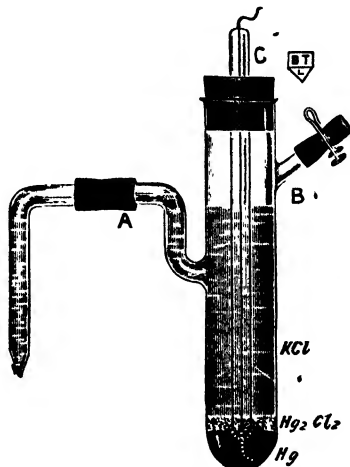
What next is the value of this electrode and how has it been obtained?

If this electrode could be put against any other electrode of which we can be sure that there is no potential difference, then the e.m.f. of the combination will be the p.d. of the calomel electrode both in magnitude and direction.

For the moment we will omit the construction of such a "no difference of potential electrode." Assume that it *has* been achieved and that with it the value of the normal calomel

electrode has been determined to be 0·56 V with the mercury positive and the solution negative. The determination of this value must later claim our attention.

The calomel electrode is then connected with an electrode of zinc standing in a normal solution of zinc sulphate. This combination of two electrodes constitutes a voltaic cell of which the e.m.f. can be determined by means of the potentiometer and standard cell. The value thus determined is 1·04 V, with zinc showing the tendency to pass into the ionic form. Diagrammatically, we have the combination of the two electrodes shown in Fig. 44, and from the data it will be seen that the p.d. value of the zinc electrode is 1·04 — 0·56 = 0·48 V.

If the zinc electrode is replaced by one of copper in a normal
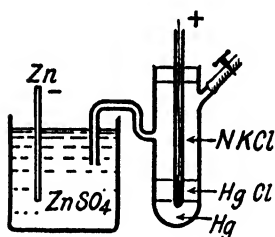
FIG. 44. ZINC AND CALOMEL ELECTRODES

solution of copper sulphate the determined e.m.f. of the combination is only 0·05 V in such direction that the copper ions are tending to come out. But before this can happen it is necessary that mercury shall be brought into the ionic form from the metal in the calomel electrode. The tendency of copper ions to come out is therefore equal first to the requirement of bringing mercury into the ionic form—this necessitating 0·56 V—after which 0·05 V still remains unabsorbed. The single potential of the copper in the normal sulphate solution is 0·56 + 0·05 = 0·61 V, copper ions tending to be deposited. Many other values can be similarly determined, and the following list (Table XLIX) shows the once commonly accepted values for the different electrodes. These metals are usually standing in normal solutions of their salts, this being the system at first adopted.

TABLE XLIX

SINGLE POTENTIALS

Magnesium	.	— 1·27 V	Nickel	.	.	+ 0·06 V
Zinc	.	— 0·48 ,,	Lead	.	.	+ 0·16 ,,
Iron	.	— 0·15 ,,	Tin	.	.	+ 0·18 ,,
Cadmium	.	— 0·12 ,,	Hydrogen	.	.	+ 0·28 ,,
			Copper	.	.	+ 0·61 ,,

The signs of these potentials must now be carefully considered. If a metal tends to pass into the ionic form, thus leaving the metal plate negatively charged, the p.d. is said to be negative. This is the case with zinc and similar chemically active metals. If the ions tend to deposit out and thus impart their positive charge to the electrode, the p.d. is said to be positive. This occurs in the cases, among others, of copper and mercury. Now in an electrolytic solution, metal ions move in one direction only, and thus the sum total of the action is the algebraic difference of the two individual single potentials. Thus in the case of the Daniell cell the combination is as follows—

$$\begin{array}{cc} \text{(Zn)} & \text{(Cu)} \\ -0.48 - (+0.61) = -1.09 \text{ V} \end{array}$$

in the direction of zinc passing into solution while copper ions come out in the metallic form.

Similarly a cell constructed with an electrode of cadmium in its normal sulphate and one of platinum in normal sulphuric acid will have the value of

$$-0.12 - (+0.28) = -0.40 \text{ V},$$

that is, in the direction of the cadmium dissolving and hydrogen being deposited in much the same way as in the simple cell.

Later, the positive or negative value of the single potential of any electrode will be readily apparent.

Electro-chemical Series. From Table XLIX the metals carrying the negative sign will be readily recognized as those which are familiar to the chemist as the active metals, while those carrying the positive sign are those usually regarded as relatively inactive. Further, the usual chemical properties of these metals and their compounds would place them in the same order as that obtained from a study of their single potentials. This order of the metals has long been known as the electro-chemical series, though commonly based on properties which do not at first appear to be electro-chemical. Years ago the more active metals were said to be positive, the term negative then signifying the less active. Since the recognition of these more definite electro-chemical properties as, for example, the single potentials, these terms have been reasonably reversed. Some confusion existed during a short

period of transition from one system to the other, but this has now passed and the present form finds general acceptance. The negative metals are those which chemically are very active, readily dissolving in acids and evolving hydrogen (though not, of course, from nitric acid). They are readily prone to corrosion except when inhibited by secondary causes, and their compounds are usually very stable, this property carrying with it the difficulty of recovering the metals from their natural occurrences. Still further, the more negative metals replace those which are positive, and this property is one which is progressive throughout the list from the most negative to those most positive. In this scheme noble metals are those which are chemically or electro-chemically inactive, quite apart from the consideration of cost.
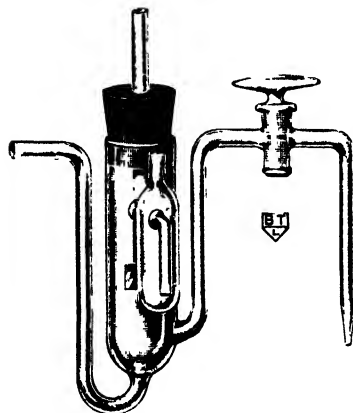
FIG. 45. HYDROGEN ELECTRODE

The Hydrogen Electrode. There are, however, other electrodes used as standards to which reference must be made in view of their extensive use and their special application to electrode potential magnitudes. One of the most important of these is the hydrogen electrode. It may at first sound strange to speak of a gaseous electrode, and for a continuous supply of hydrogen to be available as an electrode for conversion into the ionic form there must necessarily be some method of condensing the gas on to a conducting surface. Platinized platinum supplies the need. In Fig. 45 is shown a platinized platinum electrode immersed in a solution of sulphuric acid, and from below the electrode a continuous stream of pure hydrogen gas bubbles is maintained from a usual source of this gas. The gas for this purpose should be free from any impurities as these would seriously interfere with the electrochemical properties of the electrode and the electrolyte. The electrode may take a number of forms, and as a standard electrode exact conditions of setting up and maintenance must be observed. The acid solution contains hydrogen ions and is also

charged to saturation with the molecular gas, as also is the surface of the electrode. In the form usually adopted there is the aim at normal hydrogen ion concentration in the acid. It will be recalled that $N \cdot H_2SO_4$ is ionized, to the extent of about 0·52. Stronger solutions are somewhat less ionized so that it may be taken that in a 2N. sulphuric acid there is a hydrogen ion concentration of approximately normal strength. Similarly, normal hydrochloric acid is dissociated to the extent of almost exactly 0·8, so that a solution of this acid of 1·25 normal realizes normal ionic concentration of hydrogen. Imagine this electrode set up with the calomel electrode. Across the potentiometer the combination gives an e.m.f. of practically 0·28 V, the mercury of the calomel electrode proving to be the positive element of the combination. Thus the usual single potential of the calomel electrode has been reduced from + 0·56 to + 0·28, the difference, viz. 0·28 V, having been expended in the production of hydrogen ions at the hydrogen electrode, this potential being required to overcome the natural tendency of hydrogen ions to discharge themselves from this ionic concentration with the production of a p.d. of the equal value of 0·28 V. This value, with some refinement, is the value of the hydrogen electrode when that of the normal calomel electrode is taken as 0·56 V.

Hence a normal zinc electrode set up with a normal hydrogen electrode would give an e.m.f. of

$$- 0·48 - (+ 0·28) = - 0·76 \text{ V}$$

and others correspondingly.

Hydrogen and Absolute Scales of Electrode Potentials. On page 188 has been set out a list of electrode potentials on the basis of that of the calomel electrode being + 0·56 V. For reasons which will be more apparent later, electro-chemists have transferred the values to a new scale on which the value of the hydrogen electrode is taken as zero. The values on the two scales are shown in Table L, from which it will be seen that on the hydrogen scale (E_h) all negative values are increased by 0·28 V, while the positive values are reduced by the same figure. By the use of the easily set up hydrogen electrode, the combination of any metal electrode with that of hydrogen gives an e.m.f., which is at once the single potential of the metal electrode on the hydrogen scale. This may at least

be regarded as some advantage. On the other hand, the values on the absolute scale do at least show the natural tendencies of the metals to pass either from the metallic to the ionic state or vice versa in solutions of normal salt strength. Further, the difference between any two values is not influenced by the change of scale. Thus for the Daniell cell the figure, on the hydrogen scale, becomes—

$$- 0{\cdot}76 - (+ 0{\cdot}33) = - 1{\cdot}09 \text{ V},$$

the negative value indicating that the zinc is passing into solution. In conformity with general use, the values on the hydrogen scale will now be adopted. Moreover, these values refer to solutions not normal with reference to the metal salt, but normal with respect to the metal ion concentration, this being a more reasonable basis, having in mind the very varying degrees of dissociation in normal solutions and therefore the varying ion concentrations.

<div align="center">

TABLE L

ELECTRODE POTENTIALS

</div>

Metal	Process	E_A	E_h
Li . .	Li → Li.	− 2·68	− 2·96
K . .	K → K.	− 2·64	− 2·92
Na . .	Na → Na.	− 2·43	− 2·71
Mg . .	Mg → Mg..	− 1·27	− 1·55
Al . .	Al → Al...	− 1·05	− 1·33
Zn . .	Zn → Zn..	− 0·48	− 0·76
Cr . .	Cr → Cr..	− 0·32	− 0·60
Cr . .	Cr → Cr...	− 0·22	− 0·50
Fe . .	Fe → Fe..	− 0·16	− 0·44
Cd . .	Cd → Cd..	− 0·12	− 0·40
Co . .	Co → Co..	− 0·01	− 0·29
Ni . .	Ni → Ni..	+ 0·05	− 0·23
Sn . .	Sn → Sn..	+ 0·144	− 0·136
Pb . .	Pb → Pb..	+ 0·158	− 0·122
H . .	H → H.	+ 0·28	± 0
Cu . .	Cu → Cu..	+ 0·62	+ 0·34
Hg . .	Hg → Hg..	+ 1·08	+ 0·80
Ag . .	Ag → Ag.	+ 1·08	+ 0·80
Au . .	Au → Au...	+ 1·64	+ 1·36

It should be pointed out, however, that the figures refer to the metals in their normally active state. Under a number of conditions metals assume a state of passivity (Chapter XVII)

during which their potentials are practically zero, that is, set against a noble metal such as platinum they give little or no evidence of chemical activity or electrode potential.

The Salt Bridge. It will be appreciated that electrode potential measurements frequently involve the use of liquids which are not miscible without chemical reaction, and in many cases precipitation, with changes of concentration of the solutions which should be constant. In the determination of the electrode potential of silver in the nitrate solution, for example, it is obvious that the limb of the calomel electrode with its solution of potassium chloride cannot be inserted in the silver nitrate solution. In this and similar cases an intermediate or connecting cell containing a solution which is chemically indifferent is used as shown in Fig. 46. For silver nitrate with the calomel electrode this solution might conveniently be potassium nitrate. This liquid connection is commonly known as a "salt bridge."
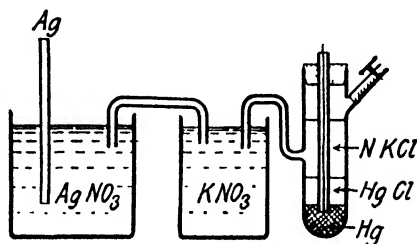
FIG. 46. SALT BRIDGE

The Dropping Electrode. The calomel electrode was the first to be used in any electro-chemical research work, and upon it the first values for single potentials were based. Obviously before this could be done it was necessary to attach to it some determined value and at that time there were no known single potentials. In order to get some first value for what was afterwards to be regarded as a standard, some experimental search had to be made for an electrode which should be free from a difference of potential from that of the solution in which it stood. This "no difference of potential electrode" engaged the attention of Helmholtz, Ostwald, König and others and was attained with some measure of success, insufficient, however, to admit of its being regarded as an ultimate and accurate basis upon which some of these most important values could with confidence be based.

It was achieved by allowing a fine stream of mercury to drop into an electrolyte in such a manner that there could be no

possibility of the presence of mercury ions in the immediate
vicinity of the dropping mercury and therefore no tendency
for positively charged mercury ions to be precipitated on the
mercury and giving to it its positive charge. Such an electrode
was called a "dropping electrode." The arrangement was that
shown in Fig. 47A.

A tube with a capillary terminal was charged with mercury
in contact with a platinum wire fused into the side of the tube.
By no conceivable method could the potassium chloride
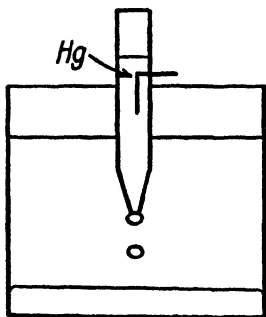
FIG. 47A.
DROPPING ELECTRODE
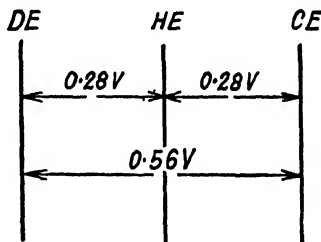
FIG. 47B.
RELATIVE ELECTRODE VALUES

electrolyte be regarded as entirely free from mercury ions. The
slightest oxidation of the mercury at the bottom of the electro-
lyte would lead to some solution of the mercury with the
formation of mercury ions. By the process of the formation
of the individual and successive drops of mercury each with
its increasing surface, it was assumed that, with a rapid stream,
the film of electrolyte immediately in contact with the mercury
drops would be so depleted of mercury ions as to reduce the
p.d. to zero. Manipulative design and accuracy in carrying
out the process failed to reveal any trace of electric potential
of the mercury falling from the tube. If now this is regarded as
a half-cell in conjunction with which the carefully prepared
calomel electrode is associated, then the e.m.f. of the combina-
tion must be due to the potential of the calomel electrode. It
was by this method, carried out with the utmost care, that the
value of 0·56 V was determined for the calomel electrode
containing normal potassium chloride solution, and it was on

this standard that single potentials were first based. It was a case of some carefully determined and accepted value, upon which other calomel electrodes could be prepared and this value attached. The relation of the three electrodes, dropping (DE), hydrogen (HE) and normal calomel (CE), is shown in Fig. 47B, approximate figures only being used.

The Value of the Calomel Electrode. The method, however, has always been open to criticism, and this led to the change from the calomel electrode to the normal hydrogen electrode as the accepted standard. Values referred to the calomel electrode thus standardized were, and are still, known as absolute values (E_A), while those referred to the normal hydrogen electrode are admittedly only relative. Thus the figure of -0.76 V for zinc on the hydrogen standard embodies at least two differences of potential, that of the hydrogen electrode itself and that of the zinc electrode. By taking the value of the hydrogen electrode as zero in every case and at all temperatures, the values on the hydrogen scale refer to the differences of potentials of the metals from that of the hydrogen electrode. These values are capable of accurate determination free from any doubts as to the reliability of the first standard, the only necessity being that of setting up the hydrogen electrode strictly on the specification laid down with regard to the preparation of the platinum electrode and the ionic strength of the electrolyte. Subsequently there was a reversion to the use of the calomel electrode in several forms, each having first been standardized against the hydrogen electrode. Again, calomel electrodes of different potassium chloride concentrations are in common use, these being shown and with their corresponding values in Table LI.

<div align="center">

TABLE LI

CALOMEL ELECTRODES

</div>

Strength of KCl			18° C.	25° C.
Decinormal	.	.	0.334 6 V	0.334 1 V
Normal	.	.	0.283 ,,	0.281 6 ,,
Saturated	.	.	0.249 ,,	0.244 ,,

From these values it will be seen that the stronger potassium chloride solutions give the lower values, due to the lower

mercury ion concentration representing a lower solubility of the mercurous chloride in the electrolyte with a common ion, other examples of which have previously been pointed out (see page 197).

Electrode Potential Diagrams. A conception of the meaning of these single potentials in a depositing solution is illustrated in the diagrams (Fig. 48), in which it is assumed that there is only the smallest amount of current flowing in order that there shall be the minimum change of the electrode potential from the "single" values.
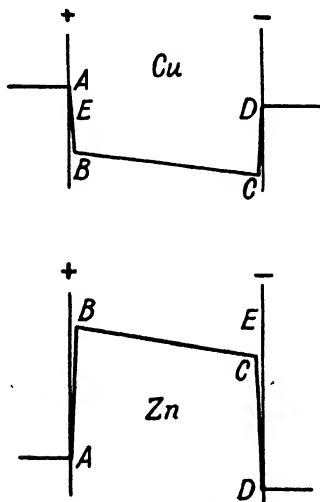
In the case of copper the copper ions are discharged, this process producing a p.d. of practically 0·34 V. At the anode copper passes into the ionic form with an absorption of practically 0·34 V. Thus the voltmeter records at least three components, the potentials at the anode and cathode, which in this case are assumed to be equal and opposite, and also the drop in potential due to the resistance of the electrolyte. As will later ·be seen, these electrode potentials in the process of deposition are not equal. Each suffers some change so that the voltmeter records the summation of three different components.

FIG. 48. ELECTRODE POTENTIAL DIAGRAMS

Here *AB* represents the fall of potential in the production of copper ions, *BC* then representing the fall due to ohmic resistance. At the cathode the discharge of copper ions is attended with the development of about 0·34 V, thus increasing the potential at which the current leaves the cell.

In the case of the zinc a p.d. of 0·76 V is developed at the anode with the production of zinc ions, while a practically equal potential is absorbed at the cathode by the precipitation of zinc ions on the cathode.

In this case *AB* represents the development of potential with the production of zinc ions at the anode, after which *BC* again represents the fall through the solution due to ohmic

resistance. At the cathode the discharge of zinc ions into the metallic form necessitates the absorption of a potential equal to that produced at the anode, and if anodic and cathodic processes are theoretically efficient, then the voltmeter reading across the bath is a measure of the ohmic resistance with the exception of a slight error for concentration at both electrodes.

A study of these electrode potentials with, in some cases, their bearing on the attendant deposition process, has been made by a number of investigators. For example, Fink and Hogaboom* have shown that in the case of silver in cyanide solutions, the accepted standard methods for the determination of polarization yield discordant results. With solid silver plate electrodes, they found that the polarization potentials are highest at the upper edge of the plate and lowest at the lower edge. This difference was considered to be due to the solution films next to the electrodes, and it is suggested that uniformly consistent results are possible only when these surface films are uniform throughout, both in composition and structure.

The Nernst Equation. From an entirely different angle and based on thermodynamical principles, Nernst deduced the following expression for the potential of a metal immersed in a solution of one of its salts—

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

where E is the electrode potential

R is the gas constant referred to on page 49

T is the absolute temperature

n is the valency of the metal ions

F is the Faraday

P is the electrolytic solution pressure of the metal

and p is the osmotic pressure of the ions in the solution

Some comments must be made on these individual items in the expression. The term osmotic pressure of the ions might better be termed ionic pressure. It has previously been emphasized that osmotic phenomena occur around semi-permeable membranes, but the use of the term in this connection will be readily understood.

* *Amer. Electro-chem. Soc.*, (1930).

The gas constant R should be expressed in electrical terms thus—

$$R = 84\ 500 \text{ g.-cm} \quad \text{and} \quad 42\ 500 \text{ g.-cm} = 1 \text{ g.cal.}$$

Further, 1 g.cal. $= 4{\cdot}18$ J so that

$$R = \frac{84\ 500 \times 4{\cdot}18}{42\ 500} = 8{\cdot}28 \text{ J}$$

Log_e refers to logarithms calculated to the base $2{\cdot}718\ 28\ldots$. This is an important number in the realm of natural phenomena. It was discovered by Euler and is made up as follows—

$$e = 1 + 1 + \frac{1}{2} + \frac{1}{2 \times 3} + \frac{1}{2 \times 3 \times 4} + \frac{1}{2 \times 3 \times 4 \times 5} + \text{etc.}$$

Taken to its limit this result is $2{\cdot}718\ 28..$ the logarithm of which to the ordinary base of 10 is $0{\cdot}434\ 3$. Logs to the base e are therefore converted to ordinary logs by multiplying by $1/0{\cdot}434\ 3 = 2{\cdot}3$. The expression then simplifies to—

$$E = \frac{8{\cdot}28 \times T \times 2{\cdot}3}{n \times 96\ 540} \log_{10} \frac{P}{p}$$

$$= \frac{0{\cdot}000\ 198 \times T}{n} \log \frac{P}{p}$$

While P is at present quite an unknown quantity, the presence of p indicates that the potential of the metal is to some extent dependent upon the concentration of the metal ions in the solution. This is, of course, reasonable and recognized.

In the absence of definite knowledge of the magnitude of the electrolytic solution pressure (to which reference will be made later), we can use the Nernst expression to calculate the e.m.f. developed by a metal standing in two solutions of one of its salts of different concentrations. In this case P and p are replaced by C and c representing the ionic concentrations in the two solutions. Take a simple case in which C and c represent normal and decinormal ionic concentrations. Hence $C/c = 10$ and its log unity. This factor therefore disappears. At a temperature of $18°$ C. ($291°$ Abs.) the expression becomes—

$$E = \frac{0{\cdot}000\ 198 \times (273 + 18)}{n} = \frac{0{\cdot}058}{n} \text{ V}$$

This combination of a metal in two solutions of its salt of different ionic concentrations is known as a concentration cell. When these ionic concentrations vary to the ratio of 10, the developed e.m.f. is $0·058/n$ V, that is, $0·058$ V for a univalent ion, $0·058/2 = 0·029$ V for a divalent ion, etc. These are values which are in exact accordance with those already determined, so that the Nernst equation will seem to have many applications in the study of electro-chemical potential differences without an exact knowledge of the more or less hypothetical factor of the electrolytic solution pressure, which is, after all, only a conception to account for the observed facts.

Having, however, the accurately measured potential of, say, zinc in a solution of zinc sulphate with normal metal ionic concentration, some attempt can be made by working backwards with a view to calculating this electrolytic solution pressure. For this purpose use the approximate value of $0·48$ V on the absolute scale for zinc in a solution of normal zinc ion concentration. At 18° C. the expression becomes—

$$0·48 = \frac{0·000\ 198 \times 291}{2} \log P$$

from which—

$$\log P = \frac{0·48 \times 2}{0·000\ 198 \times 291} = 16·6$$

and P must be of a considerable order to have a log of $16·6$. It is partly on this account that the Nernst expression is open to some criticism, but it is by no means the first case in which an expression has useful applications over restricted ranges without being exactly applicable to all conditions. The equation will therefore be used on much the same lines as in the calculation of the e.m.f. of the concentration cell.

The number with log of $16·632$ is $4·29 \times 10^{16}$ and thus the electrolytic solution pressure of zinc is this figure times the ionic pressure of a normal ionic solution. This, however, is of the order of 22 atm, and thus the electrolytic solution pressure of zinc is of the order of $22 \times 4·29 \times 10^{16} = 9·4 \times 10^{17}$ atm, an altogether unimaginable figure. Similar figures for other metals can be calculated from their measured single potentials. These high values will naturally stand in the same order as

the single potentials, but no useful purpose will be served in extending the calculation.

Electrode Potentials of Anions. Anions, too, have electrode potentials. If that of hydrogen can be dealt with and so successfully turned to account in the hydrogen cell, those of other gases might be capable of similar treatment. A platinum plate, for example, will absorb small amounts of chlorine gas, which element can be kept in solution in·some electrolyte containing chlorine ions, for example, KCl. This chlorine gas tends to pass into the ionic form producing negative chlorions and leaving the platinum plate positively charged. Other halogens can be similarly dealt with and their determined potentials are as follows—

<div align="center">

TABLE LII

ELECTRODE POTENTIALS OF ANIONS

</div>

Element	Ion	Potential
I	I⁻	+ 0·54
O	OH⁻	+ 0·40
Br	Br⁻	+ 0·99
Cl	Cl⁻	+ 1·36
F	F⁻	+ 1·90

Consequently a half-cell with zinc in its sulphate and another with chlorine in potassium chloride with a Pt electrode can be joined together. Both elements tend to pass into solution and their effects are added together as they are producing oppositely charged ions in opposite directions. The e.m.f. of the combination becomes the algebraic difference between their individual values thus—

$$- 0.76 - (+ 1.36) = - 2.12 \text{ V}$$

This is a possible voltaic cell though, of course, an unusual one.

Liquid Junction Potentials. The possibility of the existence of potentials at the junction of the liquids comprising the electrolytic cell has not been overlooked. It has, by reason of its very small dimensions, been regarded as negligible in the usual potential measurements with which we have been concerned. Some idea of the several values which have been determined may, however, be given. With two solutions of the same electrolyte the determination is relatively simple, but with differing electrolytes the matter is more difficult. Generally the method

adopted is that of maintaining a constant flow of the two solutions on opposite sides of a mica plate with a small hole. A few values so determined are as follows—

<div style="text-align:center">

0·1 N HCl/0·1 N KCl   0·027 V

0·1 N HCl/N KCl   0·007 6 V

0·1 N HCl/Sat. KCl   zero

</div>

From these figures it will be seen that the appreciable difference of potential between decinormal solutions of HCl and KCl disappears with saturated KCl, this fact being utilized in adopting saturated potassium chloride solution as an inert liquid junction in potential measurements.

ELECTRODE POTENTIALS (*contd.*)

Introduction. We can now pass on to a consideration of the changes which take place in the potentials of metals standing in solutions of their salts and functioning as electrodes either as cathode or anode. With these changes of potentials many problems in electrodeposition are intimately concerned, and the study throws considerable light on many aspects of this phase of electro-chemistry. That such changes do occur will be obvious. Zinc, for example, in a solution of its sulphate of normal zinc ion concentration develops a potential of − 0·76 V on the hydrogen scale, the negative sign indicating that the metal tends to pass into the ionic form against the ionic pressure already existing there. If the zinc now constitutes an anode, the metal passes into solution with an increase in the zinc ion concentration in the solution in contact with the zinc plate. Against this greater ion concentration the metal plate will develop a smaller potential, the figure being less than 0·76 V, but still carrying the negative sign. The plate has thus become less negative or more positive. On the other hand, as a cathode, the zinc plate will receive a deposit, thereby inducing a lower zinc ion concentration in the layer of solution in contact with it. Against this weaker solution the zinc plate will develop a greater potential so that the figure will be in excess of 0·76 V still with the negative sign. As a cathode, the zinc becomes more negative, and these variations would seem to increase with an increasing current or current density. Take also the case of copper which in N. ionic copper sulphate develops + 0·34 V. As an anode, more copper ions are formed, increasing their concentration in the anode film of solution, from which stronger solution copper ions would tend to more easily discharge, thereby raising the positive value of the copper potential. The metal anode thus becomes more positive, while at the cathode the discharge of copper ions as a deposit weakens the solution, reduces the tendency to the

separation of the copper, and thus lowers the potential which becomes less positive or more negative.

Static Potential and Dynamic Potentials. To differentiate between these potentials the terms "static" and "dynamic" potentials are applied to those developed without and with the presence of a current. So far we have considered only the static potentials and we now turn our attention to the dynamic
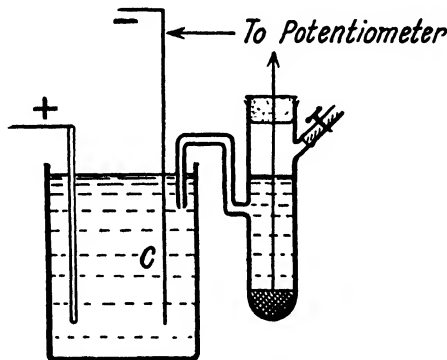
FIG. 49. MEASUREMENT OF DYNAMIC POTENTIAL

potentials, the term dynamie being usually omitted but clearly understood.

These are determined in exactly the same manner as the single potentials as illustrated in the previous chapter.

In Fig. 49 is shown a small deposition cell fitted up for the deposition of a metal upon the cathode C. Into the solution, and preferably near to the cathode, is inserted the connecting limb of the calomel electrode. When no current is flowing the electrode potential ("cathode") is obtained from the e.m.f. across the "cathode" terminal and the mercury of the standard electrode. The figure obtained is quite independent of the fact that the plate is shortly intended to function as a cathode and to receive a deposit. A small current is then passed through the cell with metal deposition. In endeavouring to obtain the new potential some difficulty may at first be experienced. This is due to the fact that with different metals there are widely different potentials to be dealt with. In the first place there can be no zero point obtained on the potentiometer wire

until both positive terminals meet at one end of the wire. Imagine first the case of the deposition of copper in the cell. Copper is a less positive metal than the mercury in the calomel cell and the difference between the two potentials will therefore be measured on the potentiometer wire. The electrode potential of the copper plate will therefore be computed by adding the figure for the calomel electrode to that determined on the potentiometer. For the normal calomel electrode the value is $+ 0 \cdot 28$ V while that for copper in normal ionic copper solution is $+ 0 \cdot 34$ V. In this case, therefore, there will be a measurable potential difference over the two half-cells of $0 \cdot 34 - 0 \cdot 28 = 0 \cdot 06$ V. The accurate measurement of such small potentials obviously presents difficulty, and it is therefore customary to introduce into the circuit a Weston cell, to the e.m.f. of which these small potential differences, whether positive or negative, are added, giving a readily measurable figure, in the case of the simple potentiometer wire, somewhere more nearly in the middle of the length of the wire rather than a centimetre of two from the end. Alternatively, if zinc is under test the mercury of the calomel electrode will need to be connected with the positive end of the potentiometer, the measured e.m.f. then being the arithmetical sum of the two values or their algebraic difference. These simple rules serve to convert the actual readings of potential differences on the potentiometer to those for the electrode under examination.

Such results clearly show that with increasing current the cathode becomes less positive or more negative, and that the anode becomes more positive or less negative. In other words, the plates originally static become, when a current is passing, differently charged and this difference increases with increasing current density.

This variation of potential with increasing current density is known as electrode polarization, meaning the difference in the electrode potential in the static and dynamic conditions. This polarization affects both electrodes and not necessarily to the same extent, so that both cathode and anode polarization need to be separately determined.

