ALKALINE ACCUMULATORS

BY

J. T. CRENNELL, B.A.

AND

F. M. LEA, M.Sc., A.I.C.

WITH ILLUSTRATIONS AND DIAGRAMS

LONGMANS, GREEN AND CO.
LONDON ✦ NEW YORK ✦ TORONTO
1928

ALKALINE ACCUMULATORS

LONGMANS, GREEN AND CO. LTD.
39 PATERNOSTER ROW, LONDON, E.C.4
6 OLD COURT HOUSE STREET, CALCUTTA
53 NICOL ROAD, BOMBAY
167 MOUNT ROAD, MADRAS

LONGMANS, GREEN AND CO.
55 FIFTH AVENUE, NEW YORK
221 EAST 20TH STREET, CHICAGO
TREMONT TEMPLE, BOSTON
210 VICTORIA STREET, TORONTO

PREFACE

ALKALINE accumulators are entirely a development of the present century, and all present types, excepting the Edison cell, are products of the last twelve or fifteen years. Their existence and their spheres of usefulness have not yet been fully appreciated, and, indeed, it is often not realised that more than one type exists.

It has been the authors' aim in this book to give a general account of alkaline accumulators, and to emphasise those characteristics in which they differ from lead cells. Their deficiencies have been described, as well as their advantages, and the various fields in which they excel, by virtue of their characteristic properties, have been indicated.

The authors have endeavoured to preserve a fair balance between theory and practice, and, the field being relatively small, they hope that the combination of the two in one volume has been attended with some measure of success.

Considerable emphasis has been laid on the general principles of the working of accumulators and on the factors affecting their operation. In this way a truer appreciation of the relative characteristics of different types of accumulators is obtained. At the same time the text has been kept as non-specialised as possible, with the exception of one chapter on the theory of cell reactions.

It is hoped that the gaps revealed in the theory of alkaline accumulators, and particularly in the mechanism of the reactions of the composite cadmium-iron plate, may stimulate some worker to enter this field. Further data on the capacities of individual plates and their variation with conditions of operation, *e.g.* temperature and discharge rate, are also needed.

The authors have to express their thanks to the following firms for the loan of blocks for illustrations: Messrs. Batteries, Ltd.; Edison Accumulators, Ltd.; the Iron and Nickel Battery Co., Ltd.; and Worsnop and Co., Ltd. They have further pleasure in expressing their indebtedness to Mr. A. G. Milligan, M.Sc., A.I.C., for reading and criticising the proofs of this book.

J. T. CRENNELL
F. M. LEA.

CONTENTS

CHAPTER I

INTRODUCTORY

CHAPTER II

DEVELOPMENT, CONSTRUCTION, AND MANUFACTURE OF ALKALINE CELLS

CHAPTER III

ELECTROCHEMICAL THEORY

CHAPTER IV

ELECTRICAL CHARACTERISTICS

CHAPTER V

OPERATION AND MAINTENANCE

CHAPTER VI

THEORY OF THE REACTIONS IN ALKALINE CELLS

CHAPTER VII

FACTORS AFFECTING THE PERFORMANCE OF ALKALINE CELLS

CHAPTER VIII

CHAPTER IX

APPLICATIONS

APPENDIX

LIST OF PLATES

ALKALINE ACCUMULATORS

CHAPTER I

INTRODUCTORY

THE function of a secondary cell, accumulator, or storage battery is, as the alternative names imply, the "storage" of energy. There is no known means of storing considerable quantities of electrical energy as such, and the only convenient method by which it can be stored is its conversion into chemical energy.

An accumulator consists essentially of two different plates, known as the *positive* and *negative* plates, immersed in an *electrolyte* which is usually a conducting liquid, though occasionally it is immobilised as a jelly. When a current is passed from an external source through an accumulator, entering the cell at the positive plate and leaving it at the negative plate, its action on the chemical compounds in the cell produces a new set of compounds. This process is known as *charging* the cell. If now the terminals of the charged accumulator are connected by an external circuit, for example, a resistance wire, an electric current is delivered, leaving the cell at the positive plate and entering at the negative plate, and the chemical changes in the cell take place in the reverse direction to those occurring during charge. This process is known as *discharging*.