Concentration Polarization. This polarization is graphically shown in Fig. 50. It represents an added e.m.f., which must be applied with increasing current density to that already required

to overcome the ohmic resistance of the solution. It arises from the difference in the concentrations of the metal salts and therefore of the metal ions in the films of electrolyte on the surface of the electrodes. It is, in fact, concentration polarization and would not occur if the films of anolyte and catho-

lyte in contact with the electrodes could be continuously maintained at their normal concentration during the passage of the current. The figure shows, though not to scale, the changes at each electrode, that at the anode making this electrode less negative or more positive while that at the cathode makes this electrode less positive or more negative.

Still assuming that the current efficiency is 100 per cent at both the anode and cathode, the e.m.f. across the cell can now be seen to comprise three components,

Fig. 50. Concentration Polarization

viz., that required to overcome ohmic resistance, and this increases proportionally with increasing current, and also those required to overcome these increasing polarizations and the electrodes. This is indicated in Fig. 51 and from it, it will become increasingly apparent that a single voltmeter reading across a deposition bath does not necessarily convey any very definite information regarding the processes going on in the bath.

Thus in Fig. 51 (a) the components are set out for the anode and cathode compartments of the cell while in (b) they are presented in a somewhat different form, both of these being self-explanatory.

Concentration polarization of this type is readily illustrated by setting up in a glass cylinder a strong solution of copper sulphate over which is poured carefully, to avoid mixing, a solution of lower concentration (Fig. 52). For the upper layer a dilute sulphuric acid would suffice. A clean copper rod stands in the two solutions as shown, and in the course of a few hours there is definite evidence of copper deposition on the lower part of the rod while the upper portion shows evidence of anodic solution.
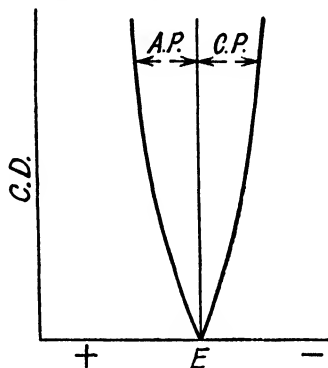
The magnitude of the developed e.m.f. is that calculated from the Nernst equation in the previous chapter and in the case of copper (a divalent metal) amounts to $0.058/2 = 0.029$
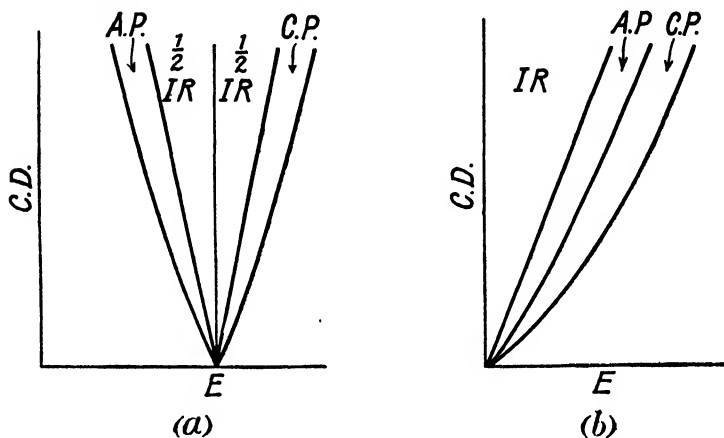
FIG. 51. P.D.'s, TO OVERCOME OHMIC RESISTANCE AND CONCENTRATION POLARIZATIONS

volt approximately for solutions differing ten times in their ion concentration. Theoretically the process of copper deposition on the lower portion of the rod and the anodic solution of the upper portion will go on until the two solutions acquire the same concentration of copper ions. Its presence prevents the accurate determination of resistivity in electrolytes even though no actual chemical action takes place at the electrodes, and hence the use of alternating current. It may be regarded as probable that these phenomena will have an important bearing on many matters electrochemical.
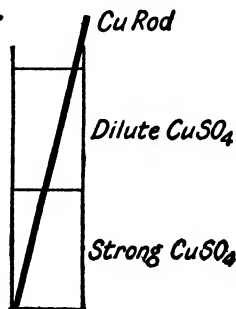
FIG. 52. CONCENTRATION CELL

Cathode Polarization. It will now be convenient to set out these effects to some sort of scale so that the behaviour of the different metals will be more easily comparable. Fig. 53 shows the polarizations of the cathodes for the metals referred to, and they are, moreover,

set out to a scale which indicates the negative or positive character of the metal in the static form. They cover a wide range from mercury, a very positive metal, on the one hand, to zinc in a potassium cyanide electrolyte, which is very negative, on the other. These curves express the changes of potential with changes of current density.
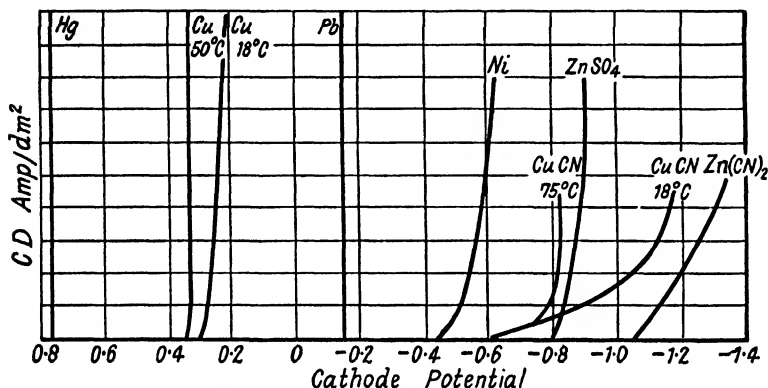
FIG. 53. CATHODE POTENTIAL AND CURRENT DENSITY

In this arrangement it will be seen that some grouping may be effected as follows—

Group 1 includes such metals as lead and mercury (to which may be added silver in the nitrate solution), which show little polarization.

Group 2 includes copper, nickel and zinc in solutions of their mineral acid salts, while

Group 3 includes such metals as copper, cadmium and zinc in solutions of either the single alkali cyanides or the double cyanides.

Later it will be seen that this rough classification finds some application in the behaviour of the several metals in deposition processes, but for the moment it will be observed that in some cases these polarization curves are far apart while in others they fall more closely together and even in some cases overlap. This problem will be explored later.

Electrode Polarization (Simple Determination). These variations of electrode potentials may be approximately determined in a simple manner by the use of a cell divided into three equal

compartments by the introduction of gauze screens as shown in
Fig. 54. These gauzes are such that the current passes through
without making any contact with the metallic partition. [In
the latter case the screens would, act as bi-polar electrodes
(see Chapter XXII) and each compartment would then exhibit
the usual properties of an electrolytic cell.] Voltmeter readings
are then taken across the anode, middle and cathode compart-
ments. That across the middle compartment accounts only,
for the ohmic resistance of the electrolyte. An equal p.d. is
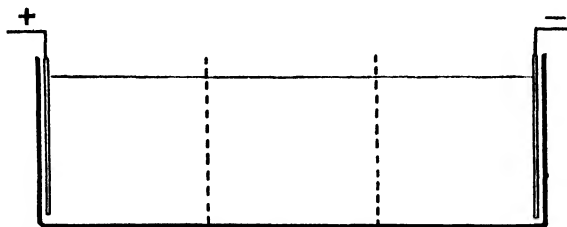
FIG. 54. CELL FOR APPROXIMATELY MEASURING POLARIZATION

used for the same purpose in the anode and cathode compart-
ments, and the varied readings obtained in these compartments
are due to the electrode potential changes or polarizations with
the variations of current density.

With a high resistance voltmeter such results give a good
indication of these electrode polarizations, but much more
accurate data are determinable by the usual method of measur-
ing electrode potentials by the potentiometric method with a
standard electrode as previously described.

Polarization with Insoluble Anodes. It will be appreciated
that with insoluble anodes a new set of conditions arises from
the fact that definite chemical changes occur as the result of the
migration and discharge of the ions. Thus with acidulated
water there is the definite decomposition of the water with the
absorption of a considerable amount of energy. For the moment
we will set this figure at $1 \cdot 25$ V required for the discharge
of the hydrogen ion at the cathode and the hydroxyl ion at the
anode. This is practically a constant figure over different
current densities. On to this has then to be added the increasing
p.d. required for overcoming the ohmic resistance of the
electrolyte together with the p.d.'s of anodic and cathodic

polarizations. This is diagrammatically set out in Fig. 55, from which will be seen that the total e.m.f. over the electrolytic cell is made up of (1) the electrolytic reversible potential *ERP*, that required for decomposition, (2) *IR*, that for overcoming ohmic resistance, and (3) *CP* and *AP*, two differing electrode polarizations, altogether a somewhat complex figure. Voltmeter readings across any electrolytic bath are not so simple as sometimes imagined and indeed require some interpretation.
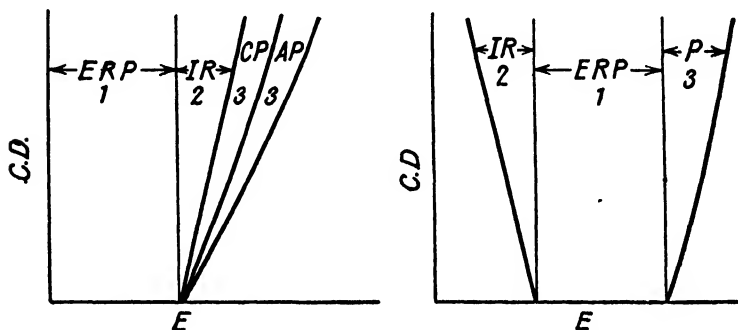
Fig. 55. Components of Bath Voltage with Insoluble Anode

Depolarization. This term of frequent use refers to the counteraction of the conditions leading to polarization. Substances reducing the tendencies to polarization are called depolarizers.

Over-voltage. Under normal conditions the evolution of hydrogen and oxygen from acidulated water might be anticipated with a p.d. across the electrodes of about 1·12 V. Such anticipation is confirmed by the use of platinized platinum electrodes. By the substitution of smooth platinum electrodes, no such evolution of gases takes place under a p.d. of 1·7 V. Hence where the discharge of gases is concerned, a new set of conditions seems to arise from the fact that different electrode materials offer different facilities for the discharge of these gaseous products. For example, hydrogen is eliminated at the cathode, but the ease of discharge of this ion is dependent to some extent upon the physical and, more strikingly, the chemical nature of the cathode material. Under

precisely the same conditions, metals like zinc and mercury offer a considerable opposition to the discharge of the hydrogen ion on their surfaces in comparison with that offered by platinum. This opposition is measurable by an increased cathode potential above that required for some standard material, and this excess voltage is called "over-voltage." Values for this phenomenon vary slightly according to different observers, but the following may be taken as generally recognized for hydrogen from normal sulphuric acid—

TABLE LIII
OVER-VOLTAGE OF HYDROGEN

Platinized Pt. .	.	.	.	.	0·005 V
Gold	.	.	.	.	0·02 ,,
Polished Pt.	.	.	.	.	0·09 ,,
Silver	.	.	.	.	0·15 ,,
Nickel	.	.	.	.	0·21 ,,
Copper	.	.	.	.	0·23 ,,
Cadmium	.	.	.	.	0·48 ,,
Tin	.	.	.	.	0·53 ,,
Lead	.	.	.	.	0·64 ,,
Zinc	.	.	.	.	0·70 ,,
Mercury .	.	.	.	.	0·78 ,,

Over-voltage varies with temperature, the values usually being lower at elevated temperature, but increases with current density. The phenomenon is one to be reckoned with in many examples of commercial electrolysis.

Over-voltage, too, is reduced by the super-imposition of an alternating current, this method having some application in electrodeposition problems.

Similar figures for the over-voltage of oxygen are shown in Table LIV.

TABLE LIV
OVER-VOLTAGE OF OXYGEN
(In normal KOH)

Nickel	.	.	.	.	0·06 V
Cobalt	.	.	.	.	0·14 ,,
Platinized Pt. .	.	.	.	.	0·25 ,,
Iron	.	.	.	.	0·25 ,,
Lead	.	.	.	.	0·31 ,,
Silver	.	.	.	.	0·41 ,,
Cadmium	.	.	.	.	0·43 ,,
Palladium	.	.	.	.	0·43 ,,
Pt. (smooth)	.	.	.	.	0·45 ,,
Gold	.	.	.	.	0·53 ,,

Assuming for the moment that these values are not widely different in various electrolytes there will be a marked difference in the voltages required for electrolytic decomposition of water with (a) a nickel anode and gold cathode and (b) a gold anode and mercury cathode.

In (a) the combined over-voltages are $0.06 + 0.02 = 0.08$, while in (b) they are $0.53 + 0.78 = 1.31$ which is 1.23 V in excess of (a). Some effects of these phenomena may be gleaned from the thought that with a low over-voltage of hydrogen the gas will prefer evolution to undertaking possible chemical reactions in the solution. The similar case arises with oxygen, and thus in many electro-chemical reactions changes in the materials of the electrodes frequently alter entirely the course of the secondary reactions.

After making some calculations relating the thermo-chemical properties of the various compounds with the e.m.f. required for their decomposition, it may be pointed out that the additional e.m.f. concerned with over-voltage problems makes its appearance by transformation to the form of heat, being an addition to the energy required for decomposition.

Applications of Over-voltage. Many suggestions have been ventured to account for this phenomenon of over-voltage. In the case of hydrogen it has been suggested that it may be due to the production of highly condensed films of hydrogen on the surface of the cathode. From the values for over-voltage it should be possible to apply the Nernst equation to the calculation of the pressure of these assumed hydrogen films, and the figures thus obtained are altogether beyond reason.

A more likely explanation is that of the production of hydrides on the surface of the cathode giving rise to high electrode potentials. This would seem to be a reasonable suggestion in view of the known existence of many metal hydrides, and, moreover, from the fact that the activity of the hydrogen on the cathode would seem to favour the production of these hydrides if only in the merest yet appreciable amounts.

In the case of chemical reductions at the cathode yet another factor may have a determining influence. In Table LV, p. 212, is given the data for the reduction of nitric acid to (1) hydroxylamine and (2) ammonia. These may be regarded as progressive stages in the reduction.

Now amalgamated lead has a recognized high over-voltage against hydrogen while that of spongy copper is notoriously low. Another factor must therefore be responsible for the reduction of the acid, and it is apparent that the individual metals may act catalytically in promoting the reduction of the acid to a much more marked extent than the hydrogen over-voltage.

TABLE LV

REDUCTION OF NITRIC ACID

Cathode Material	Percentage Current Forming	
	Hydroxylamine	Ammonia
Lead, amalgamated	70	17
Lead, rough . .	24	60
Zinc . . .	43	40
Copper, smooth .	11	77
Copper, spongy .	1·5	9·3

This over-voltage may be regarded as another type of polarization, and a number of electro-chemical operations in which it plays an important influence may now be referred to.

1. *Behaviour of Zinc in Acid.* It is well recognized that impure zinc dissolves readily in dilute sulphuric acid while pure zinc is relatively unaffected. The explanation of this difference lies in the fact that zinc cannot enter into solution without the discharge of an equivalent amount of hydrogen. The action is electrolytic, zinc ionizing anodically, while hydrogen ions are discharged at a cathode. Unless hydrogen can be evolved, zinc cannot enter the solution. Impurities in zinc have low over-voltages for hydrogen and thus facilitate the discharge of hydrogen ions and the evolution of the gas. Pure zinc, on the other hand, has a high over-voltage for hydrogen, thereby resisting the elimination of hydrogen and, therefore, the ionization of the zinc, the p.d. of this ionization being insufficient to overcome the over-voltage. Mercury, too, has a high hydrogen over-voltage, again resisting the evolution of hydrogen and thus stabilizing the zinc. The amalgamation can be effected either by rubbing on the mercury or passing the

zinc through a weak solution of a mercury salt. With impure zinc dissolving rapidly in sulphuric acid, the addition of a small amount of a mercury salt solution at once inhibits the action.

2. An application of this principle occurs in the suggested methods for the purification of the crude zinc solutions prepared by the treatment of roasted zinc sulphide for conversion into oxide and sulphate with sulphuric acid. For this purpose the ores, the zinc content of which is mainly in the form of sulphide, are roasted to convert the sulphide into oxide, together with a small proportion of sulphate—

$$2ZnS + 3O_2 = 2ZnO + 2SO_2$$
and $$ZnS + 2O_2 = ZnSO_4$$
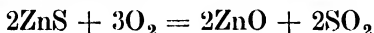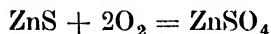
The roasted ore is then treated with sulphuric acid (in the origination of the process, but later with the partly-depleted acid zinc sulphate solution from the electrolytic cells), the zinc compounds being dissolved out as sulphate. Zinc enters into solution as the sulphate together with many metallic impurities. From such a solution it is impossible to deposit zinc with any practical success. The impurities, mainly positive with respect to zinc, are deposited in the early stages with the zinc and at once provide points of low over-voltage for the evolution of hydrogen from the relatively strong sulphuric acid solution necessary for conductance purposes, with a considerable reduction in the current efficiency of zinc deposition. The elimination of these impurities from the slightly acid solution is the crux of the process. For this purpose treatment with finely divided zinc is largely used, but one method* makes use of zinc in some finely divided form followed by an addition of mercuric sulphate, this effecting the amalgamation of the zinc and reducing to zero the solution of zinc except by the replacement of the impurities. The mercury is recoverable from the metallic sludge, entailing only a very slight consumption of the metal.

At a further stage in the process the zinc is deposited from a highly purified solution of zinc sulphate containing a notable quantity of free sulphuric acid on to aluminium cathodes. The high over-voltage of zinc against hydrogen ensures a high current efficiency of zinc deposition. From time to time the

* *Trans. Amer. Electro-chem. Soc.*, Vol. XLIV, p. 467 (1923).

cathodes are removed, the zinc deposit detached, and the aluminium cathodes, after some cleaning, are reintroduced into the electrolytic cells. Being free from zinc and of relatively low over-voltage they effect the deposition of hydrogen until covered with deposited zinc, after which the deposition of the zinc proceeds normally. The high over-voltage of zinc against hydrogen thus plays an important part in a process which in the course of twenty years or so has come to account for the production of about one-third of the world's supplies of this metal usually from resources which were not readily amenable to the usual distillation process.

3. *Electrolytic Alkali Processes using Mercury.* Several types of cell for the electrolytic production of alkalis make use of an intermediate diaphragm of mercury. Some account of the Castner-Kellner process will be found in the literature of the subject. In this process a salt solution is electrolyzed with carbon anodes (at which chlorine is evolved and led away for use) and iron cathodes between which there is a layer of mercury, which constitutes a diaphragm separating the anolyte and catholyte. Between the electrodes current must pass through the mercury, there depositing the sodium which is redissolved anodically from the mercury in the cathode compartment. This deposition of the sodium from an aqueous solution is made possible by reason of the very high over-voltage of the mercury against hydrogen, and the fact that the sodium rapidly diffuses into the mercury. The over-voltage increases with an increase in current density, and high current densities are the order of the process. The deposition of sodium into the mercury has a current efficiency of the order of 90 per cent, while that of the anodic solution on the cathode compartment of the cell is naturally of the order of 100 per cent, this necessitating some boosting of the current in the anode compartment.

The over-voltage of certain metals against hydrogen thus plays a conspicuous part in a number of electro-chemical industries.

A similar example is probably that of the addition of a small amount of mercury to the alkaline zinc bath in the deposition of the metal on cast-iron in which numerous impurities facilitate the deposition of hydrogen which is inhibited by a thin film of deposited mercury, thus facilitating the deposition of zinc.

4. *The Lead Accumulator.* The p.d. curve of the lead accumulator after a long steady period of about 2·2 V shows a sharp turn upwards towards the end of the charging process. At one time it was thought that this might be due to the formation of highly oxidized products after the conversion of the major part of the lead sulphate to active lead and lead dioxide. It is more probably due to the high over-voltages of lead dioxide against oxygen at the positive, and of lead against hydrogen at the negative plates. This high p.d. has only a temporary existence.

5. *Deposition of Chromium.* It is recognized that the deposition of chromium from chromic acid baths occurs more quantitatively on cathodes like copper and nickel. Nickel is invariably selected as the most suitable undercoat for chromium, copper being at a disadvantage on account of its conspicuous colour when the chromium may be worn through. The high over-voltage of nickel militates against the evolution of hydrogen with an increase in the proportion of chromium deposited.

Oxygen over-voltage, too, plays its important part in a number of electro-chemical processes. Reference to some of these must be made.

In the chromic acid bath for the deposition of chromium there would appear to be a choice of anode material in the absence of chromium, this metal never being used, first on account of its relatively high cost in comparison with the cost of chromic acid as a periodic addition, and, secondly, on account of its almost 100 per cent solution efficiency. With a cathode efficiency only of the order of $12\frac{1}{2}$ per cent this would lead to the large accumulation of chromic acid on the bath. Alternative metals as anodes are iron and lead. At the anode some of the trivalent chromium always present in this solution and usually as chromium chromate ($Cr_2(Cr_2O_7)_3$) is reoxidized to the hexavalent chromic acid, and this process should, as far as possible, counterbalance the reduction which invariably takes place at the cathode. Now Haring and Barrows have shown that this oxidation takes place more effectively at a lead than at an iron anode. The figures in Table LVI illustrate the point.

Further, the relative area of the anode to the cathode makes its contribution to the problem and can be chosen to maintain

TABLE LVI

COMPARISON OF LEAD AND IRON ANODES IN CHROMIC ACID
SOLUTIONS

Ratio of Areas Anode to Cathode	Anode Composition	Chromium Dichromate Normality (Cr''')		Percentage of Total CrO₃ in "Free" State	
		Initially	After Electrolysis	Initially	After Electrolysis
1 : 3	Lead	0·46	0·15	84	95
	Iron	0·46	1·24	84	50
3 : 1	Lead	0·46	0·05	84	98
	Iron	0·46	0·93	84	65

an original and desirable amount of chromium dichromate in the bath.

Alternatively, a method of rectification of this excessive trivalent chromium is that of passing the current through the solution using a cathode immersed in a porous pot, or even such a cathode can be maintained in the ordinary working of the bath. Experiments have shown that this rectification may be accomplished with a current efficiency of the order of 33 per cent.*

Over-voltage of Metals Against Metals. A further point, and one of considerable interest in electrodeposition, is that of the possibility of the occurrence of over-voltage problems in the deposition of metals, if, for example, some metals will facilitate the deposition of a metal more readily than others. The problem is not capable of a simple solution in view of the recognized chemical or electro-chemical differences between the metals concerned. Some data on this matter have been published. If reliable, it would give some indication as to the suitability of metals as undercoats for other deposits. There are, however, complications, one of which is that of the over-voltage of hydrogen which is so usually an accompaniment of metal deposition. The matter is one which will command attention in view of its practical aspect, and the empirical results of long-established practice may give some lead in the further investigations. At present there seems to be little which can with confidence be recorded.

* Field and Weill: *Electro-plating*, 5th Edn., p. 356.

ACCUMULATORS

Introduction. Reference has frequently been made to the fact that in many reactions brought about by the conversion of electrical energy into the chemical energy, the resulting products show marked tendencies to a reaction in the opposite direction, with the consumption of some of the product and the generation of an equivalent amount of electrical energy. In general, this phenomenon has been called chemical polarization, which may be roughly defined as the tendency of the products of electrolysis to revert to their original condition. This phenomenon will now be examined in some detail.

The Daniell Cell. This originally has the composition—

$$Zn/ZnSO_4/CuSO_4/Cu$$
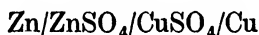
Assume that it has run down by the consumption of the whole of the zinc. Substitute a platinum sheet and develop a current from an external source of energy in the opposite direction, so that copper is dissolved and zinc is deposited. This latter reaction is one of the type to which reference has been made. As soon as zinc begins to be deposited the cell is restored to its original chemical constitution, and with the removal of the applied e.m.f. will, with a completed circuit, reproduce current. This reaction is repeatedly reversible, and a reversible process is defined as one "in which, electrochemical transformations having occurred, reversion to the original state is possible within the system."

While, however, the cell is theoretically reversible, there are narrow limits of practical reversibility. For example, the deposit of zinc would be soft, spongy and loose. Diffusion of the copper sulphate into the zinc compartment gives rise to serious local action, thus diminishing the effectiveness of the cell. If these defects could be overcome we should have a system into which electrical energy could be impressed and subsequently recovered with, obviously, a certain small amount of inefficiency. One persistent loss would be occasioned by the

electrical resistance of the electrolyte, but the system partakes of the nature of what might be called a storage cell or accumulator. It apparently only remains to secure that reversibility should be practical as well as theoretical to achieve a workable accumulator.

The Lead Accumulator. The simple constitution of this cell is well known. In its simplest form it comprises two suitably prepared plates of antimonial lead, one charged with lead dioxide and constituting the positive plate (connection usually painted red) and the other containing spongy lead, this being the negative plate (terminal usually painted black). These plates are immersed in dilute sulphuric acid. On connection to an external circuit an e.m.f. of something of the order of 1·95 V is developed. Sooner or later the system ceases to yield electrical energy. It has become discharged, and an examination of the plates reveals the presence of lead sulphate on both positive and negative.

If now current is passed in the reverse direction from an external source and with a voltage which must obviously be greater than 1·95 V, the plates are restored to their original condition. They are thus being "charged," and are then able again to supply electrical energy.

In this case the products of this reversed action are stable and adhesive. There is ordinarily a little disintegration, but the process of reversion can be repeated indefinitely. We have here a practical type of accumulator.

Simple Chemistry of the Lead Cell. The chemical reactions stated in their simplest form, and omitting any reference to the electrical energy changes involved, may be set out as follows—

DISCHARGING

    (*a*) Positive plate—

$$PbO_2 + 2H + H_2SO_4 = PbSO_4 + 2H_2O$$

    (*b*) Negative plate—

$$Pb + SO_4 = PbSO_4$$
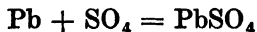
In the process, acid is absorbed and the strength of the electrolyte is therefore reduced.

CHARGING

(a) Positive plate—

$$PbSO_4 + SO_4 + 2H_2O = PbO_2 + 2H_2SO_4$$

(b) Negative plate—

$$PbSO_4 + 2H = Pb + H_2SO_4$$
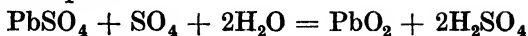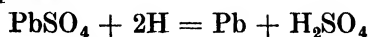
In this process acid is produced and the changes of concentration of the acid constitute some indication of the state of the accumulator relative to the charge which it retains.
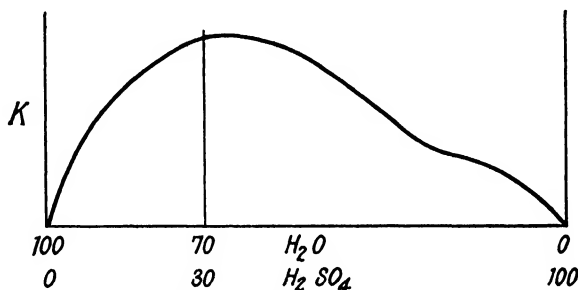
FIG. 56. CONDUCTANCE OF SULPHURIC ACID SOLUTIONS

In following these reactions it must be clearly understood that under ordinary use not more than 50 per cent of the active materials on the plates is subject to these reactions, there being always an excess of the original materials on the "discharged" plates.

Properties of Reacting Substances. Essential to the electrochemical reactions in the lead accumulator are a number of substances the properties of which should be appreciated. These substances include lead dioxide, lead sulphate, spongy lead, and sulphuric acid.

The properties of the acid are well known, and it suffices to say that the concentration of acid used is that attended by the maximum conductance. This is of the order of 1·22 density and approximately 30 per cent strength by weight. There is obviously some point in keeping down the internal resistance of the cell with an increase in the efficiency of the combined charging and discharging process. The relative conductances of sulphuric acid solutions are shown in Fig. 56.

Lead sulphate is a white insoluble substance not characterized

by any degree of conductance. Its density is of the order of 6·93. Its production in the path of the current may be expected to effect an increase in the electrical resistance. Normally this substance, as produced by the reactions of the cell, is porous and soft. Its porosity is an important factor, as through this material the acid must pass when, during charge, it is being liberated at both electrodes, and during discharge is being absorbed from the electrolyte. Its porosity facilitates the chemical reactions which it undergoes in conversion to the dioxide on the positive and to lead on the negative. The cell ceases to function correctly when, by long standing, the lead sulphate becomes hard and compact, and is then much less susceptible to the essential changes which it is called upon to undergo. The phenomenon is called sulphation and is largely avoided by fully charging the cell prior to standing unused.

Desulphation is sometimes attempted by charging and discharging with sodium sulphate as the electrolyte, subsequently rinsing out before replacing the acid. The sodium ion may be more effective in attacking dense $PbSO_4$.

Lead dioxide (PbO_2) is another important constituent. Its density is of the order of 9·38 and it exhibits marked electrical conductance, which is gathered from its resistance of from 6 to 7 Ω/cm^3. It conducts metallically. The active lead on the negative plate is the spongy variety produced by the reduction of the sulphate. Ordinarily pure lead which might be present in the solid form would be subject to some slight attack. The lead framework of the plates is therefore of antimonial lead containing from 6 to 8 per cent of antimony, this alloy being highly resistant to attack by sulphuric acid, for which reason therefore it finds extensive application as an anode material in a number of commercial processes in which sulphate solutions are electrolyzed.

The spongy form of lead may be regarded as having a density of 11·3 and a specific resistance of 0·000 019 5 Ω.

Volume Changes of Active Materials. Ordinarily the active materials of the two plates are subject to some disintegration, The trouble is considerably accentuated with improper use, particularly that of sudden and too rapid discharge. This difficulty has, however, claimed the attention of the manufacturer which it demands, with the result that modern cells are far more

robust than was formerly the case. They withstand much more rapid charge and discharge rates without undue disintegration.

Charging and discharging processes are attended by considerable volume changes on the part of the active materials. Consider first the discharge of the negative plate which involves the conversion of—

	Spongy lead Pb	into to	lead sulphate $PbSO_4$
Equivalent weights—	207	.	303
Densities	11·3		6·3
Relative volumes	$\dfrac{207}{11·3} = 18·3$		$\dfrac{303}{6·3} = 48·6$
or as	1	:	2·65

There is thus a large increase in volume during discharge and a similar contraction on charging. In both cases the new volumes have to accommodate themselves to the space in which the materials are confined. These changes of volume are to some extent responsible for the disintegration of the active materials. Of further importance, however, is the fact that the increase in volume of the lead to lead sulphate must result in squeezing out the acid from the material at a time when it is required near the plate for the reaction to proceed. This lack of acid in the spongy material, which is the most important part of the acid, leads to some falling off in the behaviour of the cell accompanied by a reduction in the e.m.f. developed. After standing for a time, acid permeates into and through the material, with an increase in the activity and therefore the e.m.f., this recuperation on standing, particularly towards the end of the discharge, being well recognized.

Similarly, on the positive plate where there is the change from—

	Lead dioxide PbO_2	to to	lead sulphate $PbSO_4$
Equivalent weights—	239		303
Densities	9·3		6·3
Relative volumes	$\dfrac{239}{9·3} = 25·7$		$\dfrac{303}{6·3} = 48·6$
or as	1	:	1·88

This change is less marked than that on the negative plate.

Another important factor arises by the varying concentrations of the essential acid, that is, that contained in the porous material. The e.m.f. of the lead accumulator is a function of the concentration of the acid and this variation can be expressed by approximate empirical formulae. One expression of this type is—

$$\text{E.m.f.} = 1\cdot85 + 0\cdot917(S - 1)$$

where S is the specific gravity between the somewhat wide limits of from $1\cdot055$ to $1\cdot279$. Without attaching too much importance to the exactness of the expression, it is well known that stronger acid gives a higher e.m.f. while weaker acid produces a lower e.m.f. Accordingly, if two accumulators are set up, one with 15 per cent acid and the other with 25 per cent acid, the latter will have the larger e.m.f. Placed "back to back" as shown in Fig. 57 the 25 per cent acid cell will discharge through the 15 per cent acid cell, thereby charging it, and this reaction will proceed theoretically until both cells have the same strength of acid and therefore the same e.m.f.
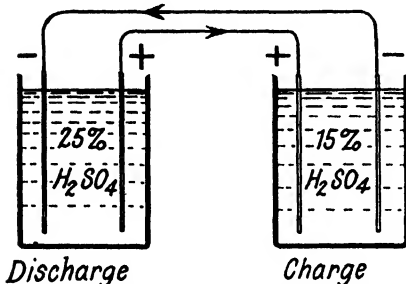
FIG. 57. ACCUMULATORS BACK TO BACK

Now the e.m.f. of the accumulator has two components, one at each plate. A review of the circumstances arising from the relatively slow motion of the acid through the active materials will reveal the fact that such impedance to the flow of acid adversely affects the p.d. of each plate and therefore the e.m.f. of the cell.

Temperature Coefficient. The accumulator, too, has a small temperature coefficient which results in variations of e.m.f. with changes of temperature. This change is least noticeable when the acid strength corresponds to a density of $1\cdot044$, far below the usual concentration. The temperature coefficient, that is, the variation of e.m.f. per degree Centigrade, is of the order of $0\cdot000\,335$ for the usual acid strength, the value decreasing with decrease in acid concentration and being negative

with concentrations below a density of 1·044. Under these latter conditions the e.m.f. produced is larger than that corresponding to the chemical reactions. The cell therefore cools by the conversion of some of its heat energy into the electrical form.

Electro-chemistry of Lead Accumulator. While the simple chemical reactions of the lead accumulator were satisfactorily expressed by Gladstone and Tribe as far back as 1883, the views which they put forward in no way accounted for the accompanying energy changes. The theory of electrolytic dissociation provides a comprehensive view of both chemical and energy changes.

In considering this, take first the case of discharge, and first again, that of the positive plate. Attribute to the active lead dioxide a slight solubility, not much of an assumption when it is recognized that no substance is in the limit insoluble.

The PbO_2 at this extreme state of dilution is completely ionized as follows—

$$PbO_2 \rightarrow Pb.... + 2O''$$

Tetravalent ions first formed pick up two electrons and thereby become reduced to divalent ions—

$$Pb.... + 2\circ = Pb..$$
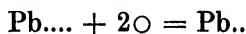
Divalent lead ions in contact with SO_4 ions combine to form first dissolved lead sulphate which is almost immediately precipitated.

On the negative plate metallic lead passes off in the form of divalent lead ions thereby releasing two electrons—

$$Pb \rightarrow Pb.. + 2\circ$$
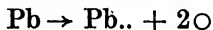
Again the divalent lead ions combine with SO_4 ions leading to the production of lead sulphate first in the soluble form which is soon precipitated. Electrons are therefore passing out from the negative plate and being drawn in at the positive, so that the conventional current is in the reverse direction. By this it will be seen that the simple electro-chemical reaction in the discharge of the cell is that of the reduction of tetravalent lead to divalent while the opposite charging process effects the conversion of the divalent lead in the sulphate into the tetravalent form of the dioxide.

Some Further Points. There are still some phenomena associated with the operation of the lead cell which require at least some explanation. That of the considerable falling off in the e.m.f. at the end of discharge and especially at high rates of discharge has already been traced to the changes of concentration of the acid in the materials of varying degrees of porosity.

Towards the end of the charge, too, there are points on the curve which require some comment (Fig. 58). While the bulk of the charging process is carried out at a p.d. of approximately 2·2 to 2·3 V, there is a marked increase in voltage required to maintain the prescribed charging rate toward the end of the process, a normal figure being 2·6 to 2·75 V. Why the increase?

At the end of the charging process the acid is at its maximum strength, especially that in the porous active materials. The electrolysis of relatively strong acid has already been shown to be attended by a number of reactions not common to the electrolysis of relatively dilute acid. While the cathode reaction is simple, involving the liberation of hydrogen, those processes at the anode admit of more possibilities. There we may have the formation of oxidized products, such, for example, as ozone, hydrogen peroxide, and persulphuric acid.

It was, however, long ago shown that the addition of such substances at an earlier stage did not affect the p.d. so that other explanation must be sought. As has already been seen, there are unusual electrode reactions occurring during the evolution of gases, both hydrogen and oxygen, at their respective electrodes. These reactions call for a higher p.d. to discharge the elements at certain electrodes in comparison with those required at some standard substance. These excess potentials or over-voltages are doubtless responsible for the higher e.m.f. required to maintain the same charging current towards the

FIG. 58. ACCUMULATOR CURVES

end of the process. Some reference to this has already been made (see Chapter XIV).

Energy Efficiency of the Cell. The energy efficiency will comprise two components, that of the current and that of the voltage. Assume average charging and discharging voltages of 2·4 and 1·9 V respectively, and an ampere-hour efficiency of 95 per cent. The energy efficiency becomes—

$$\frac{1{\cdot}9 \times 95}{2{\cdot}4} = 75 \text{ per cent}$$

which may be taken as good operation in a new cell. This from many causes related to lack of care in use, may, however, soon fall to something more of the order of 50 per cent. Accumulators generally merit more care in operation than is usually their lot.

The Iron-nickel Cell. Two great disadvantages attach to the lead accumulator: (1) its large weight per unit of energy stored, and (2) its relative fragility, this latter term signifying that some construction of a more robust type would be welcomed.

To meet this demand Edison introduced the iron-nickel type of cell which is based on the following reaction—

$$\mathrm{Fe} + 2\mathrm{Ni(OH)}_3 = \mathrm{Fe(OH)}_2 + 2\mathrm{Ni(OH)}_2$$

The following expansion of the expression will serve to indicate the determining features of the cell more clearly. The electrolyte is a 20 per cent solution of caustic potash free from other compounds and especially chlorides. This solution suffers no change of concentration during operation as does the lead cell by the absorption and liberation of sulphuric acid during discharge and charge respectively. The e.m.f. is therefore practically independent of the strength of the electrolyte.

The positive plate is of steel, in the pockets of which are pressed spirals of nickel strip together with a mixture of green nickel hydrate and nickel flakes. The negative plate is also of steel, into the small pockets of which is pressed a mixture of iron reduced from the oxide containing a small amount of mercury. Distortion of the positives is guarded against by winding the nickel spirals in opposite directions, and the two plates are separated by ebonite strips. The capacity of the cell

is determined by the amount of these active materials used in the processes and this is of the order of 75 per cent. This figure is favourable in comparison with the lead cell to which may be attached a corresponding value of 50 per cent.

Volume changes of the active materials during operation are small, and hence there is little tendency to disintegration and distortion. Charging and discharging voltage curves are shown in Fig. 59, from which it will be seen that the average p.d. of
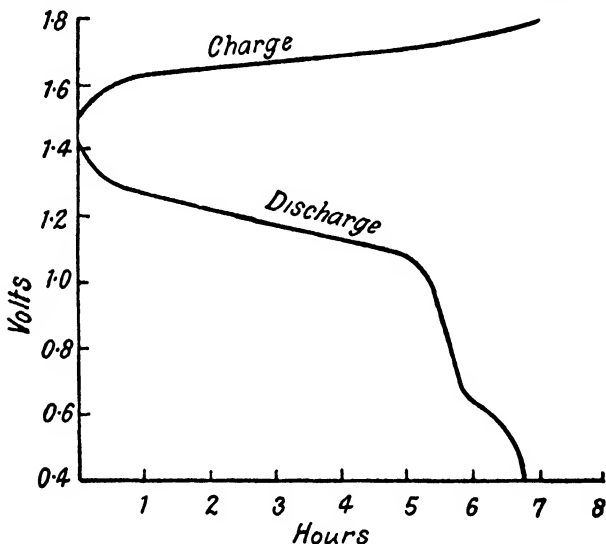
FIG. 59. IRON-NICKEL CELL CURVES

charging is 1·7 V, while that of discharge is 1·2 V. This is a disadvantageously low value in comparison with the lead cell. Again its ampere-hour efficiency is only of the order of 82 per cent as compared with 95 per cent for the lead cell, again a lower figure. Consequently the energy efficiency works out at—

$$\frac{1\cdot2 \times 82}{1\cdot7} = 58 \text{ per cent}$$

One of the advantageous features of the cell is the weight per unit of energy available. Added to this is the extreme robustness, the cell withstanding rough usage, both electrical in rapid charge and discharge, and mechanical in the form of jolting

associated with vehicle work. Disadvantages are the use of caustic potash, a not-so-convenient electrolyte as sulphuric acid, the greater space required for a given output and the rapid fall in the e.m.f. at the end of discharge, the cell therefore breaking down with very little notice.

Chemistry of the Cell. During charging the following chemical changes take place—

On the positive—

$$2Ni(OH)_2 + 2OH = 2Ni(OH)_3$$

On the negative—

$$Fe(OH)_2 + 2H = Fe + 2H_2O$$
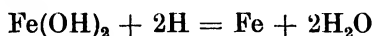
While, therefore, there is no total change in the amount of caustic potash contained in the electrolyte in the two operations of charging and discharging, there are, as these equations show, local changes accounting for the very slight differences in e.m.f. These equations represent the chemical changes in their barest simplicity. The distribution of the components of the observed e.m.f. is as follows—

		Charge	Rest	Discharge
Positive plate	.	0·6 –0·65	0·47	0·45–0·1
Negative plate	.	1·05–1·15	0·87	0·85–0·8
Cell	.	1·65–1·80	1·34	1·3 –0·9

HYDROGEN ION CONCENTRATION

Introduction. Amongst the numerous chemical reactions which take place through the medium of the ionic products of electrolytic dissociation, those related to the acids are of first importance. It has previously been pointed out that all acidic reactions must be referred back to the hydrogen ion, which is a common product of the dissociation of acids. It is, moreover, recognized that there are degrees of strength or activity in the different acids, and this in turn must be traced back to the concentration of hydrogen ions. Hence hydrogen ion concentration provides an important term in electro-chemistry, and plays an important rôle in many processes of electrodeposition.

Acids, Alkalis, and Neutralization. The action of acids on indicators, their neutralization of alkalis and other general properties must be traced to some common cause. This first cause relates to the presence and concentration of hydrogen ions which they develop. Similarly, the alkalis are alkaline because of the common OH' ion developed by dissociation. Again, there are quite different degrees of concentration of these hydroxyl ions, accounting for the range of alkalinity familiar to the chemical student. Further, the process of neutralization has already been traced to the combination of these common ions of acids and alkalis to form molecular water with its only very slight degree of dissociation.

Acids and Acidity. There is, therefore, need for distinguishing clearly between the terms acid and acidity. There are many substances called acids which in some forms show little or no sign of acidity. It is frequently said that acid is added to water to make the latter substance conductive. This is erroneous.

The added acid suffers partial dissociation. The acidic and conductive properties of the solution are due to the concentration of the hydrogen ions. Undissociated molecules take no primary part in the reactions usually attributed to the

acids. They do not add to conductance, but by the withdrawal of hydrogen ions either by electrical deposition or in the course of a chemical reaction, the reduced hydrogen ion concentration is made good by the further dissociation of more molecules of the acid.

We are here more particularly concerned with not the total amount of acid put in, but with that portion which has undergone dissociation. The total amount of acid is readily estimated by any of the usual processes of titration, but in the determination of acidity no change must be allowed to take place which would alter the hydrogen ion concentration. Alkali titration is therefore quite out of the question.

The _p_H Scale. Hydrogen ion concentration has for many years been expressed on a scale which has come to be called the _p_H scale. Quantitatively, hydrogen ion concentration is reckoned on the number of litres containing 1 gramme-equivalent of hydrogen ions. In the case of weak acids, however, the numbers of litres involved are large, and it was suggested by Sorensen that it would be convenient to express them as the logarithm of the number, this logarithm being the _p_H value. This simple principle is well illustrated by the following table (LVII)—

<div align="center">

TABLE LVII

_p_H SCALE

</div>

Litres Containing 1 g. H Ions	Logarithm or _p_H Value
1 or 10^0	0
10 ,, 10^1	1
100 ,, 10^2	2
1 000 ,, 10^3	3
10 000 ,, 10^4	4
100 000 ,, 10^5	5
1 000 000 ,, 10^6	6

The one disadvantage (if it can be regarded as such) is the fact that decreased acidity is represented with an increased numerical value, but the system is one with which it is easy to become familiar.

According to this designation—

pH $=$ log litres containing 1 g H.

$$= \log \frac{1}{\text{concentration of H. in grammes per litre}}$$

pH $= - \log$ (H.), where (H.) represents the concentration of H ions in grammes per litre

this representing the simple relationship between pH and the concentration of hydrogen ions.

To take a few examples, consider some of the well-known acids in different stages of dilution. From conductivity results we have their degrees of dissociation as follows (Table LVIII)—

<div align="center">TABLE LVIII</div>

<div align="center">DISSOCIATION OF ACIDS AND pH</div>

Acid	Normality	α	Normality H Ions	Litres per Gramme H Ions	pH
H_2SO_4 . .	1	0·52	0·52	1·923	0·28
	0·1	0·59	0·059	16·95	1·229
	0·01	0·81	0·008 1	123·4	2·091
	0·001	0·945	0·000 945	1 058·2	3·024 5
HCl . .	1	0·79	0·79	1·26	0·100 4
	0·1	0·92	0·092	10·87	1·036
	0·01	0·97	0·009 7	103·1	2·013
	0·001	0·99	0·000 99	1 010	3·004
H . $C_2H_3O_2$.	1	0·003 8	0·003 8	263	2·42
	0·1	0·013 1	0·001 3	770	2·88
	0·01	0·041	0·000 41	2 440	3·38
	0·001	0·117	0·000 117	8 550	3·93

It is not usual to express the pH value of relatively strong acid solutions, but there are numerous examples in which acidity is of a very low order and is much more conveniently expressed on this scale. A few figures will be of interest. In addition to those given in the foregoing table it may be recalled that the ionization of pure water as obtained by careful conductance measurements gives a hydrogen ion concentration of 1 g in 12 500 000 litres. The logarithm of this number is 7·097 and the pH of pure conductivity water is therefore 7·097.

The figure is usually approximately taken as 7. In this case, however, the hydrogen ion concentration is exactly balanced by a similar concentration of OH ions, and the liquid is therefore neutral though it still has a pH value expressing its concentration of hydrogen ions.

Similarly, the strongest alkali solution has a pH of about 14, this figure expressing the fact that the dissociation of the pure water in which a large amount of alkali has been dissolved has been suppressed to the extent that there is now only 1 g of hydrogen ions in 100 000 000 000 000 litres of the solution. Hence, given the hydrogen ion concentration, we can easily express this on the pH scale. Thus—

Find the pH of a solution of sulphuric acid of milli-normal strength with a degree of dissociation of 0·945. Here the normality will be 0·945/1 000 $=$ 0·000 945, and the volume containing 1 g of hydrogen ions will be 1/0·000 945 $=$ 1 058·2. The log of 1 058·2 is 3·024 5, and this therefore is the value on the pH scale.

Conversely, find the hydrogen ion concentration of a solution with a pH value of 5·6, this being somewhere near the value of an ordinary nickel plating solution. Now 0·6 is the log of 3·98, and with the characteristic of 5 this number will be multiplied by 10^5 giving the concentration of hydrogen ions as 1 g per 398 000 litres.

Influence of Hydrogen Ion Concentration in Electrodeposition. It has long been recognized that the degree of acidity markedly affects the deposition conditions in the cases of a number of metals, those especially which are operated under conditions formerly called nearly neutral. A nickel solution, for example, worked well with an acidity which just turned litmus red, while unsatisfactory results followed upon an alkalinity which just turned red litmus blue, and these were then the only tests applied. More recently it has been shown that very slight changes of acidity are severely reflected in chemical reactions of the hydrolysis type. Thus with a change of pH from 4 to 6·4 N/10 ferrous sulphate hydrolyzes, a similar reaction taking place with ferric sulphate of N/10 strength at a pH of 5 to 6 resulting in the precipitation of the hydroxides or their production in the colloidal form, either of which may influence the character of the deposit. The iron sulphates are

likely impurities in nickel solutions. Some more exact control of pH therefore becomes necessary, and the same condition applies also to the deposition of zinc from its sulphate solution requiring a more accurate control of acidity than is possible with either litmus or congo red papers.

Measurement of pH. Now it has come to be recognized that pH values are of extreme importance in many industries, and a simple method of approximately determining this value became an urgent need. The use of indicators qualitatively is familiar to every chemical student. Their application to acid and alkali titrations constitutes a step towards their quantitative use. Those in common use have their varying degrees of sensitivity and also their ranges over which they function. Some of these values are shown in Table LIX.

TABLE LIX

COMMON INDICATORS

| Indicator | Colour | | pH Range |
	Acid	Alkali	
Litmus . .	Red	Blue	5 – 8
Methyl orange .	Pink	Yellow	2·9– 4
Congo red . .	Blue	Red	3 – 5
Phenolphthalein .	Colourless	Violet	8·3–10

From this table it will appear that phenolphthalein is the most sensitive, with litmus not far behind. Methyl orange is relatively crude, and it will be recalled that its use in acidimetry is dependent upon its insensitivity to carbonic acid so that it can be used in the titration of carbonates.

Moreover, while litmus is sensitive, it suffers from the disadvantage that the change of colour from red to blue or vice versa is not sharply defined.

These indicators have ranges of usefulness rather than exact values. Thus methyl orange is pink at pH 3, orange at pH 4, and yellow at pH 5. It therefore has a range of pH 3 to 5. Similarly, the range of litmus is from pH 6 to 8, while that of phenolphthalein is pH 8 to 10.

For an indicator to be effective, a small addition of acid or

alkali near the end point should make a large change of pH. This is always the case with strong reagents. Hence methyl orange and phenolphthalein can be used. For weaker acids and alkalis, 1 cm³ may make insufficient pH change to be indicated by methyl orange with its low range, but a sufficient one for phenolphthalein with its higher range.

Again in the titration of mixtures of caustic and mild alkalis (e.g. NaOH and Na$_2$CO$_3$), the NaOH is neutralized in one stage only—

$$NaOH + HCl = NaCl + H_2O$$
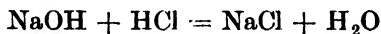
while that of Na$_2$CO$_3$ takes place in two stages—

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl$$
$$NaHCO_3 + HCl = 2NaCl + H_2O$$
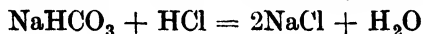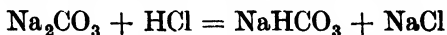
Now sodium bicarbonate is acid · to phenolphthalein and alkaline to methyl orange. Its pH value is between 5 and 8. Hence, if such a mixture is titrated with phenolphthalein, the disappearance of the violet colour indicates the completion of the caustic neutralization and the first stage of the neutralization of the carbonate. The addition of methyl orange, with further titration to a pink colour, shows the completion of the neutralization of the bicarbonate. Hence the expression that phenolphthalein indicates the caustic + half the carbonate, while the methyl orange indicates half the carbonate.

There are, however, many indicators which with their different degrees of sensitivity also show well-defined transitional colours with slightly varying degrees of acidity. A number of these are indicated in Table LX.

TABLE LX

pH OF INDICATORS

Indicator ·	Colour Range	pH Range
Thymol blue . .	Red to yellow .	1·2–2·8
Brom phenol blue .	Yellow to blue .	3·0–4·6
Methyl red . .	Red to yellow .	4·4–6·0
Brom cresol purple .	Yellow to purple .	5·3–6·8
Brom thymol blue .	Yellow to blue .	6·0–7·6

These are but a few of the many which will be found in the catalogues of the chemical supply houses. Each has its own range of application and altogether they cover a wide range.

There are, further, some indicators which give decided colour changes over a very wide range. These are generally known as universal indicators, and the following colour changes take place in the so-called "four-eleven" indicator of British Drug Houses, Ltd.

pH up to		pH up to	
3·0	Red	8·0	Green
4·0	Deeper red	8·5	Bluish green
5·0	Orange red	9·0	Greenish blue
5·5	Orange	9·5	Blue
6·0	Orange yellow	10·0	Violet
6·5	Yellow	10·5	Reddish violet
7-7·5	Greenish yellow	11·0	Deeper reddish violet

Appropriately applied (that is, in accordance with the instructions of the makers) such an indicator gives a quick and approximate idea of the pH of a solution tested.

This British Drug House universal indicator has a pH value of 3·1. Definite additions of NaOH or HCl can be made to attain further changes in pH value. Using a 0·2N acid or alkali, the addition of 1 cm³ to 100 cm³ of the indicator, and making up to 200 cm³, gives a pH change of $\pm$ 0·118 5.

Hence pH $= 3·1 \pm 0·118\ 5\ V$
where $V =$ cubic centimetres of 0·2N acid or alkali added

A more accurate figure can then be obtained by the use of one or other of the indicators previously mentioned, these being set up in definite strengths by the makers, who also prescribe the relative volumes of solution and indicator to be mixed and also supply standard colours against which these mixtures are to be matched.

Theory of Indicators. Some explanation of the behaviour of indicators is now called for to offer reason for their use and range of their application. They, for the most part, find their application by reason that they are weak acids. In solution, they are dissociated. Each produces at least one ion which is coloured differently from the molecular or undissociated substance. Being of the weak acid type, their dissociation is suppressed by the addition of acid, that is, an increase in hydrogen

ion concentration, and with this suppression of dissociation there is the marked change of colour. They exhibit markedly different degrees of sensitiveness.

As weak acids they may be regarded as dissociating thus—

$$HX \rightleftharpoons H. + X^-$$

where the ion X has a colour different from that of the molecular HX. In use, very small quantities are necessary, altogether insufficient to alter the hydrogen ion concentration of the liquid under test. In the ionic form they exhibit colour, while in the undissociated form they may even be colourless as in the case of phenolphthalein. Where the molecular material has a colour of its own the colour of the indicator in solution will vary with the degree of dissociation. If, for example, the indicator is 20 per cent dissociated, the resulting colour will be that due to 80 per cent of the molecular material and 20 per cent of the ionic. Their dissociation constants will be given by the usual expression—

$$K = \frac{C_H \times C_X}{C_{HX}}$$

and the values for some of these are given in Table LXI.

TABLE LXI

DISSOCIATION CONSTANTS OF INDICATORS

Name	Dissociation Constant
Methyl orange . .	4×10^{-4}
Methyl red . . .	1×10^{-5}
Litmus	1×10^{-7}
Thymol blue . . .	1×10^{-8}
Phenolphthalein . .	1×10^{-10}

The colour change of an indicator takes place within a narrow range of the pH corresponding with its dissociation constant.

Of these methyl orange is the least sensitive while phenolphthalein is the most sensitive, accounting for the use of methyl orange in titrating carbonates with the evolution of carbonic acid gas which would affect phenolphthalein.

The course of a titration can now be followed by observing the changes of hydrogen ion concentration with the progress of neutralization. Suppose, for example, we are titrating 50 cm^3 of decinormal hydrochloric acid with caustic soda of equivalent strength.

With the addition of 49·9 cm^3 of the alkali solution the concentration of the hydrogen ions (always assuming complete dissociation) will be—

$$\frac{0·1}{99·9} \times 10^{-1} = 0·000\,1 = 10^{-4}$$

and as the pH value is the reciprocal of the logarithm of the hydrogen ion concentration its value is now 4.

Next, with the addition of exactly 50 cm^3 of the alkali, neutrality will have been reached, when the pH of the solution will be that of pure water, that is 7.

With the addition of 0·1 cm^3 of alkali in excess of this neutral point, the concentration of the hydroxyl ions will be—

$$\frac{0·1}{100·1} \times 10^{-1} = 0·000\,1 = 10^{-4}$$

Now the product of the hydrogen and hydroxyl concentrations is, as has been seen, 10^{-14}, so that in this case the hydrogen ion concentration is $10^{-14}/10^{-4} = 10^{-10}$ and the pH of the solution is now 10.

Thus, by the addition of 0·2 cm^3 of alkali (in this case N/10) to 100 cm^3 of nearly neutralized acid there has been the sudden change of pH from 4 to 10. It is obvious therefore that the preparation of solutions as standards of pH cannot be undertaken with strong acids and alkalis. Such standards are made by the admixture of weak acids and their salts.

With reference to the use of indicators, the range of pH 4 to pH 10 is well outside the figure for methyl orange, and with it the end point is not well defined. With other indicators, however, such as litmus, methyl red, and phenolphthalein more exact neutralizations are possible. Phenolphthalein is affected by CO_2 which may be present in impure alkalis, while litmus suffers from the disadvantage of merging slowly from the alkaline blue to the acid red.

Buffering Reagents. Not only, therefore, does the measurement of the acidity become important but also its control. If

a nickel anode dissolves inefficiently, sulphuric acid is formed and the pH falls. If, on the other hand, the anode efficiency is good but that at the cathode is poor, then alkaline conditions result. Moreover, the conditions which are most important are those of the film of electrolyte on the surface of the cathode which may differ materially from those of the main bulk of the solution. This alkalinity at the cathode film may be advantageous or otherwise, but nevertheless with low cathode efficiency it is there and its possibilities should be known. It has been more than suggested by Macnaughtan and Hammond[*] that nickel hydroxide in the colloidal form at the cathode may exert a beneficial effect on the deposit in conformity with the well-known improvement in the physical characteristics of deposits in the presence of colloids, and conditions which favour the retention of the nickel hydroxide in the colloidal form, simultaneously increase the hardness of the deposit. Such stabilization of the colloid is favoured by the presence of alkali ions and also a high pH. On the other hand, flocculation of the colloid occurs in the presence of the chlorine ion, and this ion is known to reduce the hardness of nickel deposits. The maintenance of a predetermined desirable pH is therefore of importance.

This control is obtained by the use of "buffering" reagents, which may be defined as substances which, by their presence, resist changes of acidity. More generally, buffer reagents may be regarded as substances which maintain constancy of concentration of any ion. For the present the term is being applied to the maintenance of uniform pH.

As a simple illustration, equal quantities of sulphuric acid are added to equal volumes of (1) distilled water and (2) a weak solution of sodium acetate and the pH values of the mixtures determined. That of the sodium acetate is found to be much higher than that of the water. Sodium acetate has resisted a change of acidity by the chemical change indicated in the equation—

$$2Na.C_2H_3O_2 + H_2SO_4 = Na_2SO_4 + 2H.C_2H_3O_2$$
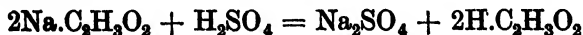
According to the equation the two acids are in exactly equivalent proportions. Their degrees of dissociation are,

[*] *Trans. Faraday Soc.* (1931), Vol. XXVII, p. 633.

however, markedly different. This is exemplified in the following data—

<div align="center">TABLE LXII</div>

<div align="center">DISSOCIATION OF SULPHURIC AND ACETIC ACIDS</div>

	Fraction Dissociated		
	N	0·1 N	0·01 N
H_2SO_4 .	0·517	0·588	0·804
$H . C_2H_3O_2$.	0·004	0·013	0·041

Acetic acid produces a far smaller proportion of hydrogen ions than an equivalent of sulphuric acid. Sodium acetate reduces the degree of acidity which would otherwise, in its absence, be developed. Formerly, when nickel anodes were far less efficient than they are now, such salts of weak acids were common additions to the nickel bath.
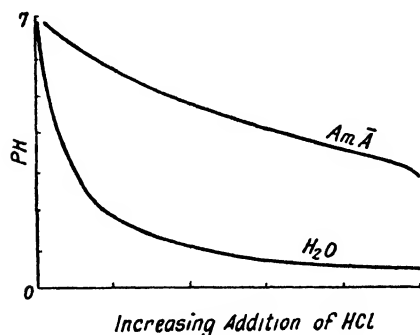
FIG. 60. BUFFERING ACTION OF AMMONIUM ACETATE

Similarly, the curve in Fig. 60 shows the result of the addition of hydrochloric acid to water and to a solution of ammonium acetate. Similar results accrue to the addition of the salts of weak acids.

Again, boric acid is a weak acid. If, to a boric acid solution, additions of alkali are made, there is little change in the $p\text{H}$ of the mixture. As hydrogen ions are removed by the alkali more are immediately forthcoming, but also to a limited extent by the further dissociation of some of the large proportion of the undissociated boric acid. Boric acid, therefore, buffers a solution against changes of $p\text{H}$ with the addition of alkalis. This is the reason for its introduction into the nickel bath, as alkaline conditions developing at the cathode may give rise to hydrolysis of the several salts contained in the solution, with possibly the detrimental precipitation of the hydroxides. A

nickel solution containing boric acid suffers less change of pH with alkali' additions than one in which this acid, or its equivalent, is absent.

Buffer Standards. Solutions of definite pH values may therefore readily be made up of mixtures of weak acids and their salts. Such mixtures are—

Citric acid and sodium citrate,
Acetic acid and·sodium acetate,
Boric acid and borax,
Sodium carbonate and sodium bicarbonate,
Disodium hydrogen phosphate and hydrogen disodium phosphate.

The following are a few examples (Table LXIII)—

TABLE LXIII

STANDARD BUFFER SOLUTIONS

pH	Composition
4	164 cm³ N/5 H$\overline{A}$. 36 cm³ N/5 Na$\overline{A}$.
5	59 cm³ ,, 141 cm³ ,,
6	9 cm³ ,, 191 cm³ ,,
7	12 cm³ M/20 borax. 188 cm³ M/5 boric acid* and M/20 NaCl
8	55 cm³ ,, ,, 145 cm³ ,, ,, ,, ,,
9	160 cm³ ,, ,, 40 cm³ ,, ,, ,, ,,

* 12·40 g H_3BO_3.