An accumulator is therefore an apparatus into which electrical energy can be passed and changed into chemical energy, stored until required, and then obtained once more as electrical energy. This energy cannot be stored indefinitely in any known type of accumulator, but gradually leaks away, and hence the storage battery in its present form is to be regarded as a temporary rather than a permanent store.

Electrical energy is the product of two factors, the *quantity* of electricity, which is measured in *ampere-hours* (A.H.) and is the product of the current in amperes and the time during which the current flows, and the *pressure* which is available for driving the current through a circuit: this pressure is measured in *volts*. The product of the current passing through an external circuit and the pressure, or voltage, at the terminals of the source of current is measured in *watts* (1 watt = 1 ampere × 1 volt). The total consumption of energy is the product of the wattage and the time during which the current flows, and is measured in *watt-hours* (W.H.)

There is a limit to the quantity of electricity which can be stored in an accumulator of given materials, size and weight, and the total quantity which can be stored is known as the *capacity*, or ampere-hour capacity, of the accumulator. The potential difference between the terminals of a cell, when no current is passing through it, is called the *electromotive force* (E.M.F.) of the cell. When a current is passing through the cell, the potential difference between the terminals is not quite equal to the E.M.F., but depends on the magnitude and direction of the current and on the time for which it has passed. This potential difference is measured in volts and is called the *voltage* of the cell.

In no case can more energy be obtained from the store than has been put in, and, indeed, in all cases there is some loss, the energy which is given out being less than that which has been put in. The ratio of the energy given out to that put in is termed the *efficiency*, or *watt-hour efficiency*, of the cell. The ratio of the quantity of current delivered by the cell on discharge to the quantity of current passed through the cell on charge is known as the *ampere-hour efficiency* of the cell.

A *primary cell* differs from a secondary cell in that, while the latter can be used repeatedly as a store of energy, the primary cell is not capable of being charged and brought back to its initial condition by passing a current through it in the reverse direction; it can therefore only give one discharge, converting the chemical energy of the initial materials of the cell into electrical energy. Primary cells are non-reversible, while secondary cells are, in this respect, reversible, and this constitutes the essential difference between them, for both depend in their action on the transformation of chemical into electrical energy. The Leclanché wet cell and the common dry cell are the best-known examples of primary cells.

It is only within the last sixty years that accumulators have been developed, and the natural trend has been in the direction of producing cells holding the largest quantity of electrical energy for a given weight and size compatible with a satisfactory life. The efficiency of an accumulator is a factor which, for most purposes, is subordinate in importance to the capacity-weight-life characteristics.

Accumulators may be conveniently divided into two distinct classes—acid cells and alkaline cells, which are so called because they have as an electrolyte an acid and an alkaline solution respectively. The former class—if it may be termed a class though it is limited to the well-known lead accumulator—is historically the older and has a considerable literature devoted to it. Alkaline cells are much less known, indeed, far less than they merit, and it is the purpose of this book to describe this class of accumulators.

The Lead Accumulator

A brief outline of the characteristics and behaviour of the lead accumulator, and of some of its defects, will indicate the considerations which led to the development of the alkaline type of cell. The positive and negative plates of the lead cell contain, as active materials, lead peroxide and metallic lead in a porous condition, respectively. These are held in a lead or antimonial-lead framework, known as the *grid*, which serves the purpose of holding the active materials in position and of conducting the current to and from the cell, but plays no part in the cell reactions. The active material is often called the *paste*. The electrolyte consists of a solution of sulphuric acid with a specific gravity of about 1·20 to 1·25 when the cell is charged. There is no metallic connection between the positive and negative plates when the cell is on "open circuit," *i.e.* when the terminals of the plate are not connected to an external circuit. If the circuit be completed by connecting the plates externally through a resistance or a source of current, a current can flow and the cell be either discharged or charged. On discharge, both the lead peroxide of the positive plate and the lead of the negative plate are converted to lead sulphate.