Many others are available. They constitute solutions of standard acidity in which definite colours can be produced with indicators for comparison purposes.

pH Control in Alkaline Plating Solutions. The pH values for the usual run of alkaline depositing solutions were formerly· not considered to be of great importance. More recently, however, definite optimum values have been determined and much closer attention is now being paid to this property with improved results in electrodeposition. The work of Springer* and Hogaboom† must be referred to in this connection. In these solutions much depends upon anode and cathode efficiencies and these have been shown to be considerably influenced

* *Metal Ind.*, N.Y., April, 1937
† *Metal Ind.*, 24th September, 1937

by changes in pH, necessitating control over this factor for successful deposition. Some of the results obtained by Hogaboom are of considerable interest. They were obtained in what may be called solutions of ordinary composition such as are in general workshop use. pH values were determined with a comparator and anode and cathode efficiencies noted. As an example of the results obtained the following figures (Table LXIV) refer to a cyanide copper solution of normal composition and working under ordinary conditions.

TABLE LXIV

pH AND ELECTRODE EFFICIENCIES IN CYANIDE COPPER
SOLUTION

pH	Anode Eff.	Cathode Eff.
11·8	101·0	88·9
12·2	101·1	88·9
12·6	101·0	87·4
13	99·2	89·3
13·4	5·9	86·3

From these figures it is obvious that a pH of 13 is critical and requires correcting, which can be done by the judicious addition of sulphuric acid with a little loss of cyanide. Again, a zinc cyanide solution gave the following results—

TABLE LXV

pH AND ELECTRODE EFFICIENCIES OF ZINC CYANIDE
SOLUTION

pH	Anode Eff.	Cathode Eff.
13·4	104	98·2
13	42·5	98·2
12·6	3·6	98·2
12·2	13·2	98·9

These are examples only, and may be regarded as sufficiently evidential of the fact that some attention to this factor is necessary in the control of these alkaline solutions. The original papers should be consulted for greater details. In the same

series of tests, silver solutions showed the widest range in pH values over good working conditions, and alloy deposition in the case of brass revealed some interesting results in that a cold solution run at pH 13·4 gave a deposit of the same colour as a warm solution at pH 12·2, although the zinc-copper ratios were different. There is evidently some connection here between pH and the crystal size and orientation.

Making the pH Test (Colorimetric Method). There are now available many forms of apparatus for this test. In general, they comprise standard tubes in which definite volumes of solution to be tested are mixed with the prescribed volumes of the specified indicator, the mixture being made uniform by shaking. The colour produced is then matched against a series of standard colours. These may be coloured solutions or discs of coloured glasses suitably mounted so that they can in turn be brought alongside the solution under test and compared.

An early type of this test involved the use of capillary tubes in which very small amounts of solution and indicator were needed, the standards also being mounted in the same type of tube. They were, however, fragile and needed replacement by a more robust type. These are now in common use under the name of Comparators. These as set up are not costly unless a wide range of pH is required. The several industries have their individual requirements regarding pH range. This simplifies the testing set and reduces the cost. Such simple sets have found extensive use in many industries.

The Lovibond Comparator (Fig. 61) comprises a bakelite case with two compartments to contain the test tubes with the solution under examination. Behind is an opal glass screen, and in front two circular openings coinciding with the test tubes. The standard colour discs are mounted in a circular bakelite frame and fitted so that the frame can be rotated to bring the individual discs opposite one of the apertures, while the tube containing the mixture of solution and indicator is opposite the other aperture. The coloured discs are then brought into position for comparison by rotating the frame carrying the discs and the colour matched. These arrangements are made so that behind the colour disc there will be a tube of solution under test, but without the addition of indicator, while through the other aperture the mixture of solution

FIG. 62. B.D.H. COMPARATOR
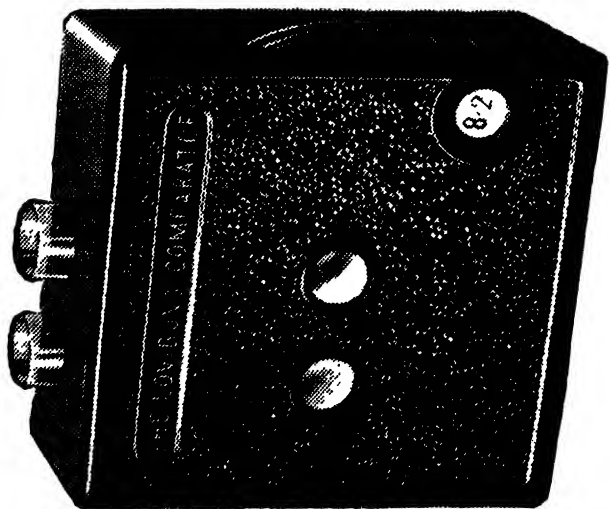
FIG. 61. LOVIBOND COMPARATOR
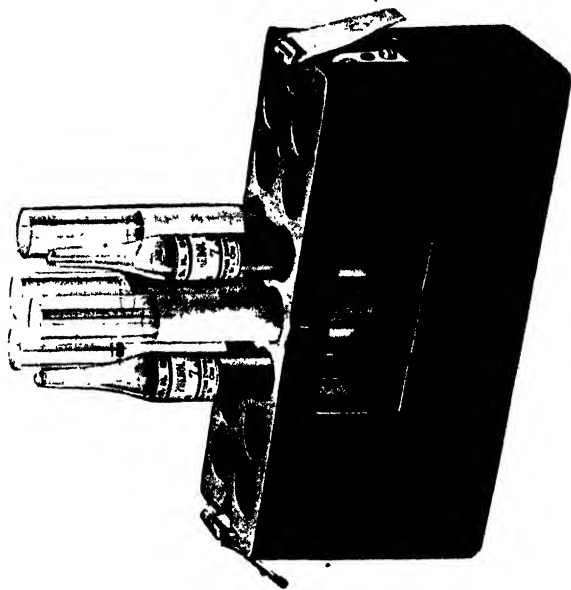
and indicator will be viewed. Nine colour discs are mounted in a frame with successive differences of pH of 0·2, so that between any two consecutive discs it will be easy to judge the intermediate pH to 0·1.

The B.D.H. Comparator is a variation in which the solution under test is placed between two standards so that a quicker and more accurate comparison can be made. Again, in a bakelite case, arrangements are made for six test tubes arranged as shown in Fig. 62 so that the mixture of solution with the standard indicator can be viewed between tubes of the solution standing behind two consecutive buffer solutions
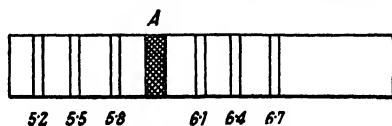
FIG. 63. pH TEST PAPER

while a tube of distilled water in front of the sample gives a similar thickness of liquid. Such standard buffers cannot be regarded as too permanent and it is recommended that they be checked against freshly made standards from time to time over periods of about six months. The case contains altogether fourteen tubes, nine of which are standard buffer solutions, another one containing the standard indicator solution which is measured out by means of a small appropriate pipette, and the remaining four tubes are available for holding the solution under test, two without and one with the indicator, while the fourth will contain the distilled water. A comparison of these results with those obtained by more accurate means will later be made.

Other and simple methods for the approximate determination of hydrogen ion concentration include the use of a series of test papers. In one type these contain a number of colour stripes with a band indicator A. Immersion in the solution changes the colour of the indicator band, this then being matched against the coloured stripes on either side of the indicator. The principle will readily be appreciated from Fig. 63.

Electro-metric Method. The determination of the pH of a solution is capable of more accurate results by the electrometric method in which the potential of an electrode immersed in the solution depends upon the concentration of the hydrogen ions. For this purpose there are a number of different electrodes three of which, in more common use, will be described.

These are the hydrogen electrode, the quinhydrone electrode, and the glass electrode.

Hydrogen Electrode. This is set up in the manner already described in the case of the normal hydrogen electrode except that, replacing the twice normal sulphuric acid, the solution under test is used. A platinized platinum plate is inserted in it and fed with pure hydrogen to constitute the electrode. The pH of this electrode is inversely proportional to the potential developed. In making a determination the same care
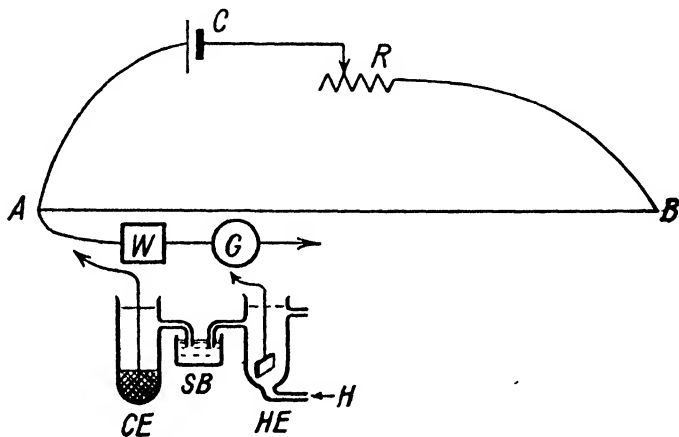
Fig. 64

is required in setting up the electrode as has already been described in Chapter XIII. The hydrogen electrode is then put in connection with a reference or standard electrode which may be either the normal hydrogen electrode or one of the three calomel half cells, and in most cases a salt bridge will be necessary in order to establish connection between the two half-cells. The e.m.f. of this arrangement is then compared with that of a standard cell, such as the Weston cell, by the use of the potentiometer. The simple arrangement is shown in Fig. 64, in which AB is the potentiometer wire carrying a fall of potential derived from the cell (C), through a rheostat (R). (W) represents the Weston cell which, through the tapping key and galvanometer (G), serves to standardize the potentiometer wire. The Weston cell is then replaced by the chain

of the hydrogen electrode (HE), salt bridge (SB), and calomel electrode ($C\overline{E}$), so that the mercury of the calomel electrode is connected with the positive terminal of the potentiometer wire. The new point of no deflection of the galvanometer needle is found so that the length can be compared with that of the Weston cell. The e.m.f. thus determined is that between the platinum of the hydrogen cell and the mercury of the calomel cell. At a temperature approximating to 18° to 20° C. this e.m.f. is converted into pH by the following formula—

$$E = 0.059p\text{H} + 0.25$$

where 0·25 is the potential of the saturated calomel electrode against the normal hydrogen standard. Then—

$$p\text{H} = \frac{E - 0.25}{0.059}$$

This method carries the advantages of accuracy with readings approximating to 0·02 on the pH scale. It is applicable to coloured solutions and involves the use of stable electrical standards. The equipment is somewhat elaborate and therefore not easily portable and, moreover, calls for skilful manipulation. It is not available for liquids the pH of which is due in some measure to the presence of dissolved gases such as CO_2, as these would be displaced by the hydrogen bubbled through with consequent change of pH.

Portable Potentiometers. The frequency with which pH readings are required in many industries, and other applications of the principle, necessitate some simple portable and compact form of apparatus with which they can be quickly and accurately taken. One such form is shown in Fig. 65. This illustrates a potentiometer on which potential measurements are made on a resistance comprising five 90 Ω coils operated with a simple dial switch in series with which a sixth coil of the same resistance is fitted with a sliding contact on a large dial switch carrying 200 divisions.

Compactly fitted in a suitable cabinet are a millivoltmeter and rheostat. By means of an external battery the adjustment of the battery rheostat effects the standardization of the voltmeter so that each coil corresponds to 0·2 V, while the 200 divisions on the larger dial each represent 0·001 V.

After standardization a second tapping key is applied to bring the millivoltmeter across the sliding contact, so that the reading can be taken when the balance is obtained on the sliding wire.

It will be appreciated that each millivolt corresponds to about $0{\cdot}02$ pH. From the Nernst equation (see page 197)—

$$E = 0{\cdot}058 \log \frac{C}{c}$$

Fig. 65. Portable Potentiometer

where C and c represent ionic concentrations. In the case of hydrogen a tenfold increase represents a variation of pH of unity, so that the corresponding E is $0{\cdot}058$ V. When $E = 1$ mV, the corresponding change in pH is therefore

$$0{\cdot}001/0{\cdot}058 = 0{\cdot}018$$

approximately. A further modification consists in the calibration of the scale in terms of pH.

The Quinhydrone Electrode. This is based on the fact that quinone ($C_6H_4O_2$) is reduced by hydrogen to hydroquinone

($C_6H_6O_2$). The reaction is reversible in a solution containing hydrogen ions when—

$$C_6H_4O_2 + 2H. \rightleftarrows C_6H_6O_2 + 2\bigcirc$$
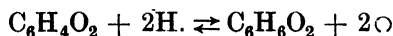
Quinhydrone is a molecular compound of these two substances quinone and hydroquinone and dissociates into the two components, which are therefore present in molecular quantities when dissolved in water. These proportions are therefore constant. The reduction of quinone to hydroquinone proceeds with the presence of hydrogen ions, but for this to take place there must be the facilities for the removal of the liberated positive electricity or, what is the same, the acquisition of electrons. This is achieved by the introduction of a platinum electrode similar to that used in the hydrogen electrode, and coupling this as a half-cell to either a calomel electrode or to a standard hydrogen electrode. Quinhydrone is a sparingly soluble substance and the addition of a few crystals to the solution to be tested assures saturation and therefore constant strength.

In this system the potential developed by the platinum electrode is a function of the hydrogen ion concentration which is thus easily determined. The system is represented as follows—

Hg/Hg_2Cl_2 . KCl (sat.)/Solution with quinhydrone/Pt
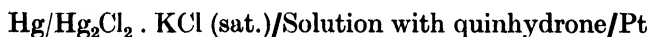
Simply stated this quinhydrone electrode has a potential expressed by the following formula—

$$p\text{H} = \frac{0\cdot453 - E}{0\cdot058}$$

If there is an excess of either quinone or hydroquinone this constant $0\cdot453$ requires modification.

Alternatively, a normal hydrogen electrode may replace the saturated calomel electrode in which case the expression becomes—

$$E = 0\cdot704 + 0\cdot058 \log_{10}(\text{H})$$

It will be remembered, however, that the usual designation of hydrogen ion concentration is on the $p\text{H}$ scale which expresses

the logarithm of the number of litres containing 1 g of hydrogen ions.

$$p\text{H is therefore} - \log_{10}(\text{H})$$

and hence

$$p\text{H} = - \log_{10}(\text{H}) = \frac{0 \cdot 704 - E}{0 \cdot 058}$$

Advantages attaching to the use of the quinhydrone electrode are (1) it attains equilibrium more rapidly than that of hydrogen, (2) it does not involve the preparation and use of a gas, and (3) more important still in the investigation of the pH of solutions in which there may be impurities which are apt to impair the spongy platinum on the hydrogen electrode, it is unaffected by these impurities. These advantages account for its extended use in connection with the determination of the pH of nickel-plating solutions. This quinhydrone electrode, however, is not suitable for the determination of pH values which exceed 8, as with any degree of alkalinity there is not the constant relation of unity between the quinone and hydroquinone. Modifications of the system can then be made with some variations of the expression of the pH values, but these need not be considered here.

The Glass Electrode. There are examples of hydrogen ion concentration in which metal electrodes are not feasible. For such determinations the glass electrode is serviceable. This is based on the fact that glass immersed in a solution containing hydrogen ions acquires a potential which is a function of the hydrogen ion concentration. A bulb is blown on the end of a glass tube, the end of which is ground and fitted with a metal terminal carrying a platinum wire immersed in a conducting solution. The bulbed· tube is then immersed in the solution to be tested. For this purpose the glass selected should have good conductance, and this is met in soda glass, though the resistance of the circuit will be of necessity high and thus require special measurements. Glass again is susceptible to attack from alkalis, and so the results obtained are not free from error. Into the solution under test also dips the arm of some standard electrode. From the e.m.f. of the combination

the potential of the glass electrode is determined, and from this the concentration is calculated from the formula—

$$E = K + R(T/F) \log_e (H)$$

where K is a constant dependent upon the nature of the glass and the electrolyte contained within it. This can first be ascertained by a test with a solution of known pH. In the formula, R is the usual gas constant expressed in the electrical form (see page 198), while F is the Faraday and T the absolute temperature. At 18° C. the expression becomes—

$$E = K + \{8\cdot28 \times (273 + 18)/96\,600\} \log_e (H\cdot)$$

and bringing this to the base 10, we have the formula as

$$E = K + 0\cdot058 \log_{10}(H\cdot)$$

from which log (H) is obtained and converted into its pH equivalent (see page 248).

Comparison of Methods. By the methods described, somewhat different figures are obtained for the same solution. The colorimetric method is obviously simple and easy of manipulation and usually gives results which are reproducible to $0\cdot1$ pH. These were for long accepted as sufficiently accurate, but later, when the quinhydrone electrode was applied with a view to obtaining more accurate results, definite discrepancies between the electro-metric and colorimetric methods came to be observed, and these, moreover, were not strictly in accordance with the two different electrodes, viz. the hydrogen and the quinhydrone electrode. Quinhydrone figures are of the order of $0\cdot1$ pH higher than the values with the hydrogen electrode, and these in turn are $0\cdot5$ pH units lower than the values obtained by colorimetric methods. The differences between colorimetric and electro-metric methods vary with different solutions. This latter difference is known as the "salt error" and can be approximately expressed for the different solutions and tabulated. The difference arises from the fact that colour standards are usually prepared for solutions of low concentration of other salts, these being common in other industries. The nickel solution, however, is relatively strong. It has not been found possible to put all these measurements upon an accurately comparable basis, but for most commercial work with

nickel-plating solutions a more accurate figure is arrived at by making a deduction of 0·5 pH from the observed colorimetric reading, but this correction, if marked on the colour standards, should be only applied in the case of nickel-plating solutions with their large concentration of nickel compounds.

Some of these corrections determined with solutions of different compositions are shown in Table LXVI in which the concentrations of the constituents are given in terms of grammes per litre, while the corrections given are deductions from the values obtained colorimetrically to bring them into line with those obtained electro-metrically.

TABLE LXVI

SALT ERRORS IN pH DETERMINATIONS OF NICKEL SOLUTIONS

Nickel sulphate cryst. .	240	240	240	210	120
Nickel chloride cryst. .	—	30	—	—	—
Boric acid . . .	30	30	30	30	—
Potassium chloride . .	—	—	—	—	8
Potassium sulphate . .	—	—	22	—	—
Ammonium sulphate .	—	—	—	—	22
pH correction . .	0·5	0·55	0·55	0·5	0·2

ELECTRODE REACTIONS

Introduction. It now becomes necessary to attempt to apply as far as possible the foregoing more theoretical considerations to the observed facts of cathodic and anodic processes, especially with those related to the electrodeposition of metals. Neither of these processes is a simple one, even apart from the fact that two or more entirely different processes may be taking place simultaneously. The deposition of a single metal offers difficulties in formulating an adequate conception free from criticism, in view of the enormously wide array of observations which have been made from time to time by numerous observers and which so far have defied simple correlation.

Deposition of Metals. The electrode or reversible potential of a metal is that at slight deviations from which the metal would be dissolved in or deposited from the surrounding solution of its salt. Thus the application of an e.m.f. reduces the potential at the cathode and this admits of the discharge of the metal ions upon it. In general, this is true, and Le Blanc confirmed this anticipation

Thus, from a mixture of copper and zinc sulphates copper begins to be deposited when the potential is somewhere of the order of 0·34 V, this value, it will be remembered, applying strictly to a solution normal with respect to copper ions. Again, it will be recalled that with a change of the ionic concentration of the solution this value varies to the extent of $0·058/n$ V for a tenfold change, where n is the valency of the ion concerned. By a reduction of the concentration of the copper to one-tenth of its original value the potential will have changed to $0·058/2 = 0·029$ V less or $0·34 - 0·029 = 0·311$ V, and by the time the potential has been reduced to zero the concentration of the copper ions will have been reduced to $0·34/0·029 = 12$ or $1/10^{12}$ of its original value. This is so infinitely small an amount as to be regarded as the complete removal of the copper before the potential at which hydrogen deposition is reached. As a matter of experience, copper is

deposited with practically 100 per cent efficiency from even strongly acid solutions, so long as the current density is kept low, a condition for good coulometric work. Thus the electrolytic separation of some metals is capable of extreme exactness. From a normal ionic mixture of the two sulphates of nickel and copper there is an almost complete separation. Reference to the electrode potentials of the two metals shows a difference of $0 \cdot 34 - (- 0 \cdot 23) = 0 \cdot 57$ V. As a reduction of the copper content to one-tenth of its concentration produces a difference of electrode potential of only $0 \cdot 029$ V, it follows that the concentration of the copper ions must be of the order of 10^{-20} normal before co-deposition should occur. This extreme dilution is equivalent to a perfect separation.

These conditions, it must be recalled, refer strictly to the films of electrolyte adjacent to the electrode. In normal practice, however, with appreciable acid content, there may be an almost complete absence of copper ions in the cathode film while a considerable copper ion concentration exists in the bulk of the solution. This allows of the precipitation of the hydrogen before the entire removal of the copper.

Again, electrode potentials are referred to the metal itself. With an inert cathode like platinum the conditions vary somewhat, but Le Blanc found that the amount of metal which must be deposited before the inert metal would exhibit the characteristic properties of the metal in the solution and therefore undergoing deposition, was so small as to be beyond the range of analysis and therefore possibly amounted to only a few atoms thick.

It is evident, therefore, that for the analytical separation of two metals quite a small difference in electrode potential amounting to, say, $0 \cdot 2$ V, will be all that is required so long as this figure is not exceeded by the conditions of the experiment.

With the evolution of hydrogen, however, and gases in general, new conditions come into play to which reference is made under the terms of "over-voltage," and this favours the separation of some negative metals with good efficiency even in the presence of hydrogen ions in considerable concentration.

On the other hand, there are a number of metals which do not deposit when their respective potentials are reached,

Among them are iron, nickel, and cobalt. Their electrode or reversible potentials and their deposition potentials are shown in Table LXVII.

These figures show marked variation of the deposition potentials from the reversible potentials, this difference being reduced at higher temperatures, and in the case of iron the value has reverted to the original. There would appear in these cases to be some effect inhibiting the free deposition of the metals, and this effect is apparently much more marked in

TABLE LXVII

DEPOSITION POTENTIALS OF METALS

Metal	Reversible Potential	Deposition Potential		
		15° C.	55° C.	95° C.
Iron . . .	— 0·46	— 0·68	— 0·49	— 0·46
Cobalt . .	— 0·31	— 0·56	— 0·46	— 0·36
Nickel . .	— 0·24	— 0·57	— 0·43	— 0·29

these than in other metals. It has been suggested by Glasstone* that this may be due to the formation of an active metastable state which with an increase in temperature passes into the more stable crystal form.

In some explanation of this behaviour it may be pointed out that obviously some time must elapse in the conversion of a metal ion into the atomic form in its definite position within the crystals of the deposit. Not only has electrical neutralization to be effected, but the neutral atom has then to take up its position either in the growing crystal or initiating a new crystal. This process, if slow, constitutes some hindrance to the deposition process and may therefore account for the excessive deposition potential.

Alternatively, it may be pointed out that hydrogen deposition inevitably accompanies the deposition of these three metals, giving rise, as is well known, to stresses in the deposits. The surface absorption of hydrogen can reasonably be made responsible for an increased potential for the deposition of these metals, and as this gas absorption will be decreased with increasing temperature, there will be some reversion towards

* *Journ. Chem. Soc.* (1926), Vol. CXXVIII, p. 2887.

normal deposition potential with increased temperature. A further possible explanation is that the deposited metal first assumes a metastable condition from which it is transformed to the stable form, this change involving time and being influenced by temperature. There would at any rate seem to be available a number of possibilities without the means for determining which may be mainly responsible for the observed facts.

Conditions Influencing the Physical Properties of Deposits. Many conditions which influence the physical properties of deposits have from time to time been observed and recorded. These include—

(1) Current density, which covers the rate at which metal ions are brought out of the solution and take their part in the formation of the crystals of the deposit.

(2) Concentration, which may have some influence on either the growth of existing crystals in the deposit or the initiation of new crystals.

(3) Ionic migration, which will affect the ion concentration on the cathode solution film.

(4) Temperature, which will influence ion migration and the degree of hydration.

(5) The simplicity or complexity of the ions.

(6) The degree of ion hydration and thus the dissipation of the water envelopes in which the ions have migrated, and from which they have to be detached for deposition.

Thus many factors have to be taken into account in forming a conception of the process or processes through which ions pass from the solution into the structure of the crystals which constitute the deposit.

A simple conception of this process of deposition is not easily arrived at nor agreed upon, and it is obvious that our conceptions of electrolytes and electrolytic action must be referred to in the search for such explanation.

A survey of the recognized facts must first be made relative to these electro-deposits. Thus, silver is a univalent metal and deposition from aqueous solution of its mineral salts results in distinct and large crystals, those of the sulphate being smaller than those from the nitrate.

Copper is a divalent metal and may be deposited from the chloride, sulphate or cyanide solutions. In the order mentioned the deposits naturally vary from coarse to fine. This seems to be a common experience. Nickel from the nickel ammonium sulphate solution is smoother than that from the single nickel sulphate solution, while lead from the fluorsilicate bath is much smoother and finer than that from the acetate solution. In these examples, smoother deposits result from solutions in which there is the greater possibility of the formation of complex salts and therefore lower metal ion concentration.

That the matter is not so simple is deducible from the fact that in very few depositing solutions are we concerned with simple ions. Such solutions are usually strong solutions of strong electrolytes. Many of the relevant ions are complex in composition and, in addition, hydrated. These complexities are referred to in more detail in Chapter XXI. It is a recognized fact that those cathions which are the least hydrated form the larger crystal structures. Examples are lead, cadmium, zinc, and silver.

Physical Properties of Deposits. The processes of electro-deposition result in the production of deposits exhibiting many physical characteristics, and the observed properties are definitely related to the arrangement of the infinitude of small parts or atoms which result from the discharge of the migrated ions.

Adopting the accepted atomic magnitudes there must be somewhere of the order of 11 000 000 000 000 000 000 000 copper ions discharged by the passage of 1 Ah, and somehow these numerous units must pass through one or more stages in the construction of the final solid metal.

Again, all deposits are crystalline. Sometimes the crystal form is large and easily observable by the naked eye. It is then said to be macroscopic. For the most part, however, the crystalline form is small and only observed after some careful preparation of a specimen and its subsequent examination under a micro-scope. This microscopic structure may again be so small as almost to defy analysis under available magnifications. As is common in metallurgical experience, large crystal form offers less strength than a smaller and more compact one. Strength seems to be associated with the number and therefore area of

crystal boundaries, rather than with the strength of the individual crystals. Again, as with the usual process of the crystallization of salts from solutions and metals from their fused forms, slow crystallization induces large crystals, while more rapid crystallization is responsible for smaller crystals. As a matter of common experience slow deposition induces obviously large crystalline deposits, while with an increase of current density the surface is smoother as a result of finer crystallization. Again, in metallurgical experience a two-constituent metal is of smaller crystalline form than a single metal, and individual metals can be manipulated for the production of single crystals of large dimensions, so large, in fact, that the usual dimensions for testing specimens may embrace only a single crystal.

In deposition, however, the process of crystallization may be seriously interfered with by the rate of deposition and the presence of other disturbing factors, and hence the production of powdery deposits. Such powdery deposits are due to—

(1) In acid solutions, the co-deposition of hydrogen in, at first, minute bubbles.

(2) In solutions of high pH basic compounds, high current density influences the pH of the cathode layer to a degree not observed in the main bulk of the solution.

The whole matter has been exhaustively examined and it will suffice to give a summary of the findings.

In the first place Hughes proposed the terms idiomorphic and hypoidiomorphic as descriptive of crystals which had freedom of growth and restriction to growth respectively, the terms being borrowed from accepted mineralogy, the processes appearing to have many points in common. Slow deposition will favour the former, while increased current density will tend towards the latter type.

One of the first problems which would seem to call for some agreement is that of the transformation of the metal ion to the metal atom within the crystal of the deposit. Several suggestions have been ventured. The first is that this change is a single process, the discharged ion at once taking its place on the crystal. For this view there is a considerable weight of evidence and support. On the other hand, it is considered by

some that the ion must first lose its charge and any associated water of hydration, and then be deposited probably first as atoms on the surface before actually taking up their final positions in the ultimate crystal. To the attempt at settlement of these conflicting views a wealth, or perhaps bulk, of evidence has been adduced, but it does seem that some simple explanation is likely to prove of the greatest service in the first formulation of an adequate conception of the process.

According to Blum and Rawdon* the process of deposition is one of a single stage from the ion to the atom within the crystal. Such a single stage must include electrical neutralization, discharge of hydration water, and finding a position within the crystal. They account for the variation of the structure of deposits almost entirely by the changes in the cathode polarization. According to their view, ions discharge at points of lowest cathode potential, and they consider that a higher potential may be required to initiate a new crystal than to develop an existing one. In favour of this view it is certain that increased current density promotes finer crystallization, and this increased current density is the product of an increased e.m.f. at the bath terminals with an increase in its component parts, including that of the cathode polarization.

Other investigators, including Hughes,† postulate the development of the crystals from material which is atomic but not carrying a charge, and even suggest that the electrical discharge takes place some distance from the cathode without venturing any explanation of the manner in which these electrically neutral atoms are finally attracted to the cathode.

This conception involves the entrance of electrons into the solution to neutralize or discharge the ion, but the neutral metal has still to find its way into the structure of the crystal.

It may be recalled that as far back as 1904 Bancroft‡ stated that "fine grained deposition is favoured by high current density and potential difference, by acidity or alkalinity, by low temperature and by colloids." This early and general statement finds confirmation in these days of more theoretical discussions, when it is remembered that these conditions tend

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* *Trans. Amer. Electro-chem. Soc.* (1923), Vol. XLIV, p. 397.

† *Dept. Sci. and Ind. Research Bull.*, 1922.

‡ *Trans. Amer. Electro-chem. Soc.* (1904), Vol. VI (ii), p. 27.

towards higher cathode polarization and the initiation of more nuclei with more numerous and finer crystals and hence smoother deposits.

All conditions which increase the difference of potential between the solution and cathode, that is, the cathode polarization, will favour the formation of nuclei with numerous crystals and smoother deposits. Such conditions are high current density and low metal ion concentration.

It is evident that some correlation and simplification of views on this difficult subject must be sooner or later forthcoming to enable the matter to pass from the realm .of the largely hypothetical to one more practical.

Theory of Chromium Deposition. This is a problem which has occasioned some discussion, and here it may be said that practice is well ahead of theory, there being at present no generally accepted explanation of the stages in the process of the conversion of hexavalent chromium in the chief constituent of the bath, viz., chromic acid, to the "nono-valent" deposited metal. The problem is beset with a number of difficulties and there must be the recognition of well-accepted facts.