The reactions are more readily understood if the positive and negative plates are considered separately. The sulphuric acid electrolyte contains hydrogen ions, each carrying a positive electronic charge, and sulphate ions, each carrying two negative charges. On discharge, hydrogen ions ($H^{\cdot}$) reach the positive plate, and give up their electric charges to it, at the same time reducing the lead peroxide, in the presence of sulphuric acid, to lead sulphate, and setting free water. This reaction is shown by the equation

$$PbO_2+H_2SO_4+2H^{\cdot}=PbSO_4+2H_2O+2\oplus \quad . \quad (1)$$

The symbol $\oplus$ indicates that a positive charge is received by the plate.

Similarly, the reaction between the lead negative plate and the sulphate ions (SO_4'') is represented by the equation

$$Pb+SO_4''=PbSO_4+2\ominus \quad . \quad . \quad . \quad . \quad (2)$$

The sum of these two equations represents the reaction of the complete cell.

$$PbO_2+2H_2SO_4+Pb=2PbSO_4+2H_2O \quad . \quad (3)$$

On charge, the direction of the current and the chemical reactions are reversed, the lead and lead peroxide are reformed and the cycle can be repeated indefinitely.

It will be noted that on discharge sulphuric acid is used up and water produced, causing the density of the electrolyte to fall, while on charge acid is reformed and water removed, raising the density until it reaches its original value on completion of the charge.

Towards the end of charge the material available for reaction becomes small and a part of the current is employed in decomposing the electrolyte, evolving hydrogen and oxygen. In other words, the cell now commences to " gas," and at the same time the voltage across the cell rises. All current which is thus utilised in decomposing the electrolyte is lost and cannot be obtained on the succeeding discharge. It is nevertheless necessary, in order to charge the cell completely, that the charge should be continued for some time after gas evolution has commenced.

The greater the loss of current by gassing, the lower will be the ampere-hour efficiency, and further, since gassing is accompanied by a rise in voltage across the cell, it will be reflected to a still greater extent in the watt-hour efficiency.

The lead accumulator suffers from certain inherent defects of which the most important are a rather large weight for a given capacity; the lack of robustness of the plates with their liability to buckle or crack; the tendency of the positive active material to fall away from the plates, though this has been much decreased by certain improved forms of construction and plate separation; and finally the gradual hardening and loss of capacity of the negative plate. A lead cell also requires care in its treatment and cannot be left indefinitely idle without serious results. The gradual attack of the spongy lead of the negative plate by the acid, resulting in "sulphation," and the slow loss of capacity from local action and other causes necessitate a regular routine of maintenance even in an idle battery. The use of an acid electrolyte introduces a risk of damage to any metalwork in contact with the battery. The lead accumulator is also rather susceptible to the action of certain impurities which may find their way into the cell.

Properties required in an Accumulator Electrode

An accumulator may be made up of any two electrodes possessing the properties necessary to form respectively a positive and negative plate. It might appear that of all the known chemical compounds there would be many possessing the required characteristics, and hence that the number of different accumulators would be large. Actually the number of electrodes possessing the necessary properties is extremely limited. The only successful cell using an acid electrolyte is the lead accumulator. In place of the negative plate others such as zinc and copper have been tried without success. In both these cases the plate is not reformed in the same mechanical condition after a discharge and charge. The metal sulphates which are formed when the plate is discharged are soluble in the electrolyte, and, on recharge, the metal is not deposited in such a way as to retain the form of the plate, with the result that the plate grows in certain places and becomes eaten away in others and finally disintegrates.