Made up from chromic trioxide, the solution contains . dichromic acid ($H_2Cr_2O_7$) which ionizes thus—.

$$H_2Cr_2O_7 \rightleftharpoons 2H. + Cr_2O_7^{--}$$

The solution is red in colour, and during the reaction these Cr_2O_7 ions become reduced in part to metal. Pure chromic acid solution, however, does not yield a chromium deposit. Chromium sulphate, $Cr_2(SO_4)_3$, was then regarded as an essential addition to supply trivalent chromium ions. However, sulphuric acid is now much more commonly used, there being apparently the need for some further anion. The solution as used is characterized by its good conductance. The addition of any basic oxide, for example, Fe_2O_3, from the iron which may be taken up from an iron or steel container forms ferric dichromate [$Fe_2(Cr_2O_7)_3$], and a similar chromium compound, chromium dichromate, will result from the reduction of the hexavalent to the trivalent chromium. The presence of the dichromates accounts for the loss of a considerable amount of free dichromic acid and, with it, a change from the bright red to a brown colour.

This chromium dichromate seems to supply the needful trivalent chromium ions and probably acts as a buffer to these ions. The reduction of dichromic acid to the lower valency compound is not possible except in the presence of an added anion, usually SO_4. Moreover, while there are still lower valency compounds of chromium, the chromous compounds, their existence in the solution is incompatible with the presence of so high a concentration of dichromic acid. According to Ollard,* if dichromic acid is increasingly reduced and the specific conductance determined, there are definite breaks in the conductivity curve when (1) 25 per cent of the chromium has been reduced and (2) when 50 per cent has undergone reduction. These percentages correspond at the first stage to compounds of the formulae $Cr_2O_3 . 6CrO_3$ or $Cr_2(Cr_2O_7)_3$ which may be regarded as chromium dichromate and may even be hydrated, while at 50 per cent reduction the formula of the product would be $Cr_2O_3 . 2CrO_3$. Both of these compounds are soluble in the excess of dichromic acid. A further stage of reduction is still possible, giving an insoluble compound to which the formula of $Cr_2O_3 . CrO_3$ has by analysis been assigned.

Various explanations of the mechanism of the deposition of the chromium have been ventured. It has been suggested that the deposited chromium results from the migration and discharge of the trivalent ions present, but this would not seem to be reasonable in view of the difficulty of producing chromium from ordinary trivalent salt solutions. Dr. Leibreich advances the view that the reduction of the CrO_3 compound takes place in successive stages through the trivalent, divalent and then to the metallic form, and some evidence seems to be forthcoming for the existence of the divalent compounds in the immediate vicinity of the cathode where the conditions may be, and very possibly are, very different from those in the main bath. The production of insoluble membranes near the cathode surface is suggested by Muller, and beneath these membranes reactions may occur in a new "atmosphere" which might be quite impossible in the strong dichromic acid solution. Such dark deposits of insoluble compounds are readily seen in solutions operated in the cold. Taking these general opinions

* *J.E.D.T.S.* (1928), Vol. III, p. 5.

into consideration, Ollard suggests that the chief reactions in the order of rising cathode potential are—

(1) Cr... → Cr.. + O

(2) H. → H + O

(3) Cr.. → Cr + 2O

These reactions are electrolytic. According to this view, trivalent chromium ions are few in number and supply the
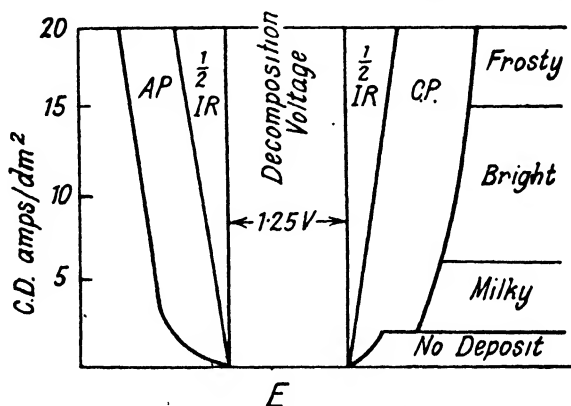
FIG. 66. POTENTIAL CHANGES IN CHROMIUM DEPOSITION

deposited metal. This is in general agreement with the recognized fact that scarcity of ions is largely responsible for nuclei formation and the production of smooth deposits, that of chromium being an outstanding example. At the same time other subsidiary reactions which are not electrolytic are—

(4) Cr.. → CrO

(4a) $3CrO + CrO_3 → 2Cr_2O_3$

(5) $2H → H_2$

(6) Cr → Cr (cryst. deposit)

The potential changes together with the usual current density ranges for the different types of chromium deposits are shown in Fig. 66* in which is expressed the fact that from a solution containing 250 g CrO_3 and 2·5 g H_2SO_4 per litre and operated at 45° C., there is no deposition of the metal

* Haring and Barrows: U.S.A. Bureau of Standards Technologic Paper No. 346.

until a current density of about 20 A/ft² is reached. A sudden change in the cathode potential now admits of the discharge of the metal from the ionic form, but these values will be markedly affected by changes in the composition of the solution and other conditions of operation.

Anodic Solution of Metals. The mechanism of the anodic solution of metals calls for some comment, this being a process which may not be as simple as appearance may suggest. This problem is of greater importance with metals which exhibit more valency than one. Similar remarks apply but in the reverse direction in the cathodic deposition of the metals. In a simple illustration iron dissolves anodically in sulphuric acid to the ferrous form. It may be later oxidized either electrolytically or purely chemically to the ferric form. Again, iron is not deposited directly from the ferric form but first suffers reduction to the ferrous. This principle may be applied to copper with its alternative of the formation of cuprous or cupric ions. It is common and perhaps convenient to consider the solution of copper as one of the direct productions of cupric ions. The electrolysis of a solution of sodium chloride with a copper anode, however, results in the precipitation of cuprous hydroxide by the interaction of cuprous ions formed at the anode with the hydroxyl ions developed as a secondary reaction at the cathode. Again, in the cyanide solution cuprous ions definitely form and pass into the form of the complex ion, $Cu(CN)_3^{--}$. Hence it is suggested* that copper invariably first assumes the cuprous ion form. In the two cases quoted this cuprous form is fixed by chemical reaction and the valency of the anode process is unity. In the case of the sulphuric acid bath or sulphates the cuprous ions first formed are then electrolytically oxidized to cupric, this involving a further Faraday per gramme-equivalent. Cuprous ions are known to exist in copper sulphate solutions. Their presence militates against correct coulometer conditions, and the alcohol addition first suppresses the dissociation of the sulphate, reducing the copper ion concentrations and, admitting some equilibrium between cuprous and cupric ions, reducing also the concentration of the cuprous ions. If cuprous ions first formed are completely electrolytically oxidized to cupric, then the apparent

* Briggs: *Trans. Amer. Electro-chem. Soc.* (1921), Vol. XL, p. 231.

valency of the reaction is two. If the cuprous ions are fixed chemically, the valency is one. A combination of these two processes will give an apparent valency always over one, usually nearing, but never exceeding, two.

Anodic Reactions. It will next be recalled that in the processes of electro-deposition there are very different circumstances attaching to the choice and behaviour of anode materials. Anode efficiency is usually less than theoretical. This varying behaviour makes an almost immediate effect on the composition of the electrolyte, such changes militating against continuity of conditions and operation.

A simple example is that of solutions which are used cold and are nearly saturated. In, for example, a cold strong acid copper bath, the copper sulphate formed at the anode may saturate the anolyte and may lead to the crystallization of the salt upon the anode, thus largely insulating it with consequent higher p.d. to maintain the necessary current, or the decrease of current at constant p.d. The removal of the anode or even one of a number, and rinsing, will restore the current, which may again fall to zero for the same reason. Again, in both depositing and refining operations there is the general aim at quantitative anode solution, thereby maintaining the composition of the electrolyte and, in turn, the cathode efficiency. Perhaps the most common type of this behaviour is that of copper in the acid solution.

In many cyanide solutions the appearance of films of insoluble compounds which impede the current is a common experience, this phenomenon varying with the current density, temperature, and composition of the solution.

These films may in some cases be quite thick without offering serious resistance owing to their porosity. There may, nevertheless, be a change in the anode reaction in view of the restricted access of the solution to the anode metal. Other deposits are, however, sufficiently dense and insoluble as to slow down the desired anode reaction even to. zero, when the anode is said to be "passive." This "passivity" is of the mechanical type definitely due to the layer of hindering material.

In yet other examples (and that of nickel well exemplifies the type) an almost complete cessation in the normal functioning

of the anode occurs with the evolution of oxygen and the production of sulphuric acid. This slowing down of the solution of the anode is due to the formation of mere films of insoluble compounds, usually oxides, and provides an example of "chemical passivity" which calls for some detailed consideration. In deposition and refining it is a definite evil, and the conditions conducive to passivity need counteracting.

Passivity. It is well known that a piece of clean iron after immersion in 50 per cent HNO_3 ceases to deposit copper from copper sulphate solution. This is but a single instance of a total change in chemical behaviour due to an invisible film of oxide. Many metals, too, develop by exposure similar films which markedly reduce their chemical activity and thus render them more noble. This accounts for the maintained brightness of a number of negative metals like aluminium. Hence the same metal in its active and passive forms occupies two totally different positions in the electro-chemical series, passivity tending to nobility. Chromium is a good example of this behaviour, its position in the electro-chemical series representing the active form, while in the passive state the metal gives little or no effect when placed opposite to platinum in an electrolyte.

A few examples of this passivity produced anodically may with advantage be referred to. Thus, copper as an anode in a solution of a chloride develops a film of insoluble cuprous chloride, which in a loose form does not too seriously affect its anodic behaviour. This occurs at low current densities. At higher current densities this film of the insoluble chloride is replaced by one of cuprous oxide that is much more resistant to the passage of the current which falls to a low value with a corresponding increase in potential, still maintaining some slow solution of the metal with, however, the evolution of oxygen. At intermediate current densities there is an alternation between these two effects with periodic variations in the behaviour of the anode and corresponding changes in the potential and therefore current. While the case has little application in deposition processes, it nevertheless illustrates a very frequent occurrence in anodic passivity.

Such inactivity does not occur to any appreciable extent with the concentrations of sulphuric acid present in the usual

deposition and refining solutions. In stronger acid, however, it becomes apparent with the formation of the blue sulphate crystals which are not readily soluble in these concentrations of the acid.

The phenomenon is, however, very apparent in the usual types of cyanide depositing solutions. These may contain small percentages of "free cyanide" added definitely to prevent the formation of insoluble films on the anode. With low free cyanide concentrations and in a still solution and even low current densities, anode films of cuprous cyanide begin to form, inducing mechanical passivity. These may disappear on standing, and constitute no great impediment in the process. With higher current densities this film is replaced by one of the oxide which is a definite example of chemical passivity. Periodicity is observable in the process with intermediate current densities, these being dependent upon other conditions, such, for example, as the temperature and proportion of free cyanide.

Similar effects are obtained with silver anodes in the usual silver potassium cyanide solution used in electrodeposition. As a rule they may be checked by the use of a sufficiency of free cyanide and, obviously too, stirring or agitation in one or other form will militate against the occurrence of passivity.

As is to be expected, similar phenomena occur with other metals in cyanide and alkaline solutions. In the case of zinc in alkaline solutions—and free alkali is present in the usual types of cyanide solution used in the deposition of zinc and cadmium—a first film of comparatively loose zinc oxide first forms, shielding the metal from the current and, therefore, increasing the current density on the unaffected parts. These high local current densities then induce the formation of a thin film of oxide which has definite protective properties, this film spreading under the loosely attached oxide and thus effecting its detachment. Such an oxide film does not produce complete passivity as zinc still continues to dissolve, though much more slowly. As may be anticipated, cadmium acts somewhat similarly except that, as cadmium oxide is not soluble in alkali, it cannot be removed by alkaline conditions and the usual periodic formation and solution do not take place.

From the electrodepositors' point of view the most striking examples of anodic passivity are those occurring with iron,

nickel, and cobalt. In the earlier days of nickel electro-deposition, anodes were of a definitely impure type containing usually not more than 92 per cent of nickel. Impurities, however, favoured the more complete solution of the anode. Difficulties became more apparent with an increase in the purity of the nickel anode the solution of which, while maintaining a purer solution with the production of much less dark yellow anode slime consisting mainly of ferric hydroxide, began
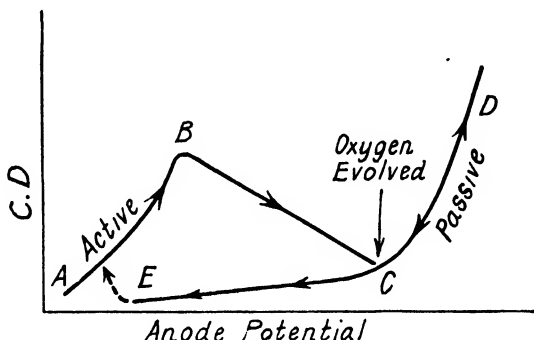
FIG. 67. PASSIVITY OF NICKEL ANODE

to show the effects of passivity. In the usual sulphate solutions these purer types of anode, while dissolving fairly quantitatively at the low current densities then in vogue, showed appreciable passivity at the increasing current densities which later became established practice with the more rapid systems of deposition. This passivity leads to the evolution of oxygen and the production of sulphuric acid which is not conducive to the maintenance of a constant pH which is usually regarded as very desirable.

The anode potential curve of a nickel anode with increasing current density is shown in Fig. 67, in which AB represents normal functioning. At B passivity begins with a decrease in current to C at which oxygen evolution takes place with increasing current density. In the reverse direction, current density decreases bring about a decreased anode potential without a break at C. At a low current density the anode re-assumes its activity.

Inhibiting Nickel Anode Passivity. Such passivity is not

produced in chloride solutions and hence the almost universal addition of a definite proportion of the chloride ion in the form of either nickel chloride or, now less frequently, some other chloride such as those of sodium or ammonium.

Methods of inhibiting passivity in nickel anodes have been investigated and one at present popular is that of the use of the so-called "depolarized" anodes. This term, however, should be replaced by that of "depassive," this type of anode having been prepared with the admixture of a small proportion of nickel oxide which, experience has proved, facilitates anode solution and thereby decreases if not entirely prevents passivity.

From these quite few experiences with the use of anodes in electrodeposition practice it is evident that some steps can be taken to reduce the defect by variations in the composition of the electrolyte—additions of free cyanide in the case of cyanide solutions and the addition of chlorides in nickel solutions together with elevation of temperature and the application of agitation of the solution; and, while these conditions have long been practised as a determination of experience, the satisfactory explanation of the phenomena involved and methods for its diminution derived from a knowledge of these phenomena adds yet another element of design in the formulation of solutions required for the continuous deposition of metals for many purposes.

In passing, reference may also be made to another method of reducing passivity, viz. that of the super-imposition of an alternating current on to the depositing current. Such reversals of current tend to make the films of oxides or other compounds thicker and therefore less protective, and some unusual results have been obtained by this method, including that of the solution of an iron anode in a caustic soda electrolyte and the solution of a gold anode in an electrolyte of the mineral salt type.

Further, this passivity must be looked upon as yet another type of polarization or change of working potential from that when the plate is at rest, and there is the considered conviction that what may be termed chemical and electro-chemical passivity is one and the same phenomenon.

Anodic Production of Oxides. There are some prominent examples of the production of metal oxides in considerable

quantities. That of lead dioxide in the accumulator may be recalled, while a similar process takes place when some polished metals such as iron and nickel are made anodes in alkaline lead solutions. There is the production of lead dioxide usually in thin films on the anode. If a cathode in the form of a pointed wire is brought near to the anode this film of dioxide is developed in the form of concentric rings of decreasing thickness
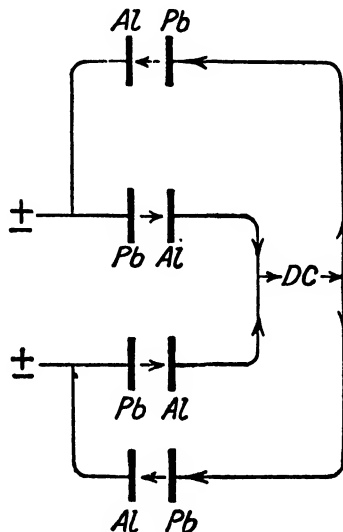
FIG. 68.   LEAD ALUMINIUM RECTIFIER

from the centre to the outside. These films are of the dimensional order to effect interference of light with the production of circular rainbow tints in the form of adjacent rings. This effect, known as Nobili's rings, has some decorative value.

Again, many lead electrodes used in electrolytic extraction processes are definitely more permanent when completely coated with the dioxide. Before bringing them into use, therefore, they are treated in a sulphuric acid electrolyte to effect this surface film of the oxide after which the electrodes are much less susceptible to attack by impurities in the solution.

Anodic oxidation of aluminium provides another largely applied formation of anodic oxide coatings. In electrolytes of chromic acid or sulphuric acid, pure aluminium becomes coated

with a continuous adherent film of its oxide which is of industrial importance. The process is termed anodic oxidation. In the first place the film is insulating. As it is formed unequally over the surface of the metal, so it diverts the current to the unaffected portions until a complete coating is produced. If the term throwing power could be applied in this process, its value would be of the order of 100 per cent, as this anodic oxidation takes place in the deepest recesses and penetrates long distances inside narrow tubes.

Further, the insulating character of the film has been turned to account in the lead-aluminium rectifier by reason of the fact that such an aluminium surface may, in an electrolyte, receive current but not admit of its passing from the plate. By the application of an alternating current some conversion to one which is uni-directional is effected.   For this purpose the arrangement shown in Fig. 68 brings about the conversion of a.c. to d.c. which may then be available for many electro-chemical processes.

This film, too, is protective against corrosive conditions and this fact has been responsible for the very wide application of the process on all aluminium and allied alloys which are subject to excessive corrosive conditions.

Finally, the film has mordant properties admitting of its decoration by immersion in many dyes which are absorbed and fixed in the oxide deposit, a fact which again has found extensive application in the decoration of this otherwise plain yet exceedingly useful metal.

THROWING POWER OF ELECTRODEPOSITING SOLUTIONS

Introduction. It may be generally assumed that in most cases of practical electrodeposition there is the desire for the production of relatively uniform deposits on the irregularly shaped work which comes in for treatment. There may be special cases in which thicker deposits are required on some portions of the surface than on others. Probably the larger share of the work upon which electrodeposits are made is flat or nearly so, in which case there is a fairly uniform distribution of current over the cathode surface and with it uniform thickness of deposit. Perfectly uniform deposits could only be assured by the rectangular type of current which would be obtained with parallel electrodes of the same shape and area enclosed so that the conducting solution will lie wholly between them. This is in some cases an attainable, indeed a very necessary, condition, but it falls well without practical conditions. In these days, too, there is the growing demand for specifications in electrodeposition and one of the factors coming within the scope of specification is that of thickness and with it some measure of uniformity over the whole surface. The choice of solution and operating conditions to achieve this desirable end is obviously of importance.
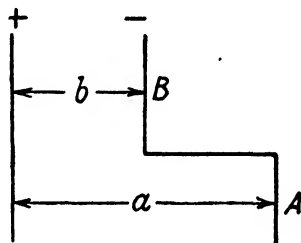
FIG. 69. THROWING POWER

Taking a simple case in which two portions (A and B) of a cathode are disposed one twice as far from the anode as the other (Fig. 69). Call these linear distances a and b. According to Ohm's law there should be twice the current density on the portion (B) nearer to the anode than on (A) the one more distant, and, other circumstances being equal (or rather omitted for the present), there should be twice the deposit per unit area on B as on A. For the discussion of the problem the term linear

ratio—in this case a/b—will be appreciated, while the term metal ratio will refer to the ratio of the masses of deposits per unit area on B and A.

Some discussion of the conditions which make for uniform deposits is therefore of importance.

If distance alone from the anode were the determining factor, two conditions would be brought into play. The first is the difference in the currents on equal areas of the prominent and depressed portions of the work. Depressed parts will receive the smaller current and therefore the thinner deposit. There may, however, be some compensating influence if there is an increased cathode efficiency with the lower current density. If inter-electrode distance is the only factor, then it will be obvious that by removing the anode further from the cathode the proportional differences between the exposed and recessed parts will be decreased with a resulting greater degree of uniformity of the thickness of the deposit. This is a practice which, where possible, is frequently followed, and this involves some linear correction for the defect. On the other hand, some further balancing out of the irregularities might be made if, with the increased current density on exposed parts, there might be some condition which would simultaneously counteract this tendency to increased thickness. Such compensation—and a most important one, too—is found in the increase in cathode polarization with increasing current density. This may be regarded as an electro-chemical corrective, and involves the choice of an electrolyte which will show high cathode polarization. The choice of an electrolyte for many examples of electrodeposition is therefore a matter of design.

By throwing power is meant the ability of a solution, and with it, its method of operation, to ensure uniform deposition upon irregular surfaces. Some quantitative methods of expression will be referred to later.

Three factors are recognized as operating to influence throwing power. These are—

1. The conductance of the solution.

2. The change of current efficiency with change of current density, and

3. Cathode polarization.

These will be examined separately.

1. *Effect of Conductance.* Statements are frequently made regarding the influence of conductance on throwing power. That there is some effect is true, but the effect is indirect rather than direct. If inter-electrode distance were the sole and determining factor then it is obvious that changes in the resistance of the solution cannot affect the linear factor. On the other hand, an increase in conductance would throw into prominence other variations due to cathode polarization and this seems to be the main effect of increased conductance. For example, the addition of free sulphuric acid to a copper sulphate solution increases the conductance, and there is apparent an increase in throwing power. This, however, is obviously due more to the suppression of the ionization of the copper salt and the resulting decrease in the copper ion concentration, and with it an increase of cathode polarization.

In another example cathode polarization may be high but not very variable with current density and in this case little change in throwing power can be expected with variation in conductance.

In connection with the conductance of the electrolyte it may be recalled that the values for many metals are of the order of millions of times more than those of depositing solutions and therefore in simple language the current will obviously take the shortest possible route in the electrolyte to the nearest part of the highly conducting cathode with, in most cases, a thickening of the deposit at this point. This, for the most part, is a condition to be avoided.

On this condition there would appear to be little possibility of varying the throwing power by a change of the conductance of the electrolyte, and it is frequently stated that increased conductance improves throwing power. Whether this is a primary effect or one secondary by reason of a variation of other influencing conditions remains to be determined, but so long as we are concerned only with the linear factor there would be no change in the ratio of inter-electrode distance with changes of conductance.

2. *The Change of Current Efficiency with Current Density.* In some electrolytes there is a decrease in current efficiency with increased current density. This is the case with copper sulphate and silver nitrate and also many cyanide solutions and so

increased current density on exposed parts is, to some extent, offset by the decreased depositing power of the increased current. In other examples, as for example with nickel and zinc sulphate solutions, there is an increase in current efficiency with increased current density. This is no advantage towards increasing throwing power. The effect is rather in the reverse direction of decreasing throwing power. This is a factor capable of examination for individual metals, some data relative to which are shown in Table LXVIII. In any case, the effect is in most cases small.

The following data refer to the current efficiencies in a straight nickel solution with high and low pH.

<div align="center">

TABLE LXVIII

CURRENT EFFICIENCY AND CURRENT DENSITY

</div>

pH	Temperature	Current Efficiency			
		30° C.		60° C.	
	Current Density (A/dm.²)	1·07	5·4	5·4	10·7
2·0		65·9	86·8	91	93·4
6·3		99	99·3	100	100

The general improvement in the current efficiency with increased current density in the nickel, as also with zinc and iron solution, and indeed with all metals more electro-negative than hydrogen, is generally recognized, and with it there is a reduction of throwing power in that there is an increase in the metal on the prominent portions which is not what is required for good throwing power.

3. *Cathode Polarization.* It is to cathode polarization that we must look for the greatest influence in the variation of throwing power. Reference again to Fig. 53 (page 207) showing cathode potential/current density curves for a number of solutions reveals the fact that in some cases there is a marked change while in others the variation is small. Large increases in cathode potential with current density are essential to good throwing power. This may be looked upon as some sort of

electro-chemical resistance. The prominent parts receive the greater current density by reason of the linear factor, but the resulting cathode potential increase counteracts, to some extent, this increased current so that it does not attain the maximum set by the linear factor. This reduces the current on the more prominent parts and, as it were, throws it into the recessed parts with a general levelling up in the current distribution and therefore improvement in the throwing power.

The obvious classification of the metals according to their cathode potential/current density curves is thus some similar grouping of the metals according to the throwing power of their solutions. Mercury, lead, and silver nitrate solutions show little cathode polarization and therefore little throwing power. Copper, nickel, and zinc sulphate solutions show marked variations of cathode polarization and therefore appreciable throwing power. But it is to the double cyanide electrolytes that we must look for the most marked throwing power, and the conclusion brought out by a study of cathode polarization curves would seem to have been known empirically, in view of the extended use of the double cyanide solutions in cases of electrodeposition in which they are not absolutely necessary from the point of view of their stability, for they are by far the best throwing solutions.

Quantitative Throwing Power. A study of these three conditions seems to have first been made by Haring and Blum, who arrived. at throwing power by a consideration of the known values for these individual properties and confirmed their results by some experimental work. More recently, Gardam* has expounded these principles with greater elaboration. He shows that cathode polarization/current density curves are in the main divisible into two groups, if in the more simple case, we exclude obviously disturbing factors in the presence of films on the cathode (of other materials such, for example, as colloids) and any abrupt changes of cathode polarization such as are occasionally met. These two types are—

1. *The Linear type* in which cathode polarization plotted against current density gives a straight line. In other words, in this type cathode polarization is proportional to current

* *Trans. Faraday Society,* 34. 698, 1938.

density. While this condition is met in some copper solutions under some conditions, it is by no means common.

2. *The Logarithmic type*, in which a straight line while not produced by plotting cathode polarization against current density, becomes possible when cathode polarization is plotted against the logarithm of the current density. This is the more common experience.

Both of these types are expressible in some simple mathematical form and it appears that the usual type of nickel
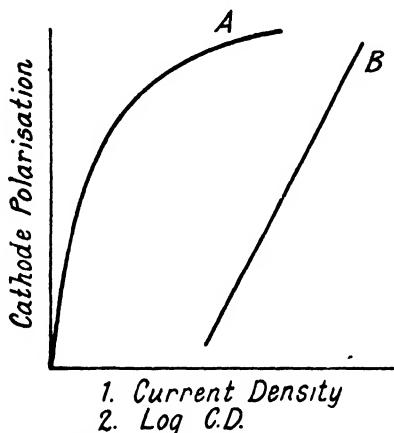
FIG. 70. CATHODE POLARIZATION/CURRENT DENSITY CURVE

solutions conform almost exactly to the second or logarithmic type. Copper solutions exhibit both types under different conditions. A curve of the logarithmic type is shown in Fig. 70, in which curve *A* shows the relation between the cathode polarization and current density, while curve *B* is obtained by plotting cathode polarization against the logarithm of the current density. When the influencing factors of throwing power are possible of mathematical expression individually, it becomes possible to calculate throwing power on some predetermined scale. This has been done by Haring and Blum* and also by Gardam, and their results have been confirmed by experimental data obtained in somewhat arbitrarily selected types of cells. Exact calculations, however, are only possible

* *Trans. Amer. Electro-chem. Soc.* (1923), Vol. XLIV, p. 313.

with a wealth of detail of each factor, and these are very varying according to several conditions, such, for example, as type of cell, current density and temperature. The problem admittedly is a complex one.

Blum and Haring also proposed a quantitative expression of this property of throwing power.

The apparatus which they used was a rectangular box of insulating material in which two half-cathodes placed at opposite ends served the purpose of near and distant parts of the same cathode. An anode of gauze was placed intermediately so that the relative distance of the two half-cathodes was as 1 : 5: Substantial connections ensured that these linear distances provided the only resistance between the anode and the separate parts of the cathode, while a gauze anode was used to ensure the same composition of electrolyte on either side and so not introduce another undesirable factor, viz., that of a difference in anode condition.

If, then, the ohmic resistance of the solution were the only factor influencing quantitative deposition, the half-cathodes would receive deposits inversely as their distances from the anode. This 5 : 1 factor—arbitrarily chosen—was termed the primary current distribution ratio. The weights of deposits on the two half-cathodes are readily obtained and this ratio was called the metal distribution ratio. Without throwing power, the metal distribution ratio is the same as the primary current distribution ratio, while throwing power is marked by a metal distribution ratio smaller than the primary current distribution ratio. Throwing power was then defined as the variation of the metal distribution ratio from the primary current distribution ratio expressed as a percentage of the latter. If, for example, the primary current distribution ratio is 5 and the metal distribution ratio 4, then throwing power was expressed as

$$\frac{5-4}{5} \times 100 = 20 \text{ per cent}$$

By this system many throwing powers of solutions were worked out and were in general shown to conform to the anticipations of the additions of the three factors already discussed, viz., conductance, current efficiency and cathode polarization.

Data for throwing powers began to find place in the literature

of electrodeposition, but not without some recognition on the part of observers that the arbitrarily chosen basis for quantitative expression was not the most desirable.

The proposals of Haring and Blum were open to some objections, as follows—

1. The ratio of 5 : 1 was unnecessarily high in view of the extended use of supplementary anodes in the cases of large and very irregular work.

2. An ideal throwing power, in which equal deposits are obtained on equal areas of the cathode irrespective of interelectrode distance, would give a metal distribution ratio of unity, and with the proposed formula the throwing power is—

$$\frac{5-1}{5} \times 100 = 80 \text{ per cent}$$

where 100 per cent would seem to be a more desirable figure.

3. Where, as occurs in some cases, the deposits on distant parts of the cathode are nearly down to zero the throwing power becomes some considerable negative value not capable of quantitative appreciation.

4. Still further, it is desirable that between the extremes of ideal deposition and that of no deposit on the distant part, there should be a uniform or graduated scale of variations.

Throwing Efficiency. It was with a view to overcoming some of these difficulties in the Haring and Blum formula that Heatley* suggested expressing throwing power as the ratio of that obtained in individual cases to the maximum possible with the linear ratio in use. To this new expression the term "throwing efficiency" was applied. This was undoubtedly a step in the right direction, but a further step towards a more ideal system was taken by the British Standards Institution† in the definition and expression published in 1934. Without specifying any linear ratio, and with the use of simplified terms as linear ratio and metal ratio, the formula adopted was—

$$\text{Throwing power} = \frac{100\,(L-M)}{L+M-2}$$

where L (linear ratio) is the ratio of the distances from the anode of the remote and the near half-cathodes respectively,

* *Trans. Amer. Electro-chem. Soc.* (1923), Vol. XLIV, p. 283.
† B.S.I. *Glossary of Electrical Terms*, No. 6321, p. 160.

and M (metal ratio) is the ratio of the weights of the metals deposited on the near and remote half-cathodes respectively. It was also recognized and stated that temperature, current density, and linear ratio should be expressed in stating the resulting throwing power.

From the following tables, LXIX–LXXI, it will be seen how far the B.S.I. formula goes to meet the conditions which have been outlined as desirable, and it will be noticed that when the deposit on the distant half-cathode becomes zero the throwing power becomes − 100 per cent.