A plate must be mechanically as well as chemically reversible if it is to function as an accumulator plate. One essential requirement for this mechanical reversibility is that the active materials, and the products resulting from the discharge reaction, shall be insoluble in the electrolyte. This ensures that when a particle of the original active material reacts the product will be precipitated at once and so take the place previously occupied by the reacting particle. It is obvious that it is also necessary that this product shall adhere to the plate and not fall away to form a sludge at the bottom of the cell.

Another disadvantage of the zinc plate is that it is attacked by the acid on open circuit, particularly when other metallic impurities are present; a continual loss of capacity of the cell results. We thus arrive at another condition for an accumulator plate, that the reaction on open circuit shall be negligible.

To summarise the characteristics required in an electrode which is to function as an accumulator plate:

(1) The substances employed must not be electrochemically inert, that is, they must be capable of undergoing chemical change in the electrolyte used when a current is passed through the cell.

(2) The electrode reactions must be chemically reversible, which necessitates that there shall be no loss from the cell of any of the resultants of the normal action. This does not include the loss of gas due to electrolysis of water towards the end of charge.

(3) Such chemical action as occurs on open circuit must be slow.

(4) In order that the electrodes may be mechanically reproduced in the same form on successive charges and discharges, the active materials in both the charged and discharged condition must be only very slightly soluble. The ions which carry the current through the electrolyte must therefore be different from the active materials, and must be provided by an electrolyte having a sufficiently high concentration and degree of dissociation to give a suitable electrolytic conductivity. In the lead cell the ions carrying

the current through the electrolyte are produced by the dissociation of the sulphuric acid.

(5) Local action must be slight, that is, there must be no continuous loss of capacity owing to the presence of impurities setting up small cells, or couples, on the electrode surface.

The following conditions for practical value may also be included as highly desirable : durability ; a low capacity-weight ratio, except for stationary battery use ; a fairly high cell voltage and low internal resistance. It is further desirable that the cell voltage should not drop excessively during the discharge.

In no existing cell are all these desiderata fully realised, and the number of combinations which satisfy even the essential conditions is very small. The lead cell, as was mentioned before, alone of cells with an acid electrolyte, fulfils a sufficient number of these conditions, and it will be seen later that the successful combinations utilising an alkaline electrolyte are similarly extremely few.

Alkaline Accumulators

Alkaline cells are a more modern development than the lead cell and represent an attempt to find an accumulator which is without the disadvantages of the lead cell. The early history of alkaline cells may be passed over very briefly as it has already been dealt with in other publications, particularly in Wade's *Storage Batteries* published in 1902.

The Lalande-Chaperon primary cell, consisting of a zinc negative plate and copper oxide positive plate, was patented in 1881 and may be regarded as the forerunner of the class of alkaline cells. During the following years several attempts were made by Desmazures and others to convert this combination into a reversible cell, or accumulator, but without much success, and as a secondary cell this zinc—copper oxide combination is now only of historical interest. It still survives, however, as a primary cell and is considerably used, particularly on the continent of Europe. Another cell containing a zinc electrode was the zinc—potassium hydroxide—mercuric oxide combination for which a German patent was taken out in 1886 by H. Aron, but this cell also proved to be of no value.

During the last ten years of the nineteenth century many other combinations which were intended to function as alkaline accumulators were patented in various countries. As a positive plate, an oxide of cobalt, copper, iron, manganese or nickel may be mentioned, together with cadmium, copper, iron or silver as a negative plate. In spite of these attempts, no success was obtained, and it was only at the commencement of the present century that the modern alkaline cell originated with the work of Edison and Jungner.