TABLE LXIX

COMPARISON OF THROWING POWER SCALES

Linear Ratio 5 : 1

Metal Ratio	Throwing Power		
	Blum and Haring	Heatley (Efficiency)	B.S.I.
1·0	80	100	100
1·5	70	87·5	77·7
2·0	60	75	60
2·5	50	62·5	45·5
3·0	40	50	33·3
3·5	30	37·5	23
4·0	20	25	12·5
4·5	10	12·5	6·6
5·0	0	0	0
6·0	−20	−25	−11·1
8·0	−60	−75	−27·3
10·0	−100	−125	−38·5
20·0	−300	−375	−65·2
100	−1 900	2 375	−92
∞ (no deposit)			−100

By the use of the B.S.I. formula, throwing power becomes more definitely a property of the solution, differences due to other conditions such as linear ratio being reduced to a minimum.

Throwing Power of Chromium Deposition. The throwing power of the standard chromic acid solution for the deposition of chromium is notoriously poor, and it is doubted whether there is any immediate hope of an appreciable increase. The throwing power is always negative. Of the three chief factors

TABLE LXX
THROWING POWER OF A CADIUM SOLUTION

Linear Ratio	Metal Ratio	Throwing Power		
		Blum and Haring	Heatley Efficiency	B.S.I.
2 : 1	1·845	8·7	17·5	8·4
3 : 1	2·6	13·3	20	11·0
4 : 1	3·33	16·7	22·3	12·5
7 : 1	5·42	22·5	26·4	15·2
10 : 1	7·455	25·5	28·3	16·4

TABLE LXXI
THROWING POWER OF AN ALKALINE ZINC SOLUTION

Linear Ratio	Metal Ratio	Throwing Power		
		Blum and Haring	Heatley Efficiency	B.S.I.
2 : 1	1·75	12·5	25	14·2
3 : 1	2·38	14·0	21	11·7
4 : 1	3·33	16·7	22·3	12·4
6 : 1	4·80	20·0	24	13·6
9 : 1	6·98	22·4	25·2	14·4

influencing throwing power, viz., conductance, cathode polarization and variation of current efficiency with current density, the second, usually important, is here almost negligible. Haring and Barrows* have shown that cathode polarization changes only very slightly with increased current density. Within the usual range of bright deposits (from 6 to 15 A/dm.²) it is only of the order of 0·01 V/A/dm². The corresponding figure for the acid copper bath (not altogether characterized by good throwing power) is 0·05 V/A/dm.², while that for cyanide copper solutions is as high as 0·8 V/A/dm.² This information alone would justify the prediction that the solution would be a poor thrower. The third factor, the increase of current

* Tech. Paper, U.S.A. Bureau of Standards, No. 346.

efficiency with current density, is the dominating influence, and is considerable.

These authors suggest as means towards the improvement of throwing power the following conditions—

1. The use of baths with relatively low CrO_3 content;

2. The use of relatively high temperatures and current densities;

3. The selection of a cathode metal with a high over-voltage for hydrogen, for example, copper or nickel;

4. The introduction of the work into the bath so that it closes the circuit; and

5. Polarizing the work for a few seconds with current in the reverse direction. Then the more prominent parts will become passive (assuming that the cathode metal is not soluble in chromic acid) and will not so readily

FIG. 71.
THROWING POWER TEST

receive the deposit, thus allowing the less prominent parts which are not, or are less, passivated, to acquire current more easily and hence chromium deposit.

An alternative method of determining throwing power is that proposed by Krombholz, who makes a stout copper wire of 1 mm. thickness, the cathode pointing towards, but some distance away from, the anode as shown in Fig. 71. The tip of the wire cathode and also the bent support are insulated with a glass cap and tube respectively so that deposits are obtained only on the horizontal portion. Deposition is then carried on for some time, the portion of the wire cathode nearest the anode acquiring a thicker deposit than that farther away. This variation of thickness can then be measured with a micrometer and a curve plotted, relating thickness with distance from the anode. With poor throwing power the curve will be steep, while with, say, a cadmium solution with good throwing power it will be less steep or more horizontal. This is a quantitative variation of the bent cathode test.

An alternative method of measurement proposed is that of cutting the plated wire into a number of equal length sections and weighing them. The weight of the copper core is determined from a number of similar sections taken from a similar

length of wire and thus the weights of the separate deposits obtained. This method finds some favour and needs some calibration in order to bring it into line with other methods. It cannot, however, claim quite the same degree of exactitude as is obtainable in the Haring cell.

SEPARATION AND CO-DEPOSITION OF METALS

Introduction. While many electrolytic processes are mainly concerned with the deposition of single metals, there are examples in which it is desired to co-deposit two or more metals in the production of alloy deposits. Notable examples are brass, bronze, and lead-tin alloys which are examples of practical processes, while others which cannot claim this degree of usefulness nevertheless attract attention on account of their inherent possibilities. Brass is the most common case. It is usually deposited from a mixed solution of the double cyanides of copper and zinc, with the alkali cyanides. These fairly simple compounds give rise to a large number of dissociation products. Thus taking the double cyanides as $CuNa_2(CN)_3$ and $ZnNa_2(CN)_4$, with a little free alkali and alkali cyanide, we get—

$$NaCN \rightarrow Na^{\cdot} + CN'$$
$$CuNa_2(CN)_3 \rightarrow 2Na^{\cdot} + Cu(CN)_3''$$
$$ZnNa_2(CN)_4 \rightarrow 2Na^{\cdot} + Zn(CN)_4''$$
$$ZnNa_2(CN)_4 + 4NaOH = Na_2ZnO_2 + 4NaCN + 2H_2O$$
$$Na_2ZnO_2 \rightarrow 2Na^{\cdot} + ZnO_2''$$
$$NaOH \rightarrow Na^{\cdot} + OH'$$
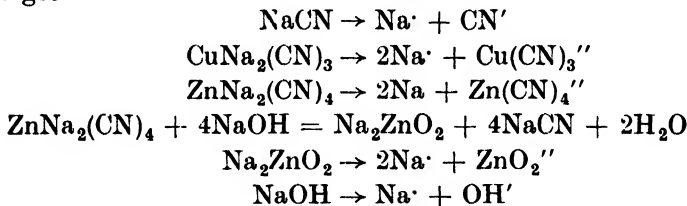
Carbonates are found to be present.

$$\therefore Na_2CO_3 \rightarrow 2Na^{\cdot} + CO_3''$$
$$Cu(CN)_3'' \rightarrow Cu^{\cdot} + 3CN'$$
$$Zn(CN)_4'' \rightarrow Zn^{\cdot\cdot} + 4CN'$$
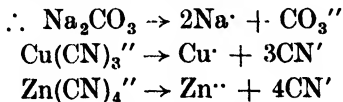
truly a complex mixture. The deposition of stainless cadmium-silver alloys and of non-corrodible iron-nickel alloys, of copper-nickel alloys of composition analogous to that of Monel metal, and, if last, certainly not the least important, the deposition of alloys of iron and chromium of the composition and properties of stainless iron and steel, are problems which offer fascinating interest and not limited commercial importance. A study of the principles upon which such possibilities may be safely based

must find some origin in fundamental facts which apply to the deposition of the individual metals.

These same principles, too, will cover the alternative cases in which, from solutions containing several metallic salts, it is desired to deposit a single metal in the purest form. Such are the examples of electrolytic refining. A similar case is that of electrolytic analysis in which it is desired to deposit one metal from a mixture of two or more compounds with quantitative accuracy which includes, therefore, the same degree of purity as that aimed at in electrolytic refining. These are new conditions somewhat different from those of commercial refining. There is also the case of most depositing solutions from which a single metal deposit is required but which contain, sometimes by design and often by unavoidable contamination, other metallic compounds, the metallic component of which is not required in the deposit.

The usual acid copper bath accumulates iron and other metallic impurities which, fortunately, do not seriously interfere with the process even when present in appreciable quantities. Metallic compounds are added to the nickel solution as conducting salts. Magnesium sulphate is one of these, and it has often been wondered whether magnesium passes into the deposit. Some observers record finding it. Thus it is claimed that from a solution of magnesium sulphate of 4 N. strength and containing nickel sulphate of 0·5 N. strength a deposit was obtained containing as much as 2 per cent of magnesium, while with an excessive current density zinc may be deposited with copper from the sulphate solution. The latter conditions, however, are so obviously abnormal with the production of powdery copper that this case need not concern us, but it is not improbable that in the case of the magnesium in nickel, we are not concerned with the deposition of magnesium upon magnesium, when the high reversible potential would be expected to hold, but rather upon nickel which seems to have a depolarizing effect, admitting of the deposition of magnesium at a markedly lower potential than its reversible value. Others are of opinion that the small traces only which they can find— and the methods of analysis must necessarily be very special— must be accounted for by unavoidable inclusion of the solution. Traces of copper and zinc in the nickel solution have detrimental

effects well known to the electrodepositor. The whole matter calls for some elementary treatment, but in passing it may be noted that in so far as alloy plating has become commercial, its development has come quite arbitrarily along practical lines, apart altogether from much or any appreciation of the fundamental electro-chemical conditions involved.

Fundamental Principles. From all solutions there is the possibility of the deposition of hydrogen, and reference to the electro-chemical series based on the single potentials of the metals at once indicates possibilities which are abundantly confirmed in practice. The single potential of copper in its sulphate solution is of the order of $+ 0.34$ V. We say "of the order of" as indicating that we must not overlook the fact that these figures apply to solutions of copper ions of normal ionic strength. The usual acid copper solution is some departure
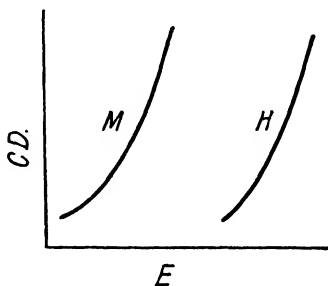
FIG. 72.
CATHODE POTENTIAL CURVES

from this strength. This figure represents the fact that hydrogen deposition may be anticipated if the cathode potential is, say by excessive current density, raised by this amount over that normally required for copper deposition. On the other hand, nickel, iron, and zinc have potential values on the negative side of hydrogen, indicating that from slightly acid solutions, hydrogen will be deposited with a diminution of the current efficiency of the metal deposition, but that increasing cathode potential will make for an increasing proportion of metal deposition with increased current efficiency.

Again, the widely different potentials of copper and zinc make it almost impossible to expect any reasonable deposition of zinc from the mixed solutions of mineral salts, and with both this metal and iron there are considerable accumulations in copper-refining electrolytes without any contamination of the deposit. This principle also guarantees the quantitative deposition of the copper from a solution which may have been prepared by dissolving brass in nitric acid for analytical purposes.

It is obvious that two metals or one metal and hydrogen

cannot be co-deposited if their cathode potential curves are of the types shown in Fig. 72 for at no current density have they a coincident potential. Some overlapping of the potential curves must be expected to ensure co-deposition.

A further glance at the potentials represented in Fig. 53 (page 207) shows the remarkably different electrode potentials of these two metals in solutions of their double cyanides with excess of the alkali cyanides. The following figures make this clear—

TABLE LXXII

ELECTRODE POTENTIALS OF COPPER AND ZINC

	Electrode Potentials		Deposition Potentials (cyanide)	
	N. Sulphate	0·1 N. Cyanide	Current Density = 1 A/ft^2	Current Density = 3 A/ft^2
Copper	0·35	— 0·6	— 0·77	— 1·12
Zinc .	— 0·76	— 1·03	— 1·12	— 1·25

Difference in cyanides; Zn > Cu by 0·35 at 1 A/ft^2
Zn > Cu by 0·13 at 3 A/ft^2.

Both copper and zinc are well on the negative side of hydrogen and are, moreover, not far distant one from the other. Their co-deposition from this solution becomes possible together with considerable quantities of hydrogen unless precautions are taken to preclude this.

And in this connection it may be noted that in the case of any individual negative metal there is always present the condition for co-deposition of hydrogen, this being evidenced by the low current efficiency at some current densities, and frequently the observed evolution of the gas at the cathode.

Separation of Metals. Brief reference to the separation of metals by electrodeposition may first be made. Two important cases arise—

1. Electrolytic refining, and
2. Electrolytic analysis.

Details of these somewhat numerous processes will have to be sought in the relevant literature but the simple cases can be outlined.

1. *Electrolytic Refining.* The case of copper is well illustrative of this applied principle. Crude copper in enormously large quantities, amounting possibly to something of the order of 1·5 million tons per annum, is highly refined by electro-deposition. Two aims are achieved in the process. These are (*a*) a high degree of purity and hence conductivity. It is well known that even the smallest quantities of even good conducting elements appreciably lower the conductivity of copper, and this at once affects the quantities to be used in any conducting proposition. (*b*) There is the concomitant recovery of precious metal impurities. These are not merely appreciable. They are frequently large, and though recoverable by dry or furnace methods, these are neither so easy nor are they so efficient. Electrodeposition admirably combines these two aims.

Without referring to any more practical details it may be said that this refining process is carried out by making crude copper the anode in an acid solution of the sulphate, the deposition of the pure metal taking place on the sheets of electrolytic copper which are specially prepared for this purpose. While there are important economic problems our chief concern is that of the elimination of the numerous impurities which may be grouped as follows—

(*a*) The very electro-positive metals, including, therefore, the precious metals. These include gold and platinum which are not dissolved, but fall into the anode slimes and are, in this much more concentrated form, easily recovered by chemical and metallurgical treatment. Silver, nearer to copper in the electro-chemical series, passes into solution. If it remained there it would inevitably pass into the deposit. The presence of a small amount of chlorides in the solution effects its precipitation into the slimes from which it is subsequently recovered. These anode slimes, which contain a considerable proportion of fine metallic copper by the unavoidable disintegration of the cast crude anode, amount to about 2 per cent of the anode weight, and hence the proportions of these precious metals are increased fifty times from the anode material to the slime.

(*b*) At the other end of the electro-chemical series are the very negative metals such as iron, zinc, and nickel. They present little difficulty. Anodically they readily pass into solution, but with the controlled current density employed, the cathode

potential never attains the figure at which their deposition becomes possible. They therefore accumulate in the solution.

(c) The greatest concern is that for the more intermediate metals such as tin, arsenic, antimony, and bismuth. Lead, of course, will pass out of the anode into the slime as lead sulphate. With the other metals there is always the possibility of the formation and subsequent precipitation of insoluble basic salts if the solution is not too acid. Both tin and bismuth are amenable to removal in this manner. Antimony, too, may thus disappear, but arsenic is more stubborn. Its removal has been effected by aerating the solution, at the same time effecting some slow circulation, so that some of the iron will be oxidized to the ferric form and then combine with the arsenic compounds to be precipitated in the form of a basic ferric arsenate. The process takes time, and there is the risk of the co-deposition of these intermediate metals with deleterious effects on the purity and properties of the deposited copper. In the presence of appreciable quantities of these metals, current density has to be limited, and this factor affects the economy of the process in the capacity of the installation required for a given output of copper. In the presence of these impurities in appreciable quantities the current density may have to be limited to 10 to 15 A/ft^2, while, when present in smaller amounts, the current density may possibly go up to 30 to 40 A/ft^2 with decreased deposition plant for a given output, though involving a larger consumption of electrical energy.

Similar principles have their application in the electrolytic refining of other metals, such, for example, as lead, while in the case of silver refining, copper accumulates in considerable quantities in the solution from which only pure silver comes out by electrodeposition.

2. *Electrolytic Analysis.* This method of analysis has many points of advantage over the more usual chemical methods with their slow process of precipitation, settling, filtration and washing prior to working up the precipitate into a weighable form. In electrolytic analysis the metal, either the impure form or as an alloy, is weighed, dissolved in acid and the solution converted into a chemical form from which one or other of the metals can be separated by electrodeposition even to the last traces without fear of the co-deposition of the other metals.

Such deposits are usually made on a platinum dish, and the weighings before and after deposition give the actual weight of the deposited component in the weighed sample of the original metal. In some cases one metal is first recovered and the solution then converted into a form which admits of the further deposition of another of its constituents. These processes have been considerably elaborated and applied, especially in the cases in which numerous routine analyses are required. They are easy, accurate and call for little attention during the major part of the time occupied in their completion.

Essential Conditions for the Co-deposition of Metals. Reverting again to the diagram of potentials in Fig. 72, the first essential condition for co-deposition becomes obvious. The potentials of copper and zinc in their sulphate solution are far removed from each other. For co-deposition a vertical line must cut through both curves.
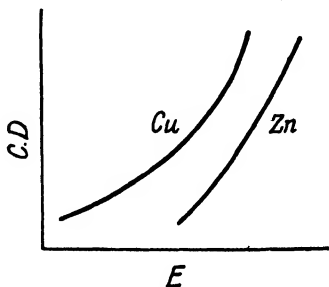
FIG. 73. CATHODE POLARIZATION/CURRENT DENSITY

In other words each metal under common conditions must be capable of deposition at a common potential. This overlapping of the current density/cathode polarization curves becomes possible when (1) the reversible potentials are nearly alike, and (2) when there are decided polarizations or increases of cathode potentials with increasing current density.

This is very clearly shown in Fig. 73 in the case of copper and zinc. The overlapping flatness of these two curves represents a wide range of electrical conditions over which co-deposition is possible. The possibilities of alloy deposition are therefore clearly indicated in the cathode polarization curves. In general, there is more chance for this overlapping in the double cyanide solutions with their very low metal ion content than in the solutions of highly dissociated mineral salts. Further, as will be seen later, the potentials of metals in organic solvents may, and do, vary very considerably from those in aqueous solutions, and this fact offers possibilities of alloy deposition which may not be within range in aqueous solutions. (See page 293.)

Another difficult factor which must influence alloy deposition

is the cathode potential of the alloy deposit. Films of solution in proximity to the cathode become unequally impoverished of their metal content according to the composition of the deposit with not easily discoverable variations in the individual potentials of the two components of the alloy.

Yet another fact may have a determining influence in the process of alloy deposition. Potentials are usually measured against single metal cathodes. Numerous properties of individual metals disappear when in the alloy form, and the
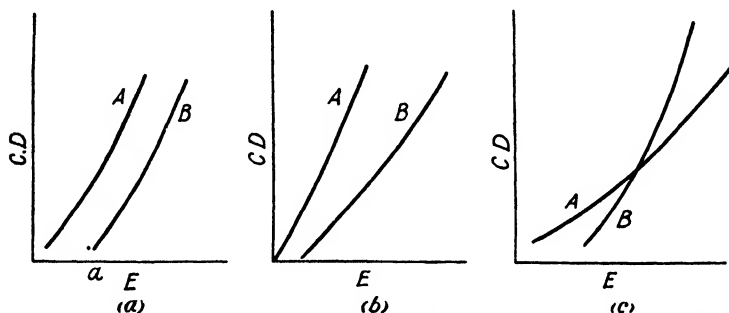
FIG. 74. INFLUENCE OF CATHODE POTENTIALS ON ALLOY DEPOSITS

potential not only may be, but is, one of them. A striking example of this is the case of the deposition of sodium on to the mercury diaphragm of the alkali cells. Here the cathode potential of the sodium as it enters the mercury must be very considerably reduced, admitting of the easy deposition of sodium, otherwise hydrogen, even with its high over-voltage, would be the sole product. Similar effects operate, though possibly not to the same degree, in other examples of alloy deposition, and although it may be possible to gather some general idea of the possibility of alloy deposition from the cathode polarization curves, many other undeterminable influences may profoundly modify these first conclusions.

Three conditions seem to co-operate to effect the co-deposition of copper and zinc in the cyanide solution. In the first case there is a much smaller concentration of copper than zinc ions. Secondly, the flatter potential curve of copper in comparison with that of zinc increases the amount of overlapping of the two curves. Thirdly, as has already been suggested in the case

of magnesium in nickel, the copper has a depolarizing effect on the zinc, lowering its deposition potential and making alloy deposition an easier proposition.

A review of the cathode potential curves of the metals with which co-deposition is possible reveals three types which are depicted in Fig. 74.

In Fig. 74 (*a*) the curves are parallel and vertical lines drawn through the curves give some indication of the relative composition of the deposits which will be obtained, assuming always the absence of hydrogen evolution. Here the deposition of metal *B* does not commence until the potential indicated at the point *a* is reached. Just beyond this point the proportion of metal *A* far outweighs that of *B*, but this proportion decreases with a further increase of potential.

In Fig. 74 (*b*) the curves diverge, and this divergence may be such that increasing the potential, and with it the current density, effects no change in this proportionality, the composi-

Fig. 75.
COMPOSITION OF BRASS DEPOSITS

tion of the deposit remaining practically constant over wide ranges of current density.

In the third case (Fig. 74(*c*)). the two potential curves intersect. At the point of intersection the two metals will be deposited in the proportion of their chemical equivalents, which is the same as saying that equal shares of the current will be concerned with the deposition of the individual metals, while below and above this potential, changes in composition will occur, the proportion of *A* to *B* decreasing with increasing potential from a positive value to one in the reverse direction.

Again, there are examples in which the two metals have close potentials, these varying with changes of concentration of the metal ions and not altogether in harmony one with the other. Lead and tin provide a case in point.

Composition of Alloy Deposits. For each alloy, assuming no

co-deposition of hydrogen, the weight of deposit per coulomb will at once indicate the composition. Let the coulombs passed through be expressed in terms of copper deposited from a coulometer. In the extreme case of the brass containing no zinc, the ratio of the "brass" to the coulometer copper will be 2 on account of the difference in the valencies of the copper under these different conditions. In the other extreme, where zinc alone constitutes the "brass" deposit, the ratio of brass to coulometer copper will be as $32\cdot5 : 31\cdot8$ or as $1\cdot022 : 1$. All ratios between these extremes represent definite compositions of deposit, these being expressed in the following table (LXXIII) and also in the curve (see Fig. 75).

TABLE LXXIII
COMPOSITION OF COPPER-ZINC DEPOSITS

% Cu	% Zn	$R = \dfrac{\text{Brass}}{\text{Cu..}}$
100	0	$2\cdot000$
80	20	$1\cdot678$
60	40	$1\cdot446$
40	60	$1\cdot271$
20	80	$1\cdot133$
0	100	$1\cdot022$

From this data the following expression is readily deduced —

$$\text{Percentage of Cu} = \frac{204}{R}(R - 1\cdot022)$$

as follows—

Consider the case of the brass containing 50 per cent each of the two metals. Then—

$$R = \frac{\text{Weight of brass}}{\text{Weight of acid copper}}$$

$$= \frac{50\ \text{Cu} + 50\ \text{Zn}}{25\ \text{Cu} + \dfrac{31\cdot8}{32\cdot5} \times 50\ \text{Cu}}$$

$$= \frac{100}{73\cdot92} = 1\cdot353.$$

$$R = \frac{\text{Weight of brass (100)}}{(\%\ \text{Cu}/2) + (100 - \%\ \text{Cu})\dfrac{31\cdot8}{32\cdot5}}$$

This on simplification gives—

$$\% \text{ Cu} = \frac{204}{R} \, (R - 1\cdot022)$$

and in the case of the alloy with the above ratio of $1\cdot353$,

$$\% \text{ Cu} = \frac{204}{1\cdot353} \, (1\cdot353 - 1\cdot022)$$

$$= 50 \text{ per cent.}$$

These expressions are only of exact quantitative use when no hydrogen is deposited. The following table (LXXIV) gives the data from a series of experiments on these lines—

<div align="center">

TABLE LXXIV

COMPOSITION OF COPPER-ZINC DEPOSITS CALCULATED
AND FOUND

</div>

	Brass $\overline{\text{Cu}^{++}}$	% Cu (Calcu-lated)	% Cu (Found)	% Current Depositing		
				Cu	Zn	Differences from 100
1	1·91	95·0	95·8	91·2	7·9	− 0·9
2	1·90	94·6	94·3	89·4	10·4	− 0·2
3	1·77	86·4	84·8	75·2	26·1	+ 1·3
4	1·60	73·5	72·8	58·4	42·0	+ 0·4
5	1·54	68·3	68·0	52·5	47·9	+ 0·4
6	1·52	66·5	65·5	50·0	50·8	+ 0·8

These figures at least indicate the possibility of depositing brass almost quantitatively, the little differences from 100 found in the last column representing either unavoidable errors or current depositing hydrogen, or possibly a little of each.

Similar expressions for other alloys are similarly deduced. In the case of the lead-tin alloys we may use a lead coulometer. Then—

Let a represent the weight of lead in the coulometer and b the weight of the alloy.

The chemical equivalents of the two metals are 103·5 for lead and 59·5 for tin. Let x represent the faradays depositing tin. The weight of tin deposited is therefore $59\cdot5x$ g. For each faraday depositing tin in the alloy there is a decrease of $103\cdot5 - 59\cdot5 = 44$ g.

Hence $\qquad a - b = 44x$

and $\qquad x = \dfrac{a - b}{44}$

Hence $\qquad 59{\cdot}5x = 59{\cdot}5\,\dfrac{(a - b)}{44}$

and the percentage of tin is

$$\frac{59{\cdot}5\,(a - b)}{44} \times \frac{100}{b} = \frac{135\,(a - b)}{b}$$

Hence with the two baths in series and the weights of lead and alloy 60 g and 45 g then—

$$\% \; \mathrm{Sn} = \frac{135\,(60 - 45)}{45} = 45 \text{ per cent.}$$

Cobalt-nickel Alloys. The co-deposition of nickel and cobalt has recently attracted a good deal of attention, especially with its association with the production of bright nickel deposits. The subject was under investigation prior to the possible application to bright nickel deposition which is effected by the addition of other reagents.

The two metals are very near to each other on the electrode potential scale and some interesting data are forthcoming from the analyses of numerous alloy deposits made in the course of the investigation on bright nickel. In the first place such solutions usually contain a small proportion of the cobalt compound of the order of one-sixteenth of that of the nickel sulphate present. Under normal operating conditions the percentage of cobalt in the deposited alloy is of the order of 15–18 per cent, and this proportion definitely decreases with increasing current density. These facts place cobalt as a metal more positive than nickel, although this is not indicated in the table of electrode potentials on page 192.

Further, Young and Gould* showed that increasing the rate of rotation of a cathode on which these alloys deposits were being made increased the cobalt content, this usually being regarded as some evidence that cobalt is more noble than nickel. Again, according to Weisberg,† the cobalt content of the alloys decreased with increased current density as shown in the following figures—

* *Trans. Amer. Electro-chem. Soc.*, Vol. LXIX, p. 585.
† *Trans. Amer. Electro-chem. Soc.*, Vol. LXXIII, p. 435.

TABLE LXXV

VARIATION OF COBALT IN DEPOSITS WITH CURRENT
DENSITY

| Current Density | | % Co in Deposit |
(A/ft²)	(A/dm²)	
20	2·15	27·7
40	4·3	17·7
60	6·45	13·4
80	8·6	11·2

This fact definitely places cobalt as more positive than nickel. There may be some anomalies in the behaviour of the two metals, being, as they are, so close together in the electro-chemical series, but the well-attested facts of decreased cobalt with increased current density and the larger proportion of cobalt in the alloy than in the solution are in agreement.

Deposition of Alloys from Organic Solvents. The industrial deposition of alloys has largely been practised from aqueous solutions. There are, however, many other possibilities, and it has, for example, been shown that silver-aluminium alloys are possible of deposition from non-aqueous solutions in spite of their very wide single potentials in aqueous solutions of their mineral salts. These and similar results were arrived at by the presence of metallic impurities in the deposited aluminium from the use of an impure anode. In this matter, a review of the potentials of the metals with respect to that of aluminium is of interest.* These are shown in Table LXXVI.

TABLE LXXVI

ELECTRODE POTENTIALS OF METALS IN AQUEOUS SOLUTIONS

Metal	Al	Zn	Fe++	Cd	Ni	Sn++	Pb	Cu+	Ag
Electrode Potential (V)	− 1·7	− 0·76	− 0·44	− 0·40	− 0·23	− 0·14	− 0·12	0·47	0·80
Differences from Al		0·94	1·26	1·30	1·47	1·56	1·58	2·17	2·50

* Blue and Mathers : *Trans. Amer. Electro-chem. Soc.*, Vol. LXIX, p. 529.

Corresponding differences from the potential of aluminium of the several metals in benzene are shown in Table LXXVII.

TABLE LXXVII

POTENTIAL DIFFERENCES OF METALS WITH RESPECT TO
ALUMINIUM IN THE BENZENE BATH

Metal	Zn	Cd	Pb	Sn	Cu	Ag	Fe	Ni
P.D. (V)	0·02	0·059	0·072	0·163	0·226	0·56	0·571	0·676

It will be seen that the differences from aluminium are quite small in comparison with those obtained in aqueous solution. This at once indicates the possibility of the deposition of alloys of aluminium with these metals. By introducing these metals into the usual bath for the deposition of aluminium, which is composed of aluminium bromide, aluminium chloride, and ethyl bromide in a mixture of benzene and xylene, alloys of aluminium with copper, zinc, cadmium, silver, tin, nickel, lead and mercury were obtained. These were usually of high aluminium content. In the case of copper, the metal was added in the form of cuprous bromide from which the metal was deposited with univalency. These results indicate possibilities in alloy deposition which have so far been little explored.

Silver Alloys. Even in aqueous cyanide solutions the deposition of silver alloys is by no means easy, for while the very positive character of the metal in its mineral salt solution largely disappears in the double cyanide compounds, it has been shown that practically pure silver can be deposited from these double cyanide solutions containing a large excess of copper,[*] and the pink colour sometimes obtained with deposited silver can therefore hardly be attributed to the presence of copper in relatively small amounts in the silver solution. Mathers and Johnson[†] have made a study of the co-deposition of silver with a number of other metals by choosing aqueous solutions containing other compounds, such, for example, as thiourea nitrate and thiocyanates, in which there is every possibility of the formation of complex salts, which condition

[*] *Trans. Faraday Soc.*, Vol. VI, p. 1.
[†] *Trans. Amer. Electro-chem. Soc.*, Vol. LXXIV, p. 229.

usually favours alloy deposition. In turn they produced alloys of silver and copper, the latter metal being present to the limit of 63·6 per cent. The copper alloys with silver decreased the resistance of the silver to tarnishing. Nickel alloys produced contained up to 74 per cent of nickel. They were characterized by their hardness but tarnished more readily than pure silver. Iron-silver alloys contained only a small proportion of iron. They were more resistant to tarnish but were not tarnish proof. With cadmium, which was obtained in alloy with silver up to 30 per cent, the deposits were only slightly more resistant to tarnish than silver alone. Co-deposited cobalt, as with nickel, increased the hardness but decreased the resistance of tarnish, while silver-lead alloys, produced from a solution containing potassium silver cyanide and potassium plumbite, developed alloys up to 72 per cent of lead, always tarnishing more readily than silver alone.

ADDITION AGENTS IN ELECTRODEPOSITION

Introduction. It has long been known, and the practice adopted, that the addition of relatively small amounts of certain substances vastly improves the physical characteristics of many electrodeposits. Thus as early as 1847 bright silver deposits were produced by Milward, and probably one-half of the silver solutions now in operation in the electro-plating of tableware yield deposits of this type, such solutions containing a minute amount of carbon disulphide. Since that time, and particularly more recently, many similar additions to electrodepositing solutions have with advantage been made. In general, these added substances are called "addition agents," and are present in such small amounts as not to appreciably alter the electrical properties of the solution. Further, their effects are only temporary. They are evidently absorbed into the deposits, necessitating periodic additions. One difficulty about their control is that of chemical estimation, and generally it can only be overcome by a close watch on the properties of the deposit with subsequent additions more or less on the basis of experience.

Many of these substances are said to be of a "colloidal" type, and some consideration of this problem is therefore called for.

Graham's Experiments on Diffusion. As far back as 1861 Graham observed marked differences in the rates of diffusion of substances ordinarily assumed to be in solution. This rate of diffusion was observed by placing the "solution" in a shallow boat made of parchment and floating it on water. The passage of solute through the parchment membrane into the water could be followed by chemical tests applied, and these quickly led to the conclusion that there was a wide variation in the rates of diffusion of different substances. Generally, the acids and their salts diffused comparatively rapidly. In the case of common salt, the addition of silver nitrate solution to what was originally pure water served to detect this diffusion. Other

substances, however, such as starch and albumen, both of which could readily be chemically detected, diffused only very slowly. Some relative rates of diffusion were determined by Graham, but in general he came to the conclusion that those substances which ordinarily crystallize also diffuse rapidly, while those of the non-crystalline type, such, for example, as gelatine and starch, diffuse only very slowly. He was thus led to divide roughly all these apparently soluble substances into two groups, (1) the *crystalloids* which diffuse rapidly and (2) the *colloids* which diffuse only very slowly.

So marked was the difference between the two classes of substances that Graham found it possible to separate crystalloids from colloids by the process of diffusion by frequently changing the water in the outer vessel. This separation was termed "dialysis," and finds many applications in the world of industrial colloidal chemistry to-day.

More recent investigation shows, however, that no such strict line of demarcation can be drawn, as a number of substances which take a definite crystalline form are, in solution, slow in diffusion, and therefore like colloids, while other non-crystalline substances behave normally when in solution.

Further, freezing-point determinations on substances in the colloid group show molecular weights of a very high order. That of starch, for example, is in the region of 33 000, indicative of a formula of the type $(C_6H_{10}O_5)_n$ where n is of the order of 200. Some determined molecular weights far exceed this value, necessitating a more definite classification.

Subdivision of Matter. It is generally recognized that solution effects the breaking down of materials to the order of molecular dimensions. Apart from dissociation we are, in solutions, dealing with individual molecules separated by mean distances determined by dilution. For these molecular dimensions we need some small units, and for this purpose two units, (1) the micron (μ) which represents $\frac{1}{10^6}$ metre, and (2) the $\mu\mu$, which represents one-millionth of a micron, have come into extended use. Molecular dimensions bring us down to the size of $\frac{1}{10^3}\mu$, while the microscope takes us down to 0·000 1 mm or $\frac{1}{10}\mu$.

Insoluble substances, on the other hand, are relatively

large, even in their smallest state of subdivision. Those fine
suspensions which are long in separating out are of the order
of $\frac{1}{10}\mu$, and here again there can be no sharp line drawn as
there is no reason to suppose that the processes of subdivision
take so sudden a jump from $\frac{1}{10}\mu$ down to 1μ. Comparisons
of these extremely small dimensions might be more easily
appreciated by multiplying them by 100 000 000, when $\frac{1}{10^3}\mu$
becomes 10 cm. Atoms would then be represented as a few
centimetres, and large colloidal particles 100–1 000 m.

In their behaviour to transmitted light suspensions are
larger than the usual light waves, and therefore cast shadows,
and are therefore readily seen by transmitted light. Molecular
dimensions, however, are below the wave-
lengths of light and are therefore "missed"
by transmitted light. They do not cast
shadows. By the use of oblique lighting,
however, their presence is seen by the scatter-
ing of light which they effect. This is known
as the Tyndall effect. The phenomenon is
similar to that of the dust particles in the beam of light in the
darkened room. By the application of this principle, diagram-
matically represented in Fig. 76, Zsigmondy made computa-
tions of the dimensions of these colloidal particles of silver and
found them to be of the order of $2 \cdot 3 \times 10^{-14}$ g in weight
and 8×10^{-6} cm in radius. Such material is said to be
ultra-microscopic. Moreover, it becomes possible actually
to count the number of particles in a given small mass
of the liquid, and we are thus getting near to counting
molecules.

FIG. 76.
PRINCIPLE OF THE
ULTRA-MICROSCOPE

This consideration thus seems to bring the matter down
to one of dimensions only, and to speak of the colloidal
state dimensionally seems preferable to the use of the term
colloids. Substances such as glue and starch are under any
circumstances definitely colloidal but, as has been said, there
is more difficulty in dealing with other substances which behave
differently in different solvents.

Classification of Colloids. In the realm of the colloidal state
there are considerable differences in dimensions and also in
properties. These differences are illustrated in the case of
colloidal gold and gelatine. Under the slightest pretext, such,

for example, as the addition of a small quantity of an electrolyte, colloidal gold separates as an insoluble powder which does not revert to the colloidal state by mere contact with the solvent. On the other hand, gelatine and its analogues separate only with difficulty, and then in contact with the solvent readily revert to their original colloidal form.

The nomenclature of colloidal substances has undergone some change. The two main groups are called—

(1) Hydrophobic (meaning water-hating) colloids, irreversible colloids, colloidal suspensions or suspensoids. These terms cover the group which includes the metal colloids which when precipitated do not easily pass back into the colloidal form.

(2) Hydrophilic (meaning water-loving) colloids, reversible colloids or emulsoids. These include glue and gelatine which, after drying, revert with water to the colloidal state with ease. They are also called colloidal solutions. The familiar glue-pot in use illustrates this.

The prefix hydro- relates to the colloidal state with water as the dispersion medium. For other liquids the prefix lyo- is substituted.

In the case of the suspensions, the terms "disperse phase" and "dispersing medium" are applied to those parts which in solutions are termed the solute and solvent.

In the case of the colloidal solutions, or sols as they are more briefly called, there appears to be a strong affinity with the solvent and, moreover, they are further divisible into two groups known as (1) colloidal electrolytes in view of the fact that they form definite groups which carry electric charges and are subject to migration under the influence of a potential difference, and (2) non-conducting colloidal solutions.

Colloidal Suspensions. In the case of colloidal suspensions in water there is little affinity between the disperse phase and the water. They are, as a rule, readily precipitated by the presence of small amounts of electrolytes. Their preparation therefore must be effected in the absence of such electrolytes. Several methods are available—

1. *Bredig's method* involves striking an arc between two points of the metal under water. The metal is vaporized under

the intense heat of the arc, and some of it is retained in the pure water in the colloidal form.

2. Chemical methods involve double decomposition in the absence of strong electrolytes. Thus sulphuretted hydrogen passed into an aqueous solution of arsenious acid yields colloidal arsenious sulphide, whereas from arsenic trichloride the sulphide comes down as an insoluble precipitate owing to the presence of the electrolyte (HCl) produced in the reaction.

Another method is that of chemical reduction, such, for example, as the reduction of auric chloride by the addition of a solution of yellow phosphorus in ether, or by tannic acid.

In some cases the mere washing of a precipitate with distilled water serves to take up the substance in the colloidal form. This occurs with cadmium sulphide, as students of analytical chemistry will know. Similarly, sodium hydroxide takes up chromium hydroxide and does not dissolve it.

Where electrolytes are produced in small and not immediately interfering quantities, they may subsequently be separated by the process of dialysis.

Properties of Colloidal Suspensions. Under the ultra-microscope, suspensions are observed with a definiteness which admits of an approximate computation of their size and mass being made. They are then shown to be considerably larger than molecular dimensions, this accounting for their slow diffusion and the low osmotic pressure which, under ordinary theory, results from large molecular weights. Moreover, under the ultra-microscope they are observed to be in a state of continuous vibratory motion. This phenomenon was observed as far back as 1823 by Brown, hence the name Brownian motion. This motion is due to the molecular bombardment of the molecules of the dispersion phase. It decreases with the increase in the size of the particle and disappears when these are of the order of 3μ diameter. Still further, these colloidal suspensions carry electrical charges and are divisible into two groups according to the charges which they carry. Thus the metallic hydroxides are positively charged while the metal colloids and the metallic sulphides are negatively charged. Another curious feature about these suspensions is the fact that they are easily coagulated by the presence of electrolytes, and further, the

precipitating power of these electrolytes has some dependence upon the valency of the coagulating ions.

Peptization and Coagulation. Further relevant terms may now be referred to. The production of colloids is termed peptization, a good example of which is the conversion of insoluble proteins into soluble peptones by enzymes in the digestive fluids.

The reverse process of converting the colloidal into insoluble material is termed coagulation or flocculation. This is often effected by heating and also by the addition of electrolytes, in which case there is some relation between the coagulating power and the valency of the ions.

Cataphoresis (Electrophoresis). Since colloidal suspensions are electrically charged they migrate to one electrode or the other under the influence of an applied p.d. This phenomenon was first called cataphoresis, in view of the fact that the observed effects were made with colloids migrating to the cathode. As, later, others migrating to the anode were observed, the more general term electrophoresis was substituted. From the point of view of electrodeposition, we are more concerned with those colloids which migrate to the cathode and there exert some beneficial effect on the character of the deposit. This cataphoretic motion is relative to the solvent. If the heavy gelatine ion migrates to the cathode it will be precipitated thereon. This is known as co-precipitation, minute quantities markedly influencing the crystalline structure and therefore the physical properties of the deposit. By the application of a diaphragm composed of the material of the disperse phase, the motion is stayed, then the solvent itself is set in motion, moving towards either electrode and, passing through the porous diaphragm, alters the levels of the water on either side. This motion of the dispersion medium is known as electro-osmosis. Some allowance for this effect must therefore be made in the determination of the hydration of the ions by the measurement of the amount of water carried with the ion into or from the catholyte.

This phenomenon has applications other than that of producing smooth electrodeposits. For example, if a current is passed through rubber latex between suitable electrodes, the colloidal rubber migrates to, and is deposited on, a zinc anode. The addition of a vulcanizing agent produces a deposit which

is then amenable to "curing," and many articles are thus producible in deposited rubber by the use of anodes of convenient forms. Normal currents of the order of 1 A/dm^2 are used for this purpose, the weight of deposit being of the order of 3 g/A min, and up to a thickness of 1 cm.

Similarly, many clays exhibit colloidal properties, and advantage is taken of this property in separating, by a process of electrophoresis, the purer form from the natural and impure clay, the process having long attained industrial importance.

Amphoteric Colloids. Again, some of these colloids do not exhibit a permanent charge of either sign. In the case of gelatine its charge varies with the $p\text{H}$ of the solution. Gelatine has a very high—yet not exactly determinable—molecular weight. It may be of the order of 30 000. It exerts very little osmotic pressure. As an amphoteric substance, it is capable of dissociation in two ways, according to the chemical nature of the "atmosphere." This amphoteric behaviour arises from its chemical constitution. Gelatine belongs to the group of complex amino acids of the general formula $R\diagup_{NH_2}^{COOH}$ in which R represents a complex organic radical, while COOH and NH_2 represent the not necessarily simple acidic and basic groups. In the presence of an acid, the amino group comes into reaction with the formation of a gelatine salt, the chloride, for example, which may be written $R\diagup_{NH_3Cl}^{COOH}$. This salt is capable of ionization as follows—

$$R\diagup_{NH_3Cl}^{COOH} \xrightarrow{\longrightarrow} \left(R\diagup_{NH_3}^{COOH} \right)^+ + Cl^-$$
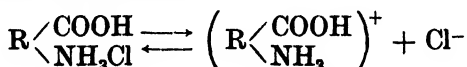
and this explains the migration of the complex gelatine radical to the cathode.

In the presence of a base, however, the COOH group enters into reaction, forming a salt of the type $R\diagup_{NH_2}^{COONa}$ which again is amenable to ionization as follows—

$$R\diagup_{NH_2}^{COONa} \xrightarrow{\longrightarrow} \left(R\diagup_{NH_2}^{COO} \right)^- + Na^+$$
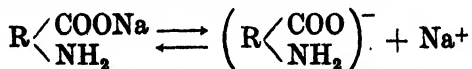
giving a complex gelatine ion which migrates to the anode. The

critical or iso-electric point for gelatine and many complex proteins is an acidity of pH 4·7, this being regarded more as a range of pH than an actual point. At this acidity gelatine is neutral, migrating neither in one direction nor the other. At lower pH, including therefore the conditions of the acid copper bath, the gelatine migrates to the cathode and there exerts some beneficial influence. This good influence, however, is not observable when gelatine is added to the alkaline bath as, at the pH then ruling, the gelatine complex is negatively charged and so migrates to the anode. Very doubtful or negative results attend the addition of gelatine to the acid zinc and nickel baths, in both of which pH's are above the iso-electric point. This view of the behaviour of gelatine based on its chemical constitution at least offers some reason for its observed results when added to electrodepositing solutions.

Applications in Electrodeposition. There are numerous applications of these migrating colloids with absorption and improved characteristics of the deposit. Probably the first record was that referred to in the case of the bright silver deposit by the addition of carbon disulphide. In 1885 Kiliani, exploring the conditions for the electrolytic refining of copper, observed the improved appearance of the deposit in the presence of tin in the crude copper, and therefore in the solution. Doubtless the tin compound in the solution hydrolized with the production of some colloidal hydroxide which was responsible for the improvement in the deposit.

Since that time many other observations have been made, recorded, and usefully applied. To mention only a few, the addition of gelatine to the acid copper bath and more recently the use of phenol-sulphonic acid are everyday applications. Lead deposits are particularly susceptible to "treeing," that is, the formation of long tree-like crystalline growths, but a miraculous change for the better is made with the addition of gelatine or glue in the fluosilicicide solution as used in the Betts' refining process, or the addition of peptone to the acid perchlorate bath. For the fluoborate solution glue makes a useful addition, while dextrine in the cadmium solution is common practice. " Acid " zinc sulphate solutions are improved by the addition of aluminium sulphate, presumably with the hydrolysis and the production of colloidal aluminium hydroxide.

Few practical depositing solutions are entirely free from such additions. Consumption of these so-called "addition agents" is definite but small, probably of the order of $\frac{1}{2}$ to 1 lb. per ton of deposited metal, and this loss is caused by the minute addition of the precipitated colloid into the deposit.

In the electrolytic extraction of zinc (page 213), gelatine has a similar effect to that in the low pH acid copper bath. This has been recorded by Pring and Tainton.* Personal experience of this process confirms this observation. The cathode efficiency is increased with a concomitant reduction in the volume of hydrogen given off. If also the gelatine has formed a froth on the surface of the electrolyte, the acid spray from the evolved gas is filtered before reaching the atmosphere, thereby also resulting in a cleaner atmosphere in the cell house.

One objection to the use of these addition agents, in spite of their recognized advantages, is the difficulty of control by analysis, and this difficulty is dependent not only on the small amount present, but also by the fact that, with continued electrolysis, the chemical characteristics of the added substance change beyond recognition. Thus after a short period of electrolysis the phenol added to the acid copper bath is not detectible, but the good influences still persist. Presumably the phenol has undergone chemical transformation with the production of other substances not readily recognizable by chemical analysis, but of even improved effects on the deposit. This process of bringing the solution into its most effective use is called "ageing," and has long been practised empirically and still obtains some use. In the absence of analytical work the further additions of the agents can only be made upon inspection of the deposit, and this is a somewhat more arbitrary method of control than one governed by exact analysis.

Glycocoll has a recognized beneficial effect in the acid copper bath. This has been studied by Fuseya and Nagari,† the amount added being 0·01 molal (0·01 gramme-molecule per litre). This addition increased the conductance. This is suspected to be due to the formation of complexes which may dissociate to a considerable extent. The glycocoll passes into the deposit proportionally to the current density. Complex

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* *J. Chem. Soc., 103,* 710 (1914).
† *Trans. Amer. Electro-chem. Soc., 1,* 235 (1926).

ions would simultaneously lower the concentration of the copper ions and this, in turn, would lead to smoother deposition.

It was early observed by Spear,* and Wen and Kern,† that the beneficial effect of gelatine in copper deposition was noticeable only "after some time," evidently another illustration of ageing.

Theory of Addition Agents. The presence of small amounts of addition agents in deposits has been repeatedly recorded. Metallurgical experience expects us to look as a first result to a reduction on the crystal size in the presence of such impurities. At the same time it is observed that usually such organic additions increase the brittleness of the deposit, and in these days when every effort is being made to improve the ductility of deposited metals the use of these additions does not offer all the advantages that could be desired. Nor is it possible to give credence to the suggestion that the extraordinarily fine grain growth of the mirror-like deposits of bright nickel—to take one example—is due to such inclusions, especially as in this case, these mirror finishes are obtained without any addition of the type which would yield colloidal constituents in the solution.

According to one definition of an addition agent there should be no marked change in the electrical properties of the solution. This would, of course, exclude sulphuric acid in the acid copper bath from effecting the rôle of an addition agent. Nevertheless sulphuric acid does improve the physical character of copper deposits, and some of these addition agents do make for an increased electrical resistance of the bath. This appears to be due to the fact that, migrating with the metal ions, they may form some type of high resistance diaphragm round those portions at which they have congregated by reason of increased current density on prominent areas. Building up such a film would divert the current from these more prominent parts of the cathode, and thus make for increased throwing power and a more uniform deposit. One observer stated that the addition of 0·1 per cent of gelatine to a copper bath doubled its resistance. The presence of gelatine in the acid copper bath has been

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* *Trans. Amer. Electro-chem. Soc.*, *22*, 277 (1912).
† *Ibid.*, *20*, 121 (1911).

observed by many workers to increase the cathode potential. This may be due to the accumulation of the heavy and slowly-diffusing ions (few of which are co-precipitated), thereby slowing up the transportation of the inorganic cathions. This effect is not observable at the anode under these acidic conditions. As a diaphragm movable in the direction of high current density at prominent spots, these colloids decrease the current on these exposed parts, and this makes for a more even deposit. This suggestion does not account for the loss of the colloid, and it has been shown that from a copper solution containing gelatine a cathode efficiency of over 100 per cent could reasonably be accounted for by the amount of gelatine added to the solution.

Again, adsorption of the migrated colloid with a reduction of the grain size of the deposit is put forward as another explanation of the improved deposit. It has, too, frequently been pointed out that many addition agents are chemically reducing, and might therefore have some good influence by the reduction of basic compounds in the liquid film adjacent to the cathode.

The chemical view to which reference has been made and which has been put forward by Frölich* provides a reasonable explanation of the presence in many cases of addition agents in the deposits by the process of "co-precipitation," the migrating colloid being discharged in contact with the cathode and deposited with the metal.

The moving diaphragm theory would account for the improved throwing power in the presence of addition agents by its deflection of the current from the prominent to the more recessed parts of the cathode. Alternatively, it would account for the greater difficulty in the migration of the copper ions towards the cathode, leading to a decrease of copper ion concentration and with it increased cathode potential and therefore improved throwing power.

Another suggestion has been made† that these addition agents are beneficial because they—being of a reducing type —effect some reduction of local basic materials, the presence of which accounts in some cases for the roughness of deposits.

The whole problem is one of interest upon which new lines

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* *Trans. Amer. Electro-chem. Soc.*, (1924).
† Betts: *Trans. Amer. Electro-chem. Soc.*, 8, 64 (1905).

of evidence will doubtless be forthcoming. In the meantime, more accurate empirical knowledge of the behaviour of these substances should facilitate the formulation of a more accurate conception of their exact rôle.

While many of these brightening effects in electrodeposition have been arrived at quite empirically, a closer examination of the problem has revealed some of the mechanism of the changes involved. Thus Egeberg and Promisel,* assuming that carbon disulphide is not the real brightening agent in the usual bright silver solution, although invariably the substance added to produce that effect, investigated the results of the addition of sulphur compounds of the thiourea and dithiocarbámate classes, which might result from the reaction of the added carbon disulphide with the other constituents of the solution. Some of these they found to be very effective in brightening silver deposits, and they were able to deduce a general formula of the type $CS_x(NA)$ (NB) where x may equal 1 or 2 and A and B might be hydrogen or hydrocarbon (preferably methyl) groups. A number of the additions gave mirror-like deposits far exceeding the usual brightness previously obtained with carbon disulphide. While, too, the brightness might be due to the co-deposition of sub-microscopic silver sulphide, which may in turn modify the crystal structure of the silver, it was thought that this did not afford a complete answer to the problem.

* *Trans. Amer. Electro-chem. Soc.*, Vol. LXXIV, p. 211

STRONG ELECTROLYTES

Introduction. Several references have already been made to the fact that strong electrolytes exhibit behaviour which is not altogether consistent with what might be anticipated from the conclusions drawn from experiments with weak electrolytes. The terms "strong" and "weak" as applied to electrolytes refer to the degree of ionization at what may, in general, be called moderate concentration. For example, acetic acid is only very feebly dissociated. It is a weak electrolyte, while potassium chloride at normal strength is considerably dissociated. It constitutes a "strong" electrolyte.

Strong electrolytes may be roughly regarded as those which at 0·1 N strength are dissociated to the extent of 50 per cent or more. Other electrolytes are weak.

All practical electrodepositing solutions come within this category of strong electrolytes. Some idea of the electrochemistry of these solutions will be necessary in order to comprehend more fully the mechanism of the depositing process. This process is by no means simple. It has obviously been desirable to treat the theory of solutions in as simple a manner as possible, as it was with the weaker electrolytes that so much of the conception of the *modus operandi* was first worked out. However, strong electrolytes constitute those in common use. Hence some, at least simple, survey of their behaviour becomes necessary.

At moderate dilutions, therefore, there are numerous ions in a given volume of strong electrolyte. A general study of the behaviour of solutes, whether dissociated or not, leads to the conclusion that they are in a form somewhat analogous to that of gases. The solid substances have in fact evaporated into an atmosphere of solvent and there behave in a manner very similar to that of a liquid which has evaporated into a vacuum. Now these gases exhibit well-defined behaviour under pressure and also with changes of temperature. These are known and have been dealt with in Chapter IV. There it was shown that

there are considerable deviations from the known simple laws when the pressure is high, that is, when the molecules are more concentrated. When, for example, the molecules are close together, intermolecular attractions are evident which are altogether negligible in the gas in the more attenuated form. These molecular attractions seem to be putting the gas under a pressure greater than that recorded. These attractions are capable of physical computation and take the form of the a/v^2 factor introduced into Van der Waal's modification of the usual $PV = RT$ equation.

Abnormalities in the behaviour of gases are thus explained and the problem of strong electrolytes might with advantage be compared with that of the "strong" or highly compressed gas.

Take, for example, the case of an equivalent solution of sodium chloride. Assume for the moment that it is undissociated. Consider its osmotic pressure. Reference to Chapter V will show that for the osmotic pressure to be the equivalent of atmospheric pressure, the concentration of the salt should be of the order of a gramme-molecule in 22·32 litres of solution. The normal solution of salt will thus have, without dissociation, an osmotic pressure of 22·32 atm. This osmotic pressure is considerably increased (almost doubled, in fact) due to ionization and we thus have the salt "vapour" in a somewhat compressed form, possibly introducing factors not present in the more attenuated material of dilute solutions.

Again, the osmotic pressure of strong sugar solutions is far greater than that in accordance with the usual simple law, and this is explained by the suggestion that sugar molecules combine, although loosely, with water molecules, leaving less free water as solvent and therefore increasing the concentration of the solution.

Here, then, are possibilities which might be explored to see whether they have any application to electrolytes. In other words: Are the ions as simple as is indicated by the well-known symbols such as Na. for sodium and Cl^- for chlorine?

Are the Ions Simple? Consider for a moment the relative rates at which these ions migrate under similar electrical conditions. These rates have already been set out in a previous chapter (IX), but for the sake of clearness a few examples are given. These are the cases of the alkali metal ions, and their

relative rates of migration are compared with their ionic masses, thus—

TABLE LXXVIII
MIGRATION RATES OF ALKALI IONS

	Li	Na	K	Rb	Cs
Ionic mass . . .	7	23	39	86	133
Relative rate of migration .	9·8	13·1	19·6	20·5	20·7

Here is shown the somewhat surprising fact that the lighter ions move more slowly than the heavier ions. The same kind of effect can also be seen in other cases of ions which, by chemical classification, are regarded as somewhat alike. We are forced to ask whether the ions are as simple as the usual expressions for them (Na. and Cl⁻) indicate.

Hydration of Non-electrolytes. Now there is plenty of evidence to suggest that when a substance dissolves in water it forms either definite chemical compounds with the water or, alternatively, some loose associations by a concentration of water molecules around the molecule of the solute.

It is, for example, well known that solutions have higher boiling-points than the solvents, and also lower freezing-points. A salt solution boils at over 100° C. and freezes at below zero. This is a very general rule. When salt or sugar molecules have been added to the water it is more difficult to separate water molecules either in the gas form by boiling, or in the solid form by freezing. There is evidently some combination or attraction between the molecules of the solute and those of the solvent.

Again, another physical property of solutions points in the same direction. Water, for example, dissolves gases and, to take the case of an inert gas, that is, one which does not combine and form compounds with water, hydrogen may be selected. The determination of the solubility of hydrogen in water is, to those experienced in this work, a relatively simple matter. Under standard conditions 1 000 g of water will dissolve a certain definite volume of hydrogen gas. The same quantity of water to which sugar has been added dissolves only a smaller volume of hydrogen. It would appear from this that in

the solution only a part of the water is "free" to perform the function of dissolving hydrogen, while the remainder is in some manner fixed and not available for dissolving hydrogen.

Moreover, the reduced volume of hydrogen dissolved gives some indication of the amount of water not now free, and it is on these lines that the problem has been explored.

In Table LXXIX we have the results of experiments carried out on the reduction of solubility of hydrogen in solutions of cane sugar ($C_{12}H_{22}O_{11}$) of varying concentrations.

TABLE LXXIX

Percentage Strength	Density	Cubic Centimetres H absorbed by		Molecular Hydration
		1 litre Solution	1 000 g Water	
0	1·000		18·83	
16·67	1·068	15·61	17·54	6·5
30·08	1·129	12·84	16·25	6·0
47·65	1·218	8·92	14·02	5·4
(1)	(2)	(3)	(4)	(5)

Take the case of the 16·67 per cent solution. A litre weighs 1 068 g of which 16·67 per cent is sugar, that is, 178 g dissolved in 890 g of water. This dissolves 15·61 cm³ hydrogen. In 1 000 g of water there would be a corresponding solution of $15·61 \times 1\,000/890 = 17·54$ cm³, which is recorded in column 4. This figure is markedly less than that for 1 000 g. of water in the absence of sugar. The difference represents the proportion of the water not free for dissolving hydrogen and, therefore, presumably, combined with the sugar. Hence—

$$\text{Fraction of water not dissolving hydrogen} = \frac{18·83 - 17·54}{18·83}$$

$$\text{Water combined with 1 g sugar} = \frac{18·83 - 17·54}{18·83} \times \frac{(100 - 16·67)}{16·67}$$

and

$$\text{Mol. water per mol. sugar} = \frac{18·83 - 17·54}{18·83} \times \frac{(100 - 16·67)}{16·67} \times \frac{342}{18}$$

$$= 6·5$$

This figure is entered in the last column of the table, and other similar values are derived for other concentrations. These are not necessarily whole numbers. The probability is that there will be a series of hydrates, in which case there should be, according to the well-known law of mass action, a greater degree of hydration in the more dilute solution, and this is indicated in the results obtained by this method.

It will thus be seen that there is clear evidence that sugar molecules become hydrated when dissolved in water. Further, the degree of hydration increases with dilution. This again is as might be expected from the law of mass action.

Many examples of inorganic salts which combine with water in more than one proportion are known. Copper sulphate crystals are $CuSO_4.5H_2O$ at ordinary temperature. With a slight elevation of temperature water is lost progressively until a fairly stable monohydrate, $CuSO_4.H_2O$, remains, the remaining molecule of water demanding a much higher temperature for its expulsion. Again, from solutions of sodium sulphate below $32 \cdot 4°$ C. the crystals obtained are $Na_2SO_4.10 H_2O$, while those obtained from solutions above this temperature are anhydrous. The temperature mentioned, therefore, is the limit for the existence of the hydrated molecules.

This combination of solvent molecules with ions or molecules is termed "solvation," and thus the term hydration becomes a specialized application to aqueous solutions. This conception of hydration was originally due to Jones, who introduced it in 1899 to account for some of the otherwise unexplainable observations on the behaviour of electrolytes.

Data for another substance, chloral hydrate ($CCl_3.CHO.H_2O$) and given in Table LXXX, show that here there is no formation of similar hydrates, this being deduced by the constancy of the figures in column 3.

Abnormal Osmotic Pressures. In this connection it may be of interest to compare some examples of abnormal osmotic pressures, especially in the case of non-electrolytes. These will be seen to bear a similar interpretation. The results shown in Table LXXXI were obtained for sucrose and dextrose.

In both cases there is an abnormally rapid increase of the osmotic pressure with increase of concentration. While this might be regarded as indicative of a loss of solvent it might

TABLE LXXX

HYDROGEN ABSORPTION BY CHLORAL HYDRATE SOLUTIONS

| Percentage Strength | Cubic Centimetres H absorbed by | |
	1 litre of Solution	1 000 g Water
4·01	18·39	18·95
7·69	18·02	18·92
14·56	17·12	18·78
18·77	16·53	18·69
29·5	15·42	19·07
(1)	(2)	(3)

TABLE LXXXI

ABNORMAL OSMOTIC PRESSURES OF SUGAR SOLUTIONS

| Sucrose | | Dextrose | |
Grammes per litre Solution	Osmotic Pressure (Atm)	Grammes per litre Solution	Osmotic Pressure (Atm)
180	13·95	99·8	13·21
300	21·77	199·5	29·17
420	43·97	319·2	53·19
540	67·51	448·6	87·87
660	100·8	548·6	121·2
750	133·7		

not be safe to regard this as the sole reason for the abnormality. Other factors, not too well explored, may make some contribution.

Hydration of Electrolytes. It will now be of interest to observe the hydration of an electrolyte. As an example, potassium chloride will be selected. Figures comparable with those obtained with sugar are embodied in Table LXXXII which show a larger degree of hydration than with sugar.

Extend this method to a number of other electrolytes. The degrees of hydration in terms of molecules of water per molecule of solute, given in Table LXXXIII, are generally accepted for normal solutions.

TABLE LXXXII

HYDRATION OF KCl

Percentage Strength KCl	Density	Cubic Centimetres H absorbed by		Molecular Hydration
		1 litre Solution	1 000 g Water	
0			18·83	
3·83	1·024	16·67	16·93	10·6
7·48	1·047	14·89	15·36	9·4
12·13	1·078	12·79	13·5	8·5
19·21	1·128	10·12	11·10	7·2

In the case of electrolytes, however, we meet with the complication that the solute is in part dissociated. The ions, too, may be hydrated and to extents which differ from the molecular material. In most of the examples recorded, the degree of dissociation is considerable, and we are therefore more concerned with ions than molecules. The problem becomes complicated, but if we for a moment assume nearly complete dissociation, we have some idea of the degree of hydration of the two ions concerned in each case.

TABLE LXXXIII

MOLECULAR HYDRATION OF N. SOLUTIONS

Sodium chloride   .   .   . 11
Potassium chloride   .   .   .   9·4
Magnesium sulphate .   .   . 25
Sodium hydroxide   .   .   . 20·5
Potassium hydroxide .   .   . 19·5
Lithium iodide 40

Taking the figures in Table LXXXIII it will be obvious that in the cases of the three alkali metal halides of lithium, sodium and potassium we have in each case the same amount of the halogen ion. We may not at present know the degree of hydration of this ion. At any rate we have no reason to believe that it is markedly different in each case. This, therefore, leads to the conclusion that the lithium ion is more heavily hydrated than that of sodium, which in turn is more hydrated than the potassium ion.

These results would therefore seem to be in harmony with the relative rates of migration. Lithium ions in migration are

dragging with them a number of molecules of water, the bulky aggregate meeting with more resistance than in the case of an ion less hydrated or even free from hydration.

Apparently, therefore, the ions are not so simple as may at first have been imagined, but at the same time it is a difficult matter to separate completely the problem to get any accurate idea of the degree of hydration attaching to the individual ions.

Assume for the moment that lithium ions are associated with water molecules. Whether in the form of a definite chemical compound or only as a relatively loose association need not for the moment matter. The migration of the lithium ion will then cause the flow of water towards the cathode, thereby increasing the quantity in the cathode compartment of the cell. There is also to be taken into account that which is similarly transported by the process known as electro-osmosis, which refers to the movement of the solvent towards electrodes under the electrostatic influence of the applied e.m.f.

Imagine a cell with a carefully prepared diaphragm made of gelatine so that the exact amount of water passing towards the cathode when lithium chloride is electrolyzed can be determined. Making a correction for electric endosmose, the quantity of water per faraday may thus be obtained and at once associated with the quantity of lithium migrating. In this case, again, some note must be taken of water which may be electrically carried in the opposite direction by the anion— seemingly a complex set of circumstances.

Yet this principle has been applied with varying degrees of success by a number of workers. While not altogether harmonious quantitatively, they do agree that there are different degrees of hydration of the alkali ions, and also that this is in the order anticipated by the apparently abnormal migration rates. The method adopted can at the most give comparative degrees of hydration, but as the result of a considerable amount of work the approximate degrees of hydration of a number of the ions are given as follows—

$$Br = 3; \ Cl = 5; \ K = 5; \ Na = 8 - 9; \ Li = 13 - 14$$

This is another example of the fact that electro-chemical phenomena are not of the most simple type, for in this case we

have not been concerned with the transport of simple ions but, as later investigation shows, that of complex hydrates, and the amount of combined water at once alters the concentration of the solution and the speed of the ion.

Several other methods have been applied to the experimental determination of the degree of ionic hydration. In one method adopted by Washburn,* the determination of the transport numbers was made in aqueous solutions containing a definite addition of a non-electrolyte, such, for example, as raffinose. This substance, which is a form of sugar, can be determined by an optical method, because its solutions rotate plane polarized light. Introduced into an electrolyte, its changes of concentration in both anolyte and catholyte will be due to the quantities of water carried in either, or both, directions by the hydrated ions. If a number of electrolytes with a common anion —chlorine in chlorides, for example— are taken, then these changes of the water carried over can be more definitely assigned to the cathions. Such experiments confirmed the expectation that lighter ions are more heavily hydrated. From the relative masses of the non-hydrated and hydrated ions some computation of their relative speeds can then be made, and from this we have some idea of the true as distinct from the apparent rates of migration of the ions. This difference is usually small and for most purposes may be neglected, though giving some slight difference to all values in which transference numbers are a factor.

By the use of such an indifferent reference substance and with some allowance for electro-osmosis, some idea of the relative degrees of hydration of the two ions concerned can be arrived at. The data can, in any case, only be relative and conversion to more absolute values is based on the recognized fact that large organic ions carry no water of hydration, and this provides a starting point in the determination of the absolute degrees of ionic hydration.

It was by this method that the following amounts of ionic hydration were determined on the assumption that the hydrogen ion is mono-hydrated—

$$Cl = 4; \ Li = 14; \ Na = 8 \cdot 4; \ K = 5 \cdot 4; \ Cs = 4 \cdot 7$$

'ʲ* *J. Amer. Chem. Soc.*, *31*, 322 (1909); *J. Amer. Chem. Soc.*, *37*, 694 (1915).

As far as the alkali ions are concerned, this hydration follows the progressive lines which might be expected from Mendeleef's classification of the elements and accounts for the somewhat unusual rates of migration to which reference has already been made.

These and similar results give clear evidence that usually light ions are more heavily hydrated than the heavier ions.

Further, these "hydrates" should be less conspicuous in dilute solutions.

As will also be anticipated, these hydrates will be less stable with elevation of temperature, and it will be recalled that the disparity between the relative rates of migration of the ions is decreased with an increase of temperature.   Illustration of this has already been given in Chapter IX, Table XXXIV, page 123.

The fact of ionic hydration, however, cannot be regarded as adequately explaining the known deviations of strong electrolytes from Ostwald's dilution law (Chapter VIII), otherwise they ought to come into line in the more dilute solutions.

Some further factors must be sought.

Complex Ionic Compounds. Referring again to Chapter IX it has been seen that there is evidence for the combination of ions with molecular material, the complex ions thus formed introducing marked deviations from simple theory. Thus, the anion I^- has been shown in relatively strong solutions to give a transport number in some cases exceeding unity, and this has been shown to be due to the combination of the iodine ion with molecular cadmium iodide leading to the transport of excess of iodine together with cadmium in the form of a complex ion to the anode.

Is this formation of complex ions a phenomenon of relatively occasional occurrence or has it a wider application than may have been imagined? Recent work goes to show that the formation of complex ions is a relatively frequent occurrence, and, if this is so, we may have another cause for the anomalous behaviour of some electrolytes. To deal with the matter quantitatively demands some mathematical treatment and the introduction of physical phenomena rather beyond the scope of an elementary treatise. It may, however, suffice to say that there is now adduced abundant evidence of the existence of

the complex ions. It has been shown, for example, that in the case of rhubidium and magnesium sulphates, the metal ions may be made to migrate to the anode in the presence of a large excess of the sulphate of the other element, and in many cases there is evidence of more metal migrating to the anode in the form of a complex ion than towards the cathode in the form of the simple metal ion.

Exceptional cases of the complex ion formation occur in the cases of the double cyanide compounds largely used in electro-depositing processes, and in which the formation of complex ions is practically complete. There is every possible tran-sitional stage from the complex ion condition to that of the simple ions in very dilute solutions. If such complexes exist, and the evidence that they do seems to be undisputed, they will certainly constitute factors with an important influence on the mechanism of electrolysis, introducing deviations from the well-defined simple laws deduced in their absence. Generally, it has been the experience of scientific discovery that the first simple observations sufficed for the formulation of the first simple laws, which required amplification as the range of knowledge with its complexities increased.

The theory of complex ions still leaves us with the thought that ionization in solution is only partial.

The Theory of Complete Dissociation. Other workers have gone much further than this and have suggested that for many electrolytes the dissociation is complete even in solutions of moderate strength. If this is the case, the idea of degree of dissociation as deduced from the relation of the equivalent conductance to the maximum value at infinite dilution, will require considerable modification. If the thought of degree of dissociation seems so simple and clear that we may be loth to have to modify it, we have still to account for this markedly abnormal behaviour of so many well-known electrolytes to the dilution law. Towards the explanation of this abnormality there has been advanced the theory of complete dissociation, and it was with this in mind that, when the relation between equivalent conductance and the maximum values was con-sidered, the term conductance ratio was introduced as an alternative to degree of dissociation. The former term simply expresses a fact, while the term degree of dissociation introduces

an interpretation of the facts which may be open to some objection.

Going still further back to the substance in the solid form we have now, by the more recently introduced methods of crystal analysis by means of X-rays, some idea of the ultimate constitution of crystals, and here it has been abundantly shown that, for example, the ultimate structures of the NaCl or KCl crystals do not consist of arrangements of molecules of these substances but rather of the ions themselves. Their freedom of motion is exceedingly small, but their presence accounts for the otherwise unaccountable, though slight, conductance of these substances in the solid form.

Again, if in the form of solution the salt is completely dissociated, we have still to explain the apparently steady increase in equivalent conductance with dilution.

To account for the observed facts the theory has been advanced by Debye and Hückel that the oppositely charged ions have some influence upon each other. Quite apart from the formation of hydrates, it may readily be conceded that a positively charged ion of sodium may constitute a nucleus around which there will be some tendency for the collection or segregation of oppositely charged chlorine ions. During their migration to the anode those chlorine ions are possibly dragging with them a sodium ion, or at least impeding its migration, towards the cathode, thereby introducing a complex circumstance not allowed for in the simple development of the theory of Arrhenius.

This ionic atmosphere, which is in equilibrium in the absence of ionic migration, at once becomes disturbed when migration begins, the atmosphere being dissipated at the rear of the ions while a new one is formed with the movement of the ion. This must involve a time factor and constitute impedance to the movement of the ion. In addition, the moving ion imparts some of its motion to the molecules of the solvent, this providing a further frictional resistance to the movement of the ion.

According to this theory of complete dissociation, the increasing equivalent conductance with dilution is due, not to an increasing proportion of ions, but rather to the greater mobility of the maximum number of ions already existing even in the strong solution.

The subject is one which calls for some advanced physical treatment, but this includes the idea that the retardation caused by the breaking up of these ionic atmospheres is in some measure dependent upon the square root of the concentration, which is in accordance with Kohlrausch's formula to which reference has been made on page 113.

The explanations of the anomalous behaviour of strong electrolytes therefore involve two diametrically opposed suggestions, one involving the complete dissociation of the substance at all concentrations, and the other definitely suggesting only partial dissociation. It may be recalled that with the introduction of the theory of dissociation by Arrhenius more than sixty years ago, this entirely new conception was opposed by prominent British chemists, who put forward an alternative suggestion that the newly observed properties of these electrolytic solutions were due in part at least to the formation of complex hydrates. Some amalgamation of these two ideas has, after many years, come to be accepted, and one wonders whether apparently opposite views on the constitution of strong electrolytes may yet come to be reconciled with each other.

These and other modifications of the conceptions of the constitution of strong electrolytes receive experimental confirmation in the case of univalent ions. In the case of divalent ions, however, the discrepancies are greater than can be attributed to experimental error, but it has been shown by Davies* that decinormal solutions of the sulphates of copper, zinc, cadmium and magnesium are approximately half dissociated, a degree exceeding that shown in the table given on page 95.

This, again, is a matter which calls for some advanced physical treatment, but it is beginning to be conceded that we have, in the suggestions made, some hope of a clearer view of what is taking place in all electrolytes. The phenomena are much more complex than was at first thought, and it is being slowly and surely unravelled. While we may regard it as unfortunate that the matter does not admit of simple treatment, there is something to be said for developing a simple conception of the process of electrolysis which, while inadequate to account for

increasing knowledge, at any rate gives a working knowledge of the operations of electrolysis and provides some simple explanation of many of the observed facts.

A more complete and satisfactory conception of the mechanism of electrolysis is apparently a problem of the future.

BI-POLAR ELECTRODES

Introduction. In all examples of electrolysis opposite types of reactions take place at the two electrodes, anode and cathode. At the anode the reactions are always of the oxidizing type, oxygen being evolved or metals taken into solution and valencies increased, such, for example, in the oxidation of ferrous to ferric compounds and those of chromic salts to chromic acid.

At the cathode, reactions of the opposite type occur. Hydrogen is commonly evolved. Metals are reduced from their salts and deposited. Hexavalent chromium is reduced to the trivalent state in the dichromate cell and further to the metallic form in the usual method for the deposition of chromium. In the Bunsen and Grove cells nitric acid is reduced to the lower oxides of nitrogen.

These reactions are persistent. We do not expect the deposition of metal on an anode nor the evolution of oxygen at a cathode. Moreover, these opposite types of reactions immediately affect the compositions of the anolyte and catholyte.

Separation of Anolyte and Catholyte. In many examples of electro-chemical work there comes the need for the separation of these two portions of the solution. In the Daniell cell the copper sulphate must be kept away from the zinc, and in the Grove cell the nitric acid and zinc are necessarily separated.

This separation can be, and is, effected in a number of ways. Sometimes the bulk of the electrolyte may constitute a sufficient separation. In other cases, one of the liquids may be separated from the other by some type of gravitational overflow as, for example, in some types of alkali cells. A very common method is that of the use of some type of porous and non-conducting medium which admits of the liquids establishing electrical contact within the pores of the material without free admixture. The usual type of porous cell exemplifies this, while on the industrial scale porous diaphragms compounded from asbestos and cement find application. If any detrimental contamination

is likely, this can be largely prevented by the adjustment of the levels of the two liquids.

Metallic Diaphragms. There is still the possibility of the use of metallic diaphragms. These will be quite impermeable to the liquids but they will be conductive. In the simplest case Fig. 77 shows a copper sulphate solution with copper electrodes. An additional thin copper plate (*a*) is placed between them without any electrical connection other than that which comes through the solution. Ammeter and voltmeter attached to the
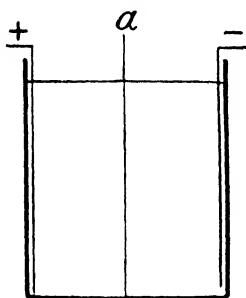
FIG. 77.
BI-POLAR ELECTRODE
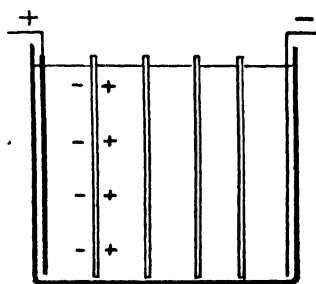
FIG. 78. SERIES SYSTEM OF
COPPER REFINING

cell indicate that the introduction of this thin plate involves little or no change in the electrical conditions of the cell. Inspection reveals the fact that a copper deposit appears on the side facing the anode, while that opposite to the cathode functions as an anode. Such a plate is called a bi-polar or secondary electrode. The only difference introduced with the copper plate is the substitution of a good conductor in place of a very thin layer of the poorly conducting solution, and it is assumed that on the secondary electrode the anode and cathode efficiencies are theoretical, involving, therefore, no consumption of electrical energy (usually registered in the form of an increased p.d.) as a result of secondary changes.

This principle finds application in what is known as the "series" system in copper refining. In Fig. 78 the end plates are definitely made anode and cathode as shown. Between them are inserted a number of thick plates of crude copper so that the current must pass through them, resulting in the deposition

of pure copper on the sides facing the anode, and the solution of the crude copper from the opposite sides. This process is allowed to proceed until probably three-quarters of the thickness of the original plates has been dissolved away, with the accumulation of a similar thickness of pure copper on the opposite sides. The plates are previously prepared so that the detachment of the pure copper deposit from the residual crude copper can be easily effected. The detached deposits constitute pure copper for the market, while the undissolved portions of the crude plates are remelted for further use. The system is very largely used on account of the very low e.m.f. required to maintain copper deposition under these conditions. Many of these crude plates are inserted in a single cell, the current being used repeatedly in the cell with, however, a corresponding increase in the p.d. of the cell. While this does not involve any appreciable economy in electrical energy, it has the advantage of rearranging the electrical supply to one of lower current and higher e.m.f., which is convenient in the supply of large-scale current for this type of work.
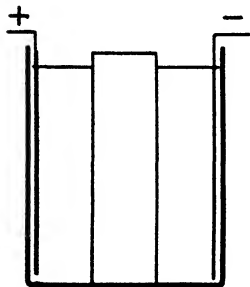
FIG. 79. THICK SOLUBLE BI-POLAR ELECTRODE

Copper refining by the series system thus exemplifies the principle of secondary electrodes in designed operation. Unintentionally, however, in other cases in which copper deposition is being carried out, it may be possible for some portions of a badly connected cathode and one of large and irregular size to pick up current from the anode and, owing to its poor contact with the cathode bar, pass it on to an adjacent cathode with a good contact to the cathode bar. The point at which the current leaves the poorly connected cathode will thus suffer loss of metal by anode solution, a condition of things altogether undesirable. The correct disposition of cathodes with good contacts will avoid the possibility.

A slight variation of this scheme is that of the use of an appreciably thick plate of copper (Fig. 79). The electrochemical changes are unaltered, but the substitution of a thick layer of highly-conducting copper in place of the relatively

poorly-conducting solution will effect a decrease in total internal resistance with the anticipated effects on the ammeter and voltmeter readings.

Lead as a Secondary Electrode. In Fig. 77 let the copper plate be replaced by one of lead. The fact that lead is a poorer conductor than copper does not enter into the problem in view of the fact that metallic conduction so far exceeds that of solutions. Definite changes on the instrument readings will indicate unusual changes in the cell. A reduced ammeter reading with increased voltage will find some explanation with the observed changes within the cell, where again copper is deposited on the side of the lead plate facing the anode, while on the opposite face of the lead plate the formation of lead dioxide with the evolution of oxygen will be the prominent observations. Added to these will be that of the decreasing blue colour of the solution with the increased acidity according to the following equation—

$$CuSO_4 + H_2O = Cu + O + H_2SO_4$$
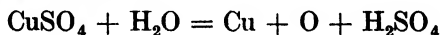
In the anode compartment of the cell the deposition of copper proceeds normally as in the copper refining process, while in the cathode compartment copper is being extracted from the solution. A voltmeter applied to the two compartments will show that something of the order of 1·2 V more is required in the cathode compartment than in the anode compartment for the maintenance of the same current. This is the e.m.f. required to effect the chemical change shown in the above equation calculated on the principle illustrated in Chapter XII.

The substitution of a thick lead plate offers a new condition in that the reduced internal resistance may to some extent offset the increased e.m.f. due to the chemical changes effected in the cathode compartment. In fact, it is not difficult to conceive a sufficiently thick plate to exactly counterbalance the increased voltage of 1·2, and thus leave the overall electrical condition of the cell unchanged, with, however, definite changes in its components and chemical constituents of the cell.

In electrodeposition practice lead-lined tanks are in common use, and with solutions of high resistance and badly-disposed electrodes it may easily happen that a shorter electrical circuit

may occur by current "leaving" the anode and passing to an adjacent portion of the lead lining with the deposition of the metal from the solution, the current subsequently passing to a portion of the cathode which lies close to the lining.   This is a
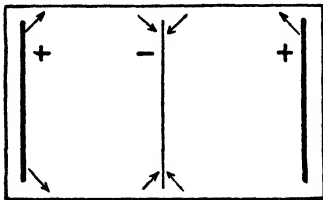
FIG. 80. LEAD LINING AS
BI-POLAR ELECTRODE
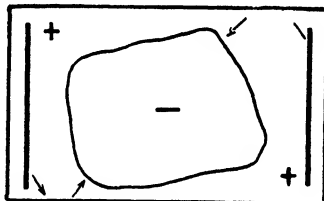
FIG. 81. LEAD LINING AS
BI-POLAR ELECTRODE

frequent experience and is mitigated by the use of thin wood or glass linings over the lead.

The point is sufficiently illustrated by reference to·Figs. 80 and 81 and, moreover, it may be recalled from experience that similar effects are possible and have been observed in a series
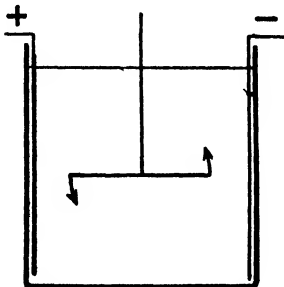
FIG. 82. SUSPENDED
BI-POLAR ELECTRODE
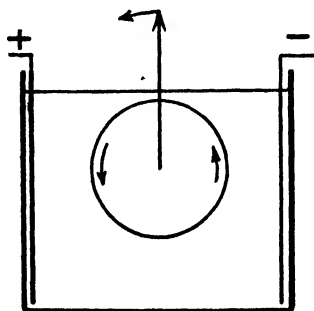
FIG. 83. COPPER DRUM AS
BI-POLAR ELECTRODE

of tanks with a continuous flow of electrolyte, especially when the p.d. of the process is relatively high.

Suspended Bi-polar Electrodes. So far the bi-polar electrodes considered have been fixed.   With freedom of motion some novel effects are possible even though without application. Thus Fig. 82 shows a bath similar to that of Fig. 77, except that,

acting as a bi-polar electrode, there is suspended a thin copper rod or needle. Under the conditions indicated the end near the anode receives a deposit of copper, while loss of metal occurs at the opposite end leading to a movement of the rod or needle in the direction indicated.

An amplification of this principle is shown in Fig. 83 in which a thin water-tight copper drum is floated between the anode and cathode. This requires some manipulation but is achieved without much difficulty. The drum may be of brass or copper sufficiently thin to ensure that it is lighter than the solution. Copper is then deposited upon it to bring its density to that of the solution. Floating is best effected by laying it on a solution of rather greater density and then adding more but some-
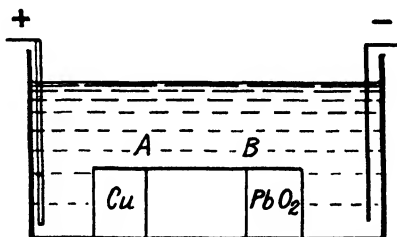
FIG. 84. A LONG LEAD BI-POLAR ELECTRODE

what lighter solution. Further, the glass cell selected should be of such dimensions as to admit of the least end movement of the drum. The cylindrical surface of the drum now represents the extreme ends of numerous rods or needles from the previous illustration. A light pointer is attached to move over a scale. Current is applied. giving rise to a slow, very slow, yet easily observed rotation in the direction indicated.

Revert next to the case of the lead bi-polar electrode which now takes the form of a substantial bar either supported in the liquid or lying on the bottom of the cell as shown in Fig. 84.

Observation soon shows that one end receives a deposit of copper while the other is peroxidized. Between these extremes there is a large portion which has apparently remained un-affected. The longer length of metallic conductor has more than compensated for the volts required to deposit copper on one end and oxidize lead at the other end. The lengths of these portions are of interest. At the point A, at which there is no obvious effect, we may imagine the current to have the choice of either entering the metal or continuing in the electro-lyte to pass on to the cathode. Entering A and emerging at B involves the expenditure of 1·2 V, which is thus an

expression of the resistance of the electrolyte over this distance. A little thought will show that with a poorly conducting electrolyte the points *A* and *B* will be nearer together while the reverse occurs with a good conducting solution.

Perforated Lead Bi-polar Electrodes. Consider next the case of a perforated lead plate substituting copper in the original example. This is illustrated in Fig. 85. Copper again is deposited on the face opposite to the anode and lead dioxide
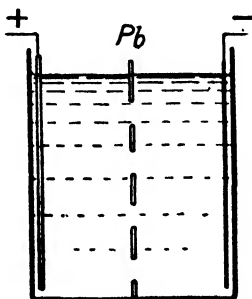
FIG. 85. PERFORATED
LEAD BI-POLAR
ELECTRODE
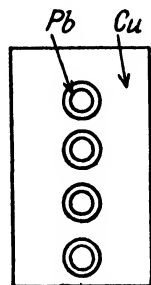
FIG. 86. SHOWING
MARGINS
WITHOUT DEPOSIT

formed on the other side, but it will be observed that these effects miss a margin around each perforation and, similarly to the case shown in Fig. 84, the width of these margins is determined by the factors which influence the resistance of the electrolyte. The result is that shown in Fig. 86.

If the perforations are brought closer together these margins may so completely overlap that no current passes through the plate at all, which therefore ceases to be a bi-polar electrode, while, still further, if the perforations are small they may be sufficient to prevent the free admixture of anolyte and catholyte, the chosen metal, in this case lead, being more free from attack by many chemical solutions than might be the case with the usual porous clay materials, especially where strong alkalis are in use.

A wire gauze is an extreme case of perforation, and may much more effectively separate anolyte and catholyte.

The Castner Sodium Cell. A conspicuous example of such use of gauze in an electrolytic cell with a view to separating

anode and cathode products is seen in the cylindrical gauze placed between the anode and cathode in the fused caustic soda from which sodium is recovered. This is depicted in Fig. 87.

At the cylindrical iron anode oxygen is being evolved in large quantities, arrangements for the collection of which are not shown. An equal volume of hydrogen is evolved at the very near iron cathode in accordance with the equation—

$$2NaOH = 2Na + H_2 + O_2$$

The cell is run at a temperature of about 350° C., always with the risk that the gases if mixed are exposed to the possibility of exploding by some chance electric spark, and wrecking the cell. The gauze diaphragm prevents this admixture. A normal size of cell takes 1 250 A. Electrodes must be close together to keep down

FIG. 87.
CASTNER SODIUM CELL

internal resistance and a simple calculation will show that from each cell 8 to 9 ft³ of gas are evolved per hour in this very limited space. The gauze is depended upon to effectively keep apart these volumes of the two gases. The important point about this gauze is that it must not under any circumstances act as a secondary electrode, otherwise an explosive mixture of gases may occur on both compartments. There must obviously be some note of "design" in the selection of this gauze in order to prevent the mixture of the two gases. The large-scale production of sodium in this type of cell is a sufficient expression of the measure of success realized in the application of this metallic diaphragm.

Carbon as a Bi-polar Electrode. Carbon is another example of a substance highly resistant to corrosive attack of many chemical substances and yet of good practical conductance. We can imagine it acting in much the same way as lead. One interesting case is shown in Fig. 88, in which *A* represents a carbon rod rotating in a space cut in a non-porous and
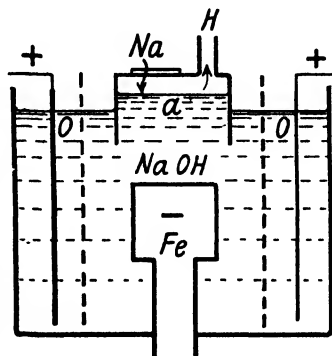
non-conducting material such as ebonite. The solution is copper sulphate. At first assume the rod to be at rest. Copper will be deposited on the surface facing the anode, while oxygen will be evolved from the surface facing the cathode, this portion of the carbon functioning as an insoluble anode. If the rod is now turned through 180 degrees the copper deposit becomes a soluble anode, while the opposite side receives a deposit, and this condition of things will continue so long as there is copper on the side facing the cathode.
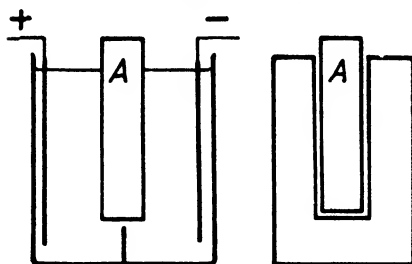
FIG. 88. ROTATING GRAPHITE ROD AS BI-POLAR ELECTRODE

The rod may now be rotated when, however short the period of exposure of any portion of the carbon rod to the anode, it will receive some copper which will be dissolved away in the next half-revolution, and so the rotating carbon rod will function as a rod of copper acting as a secondary electrode without necessitating a higher p.d. to maintain a constant current as would be the case if the rod were at rest.

That this actually happens is shown in the data embodied in Table LXXXIV and obtained from such an experiment.

TABLE LXXXIV
GRAPHITE DIAPHRAGM

| I (A) | P.D.'s across Cell | | |
| | Graphite Diaphragm | | No Diaphragm |
	Still	Rotating	
0·63	3·2	1·7	2·5
1·1	5·1	2·9	4·1
1·5	6·2	3·85	5·3
2·0	7·5	5·1	6·8

The higher figures for no diaphragm are due to the narrow section of the electrolyte which, with the rotating diaphragm, is occupied by a relatively good conductor.

The case is at least an interesting one even without immediate application.

Mercury as a Metallic Diaphragm. Even the element mercury has found application as a conducting diaphragm in an electrolytic process. This is in the Castner-Kellner cell for the production of chlorine and caustic soda by the electrolysis of brine. This process is described and illustrated in many text-books and so need not be detailed here. Briefly, however, it may be said that from suitably disposed carbon rods current is passed through brine with the evolution of chlorine at the carbon rod anodes. The cell comprises two compartments separated by a

FIG. 89.
CASTNER-KELLNER ALKALI CELL

wall through the bottom of which there are openings on the floor level of the cell. Opposite to this wall there is a depression in the floor of the cell into which is introduced a quantity of mercury sufficient to fill the groove and cover the floor to a depth sufficient to prevent liquids on either side of the wall from mixing. On the other side of the wall in the other compartment there is a solution of caustic soda in course of preparation, the current passing on to an iron cathode. This is diagrammatically shown in Fig. 89.

From the anode, current passes through the anolyte and into the mercury on the floor of the cell, sodium being deposited into the mercury. A gentle rocking motion imparted to the cell keeps the mercury in motion so that the sodium is spread into the cathode compartment. Current leaves the mercury in the cathode compartment with the accompanying solution of the sodium anodically and the evolution of hydrogen on the iron cathode which is permanent in the caustic solution. Unless, therefore, there is always a sufficiency of sodium in the mercury, the latter metal will be oxidized with the production of black mercurous oxide which involves appreciable annual loss of

mercury detrimental to the economy of the process. In other words, while the metallic mercury diaphragm is essential, as the current appears to leave it in the cathode compartment, it must do so only by the anodic solution of the contained sodium and not from the mercury itself. The mercury must *not* function as a bi-polar electrode. Incidentally, it may be correctly surmised that the deposition of sodium in the mercury in the anode compartment does not take place with an efficiency equal to that of its solution from mercury in the cathode end of the cell. There is thus a deficiency of sodium in the mercury in comparison with the current passing, and this leads to the attack of the mercury in the cathode compartment. To avoid this error, the current in the anode section of the cell is boosted up to the extent of about 10 per cent of the total by the use of an auxiliary generator which passes additional current through the anode compartment only, collecting it from the mercury. The reactions in the two compartments are thus balanced.

A more recent type of cell, however, avoids this defect by making the mercury the cathode of the cell and transferring the sodium amalgam to an adjacent compartment, from which the sodium is dissolved out chemically by contact with water, the mercury then being pumped back to the electrolytic compartment. Losses of mercury by blackening are thus avoided, but, at the same time, so is the energy of the solution of the sodium. Costs have presumably determined this change of procedure.

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