Edison's name had already been associated with the Lalande primary cell, which is often known as the Edison-Lalande cell, and in 1900 Edison[1] took out a patent for a cadmium—copper oxide combination in an alkali hydroxide electrolyte. This cell was similar to the Lalande primary cell with cadmium replacing zinc. This substitution alone was a considerable step towards making a reversible cell, since cadmium oxide is insoluble in alkali hydroxides in contrast to zinc oxide, which is soluble. The difficulties with the Lalande cell when attempts were made to convert it into a secondary cell had not, however, been limited to the zinc plate, but included the copper oxide plate. The reactions on discharge in this cell are :

$$Zn+2KOH+CuO=Zn(OK)_2+H_2O+Cu \quad . \quad (4)$$

and

$$Zn+2KOH+Cu_2O=Zn(OK)_2+H_2O+2Cu \quad . \quad (5)$$

the first equation applying to the primary cell in which black cupric oxide is used, and the second to a cell which has been recharged, the copper having been converted to cuprous oxide. The oxidation unfortunately does not stop at this point, but proceeds to form cupric oxide. This reformed oxide is soluble in the alkali hydroxide electrolyte, unlike the black oxide used in the primary cell, which is insoluble. The solubility of this reformed product proved a serious trouble. The dissolved copper diffused to the zinc plate, was reduced there to metallic copper and deposited on the plate, and set up rapid local action leading to solution of the zinc.

It had been found possible to prevent the formation of cupric oxide to a large extent by maintaining the cell during charge and discharge at 55° C., at which temperature any cupric oxide formed was decomposed. Edison claimed that

---

[1] Brit. Pat. 20960, 1900.

if the copper were prepared in an extremely fine state of division there was no tendency to form cupric oxide on charge, the reaction stopping at cuprous oxide.

The method described for obtaining the copper in the necessary condition was as follows: copper carbonate was reduced in a hydrogen atmosphere at as low a temperature as possible, and the finely divided metal obtained was moulded into thin slabs under slight pressure. This was converted into black cupric oxide by heating for 6–7 hours at a temperature not exceeding 260° C., and then reduced electrolytically to the metallic state once more. The blocks were inserted in pockets of perforated nickel, or nickel-plated iron, to form the electrode. On charging this plate red cuprous oxide was formed and the electrode was ready for use. The cadmium for the negative plate was prepared by electro-deposition from a weak solution of cadmium sulphate. The metal obtained was washed and packed into pockets similar to those of the positive plate. In spite of the work which had been done, this cell was not produced on a commercial scale, and was abandoned in favour of the now well-known iron—nickel oxide cell.

Nickel oxide as an accumulator plate had been named as an alternative to copper oxide in the first of the series of patents leading up to the Desmazures cell, but was omitted in the final patent. It had been again mentioned in a patent taken out by A. Dun and F. Hasslacher in 1887, and in 1899 T. de Michalowsky [1] once more patented it. To this worker must be ascribed the credit of making the first investigations of any real value, and in his patent the qualifications of the nickel oxide electrode and methods for its commercial preparation were described.

In 1901 Edison [2] patented the combination iron—nickel oxide, mentioning at the same time cobalt oxide as a substitute for nickel oxide. Jungner,[3] working in Europe, had a year previously patented a cell containing a cadmium negative plate, and, with these patents of Edison and Jungner, the genesis of modern alkaline accumulators has been reached. The later patents of these two workers need not be touched on here as they will be discussed in the succeeding chapter. Edison [4] in 1901 patented a cell composed of zinc, plated

[1] Brit. Pat. 15370, 1899.

[2] Brit. Pats. 2490, 10505, 1901.

[3] Brit. Pat. 7768, 1900.

[4] Brit. Pat. 20072, 1901.

on a magnesium support, as a negative plate, and an oxide of nickel, cobalt, or copper as a positive plate. It was also stated that copper oxide was not so efficient as nickel or cobalt oxides. The electrolyte was a 20 per cent. solution of sodium hydroxide nearly saturated with zinc. This cell was never developed on a commercial basis.

The position in the early years of the present century was that the Edison cell and the Jungner cell had reached a commercial stage, but their value still remained to be proved. Edison did not persevere further with the suggested cobalt oxide electrode, and Jungner finally substituted a mixture of iron and cadmium for the original cadmium negative plate.

The two alkaline cells now produced commercially are :

(1) Iron	Potassium hydroxide solution	Nickel oxide	*Edison type*
(2) Cadmium-Iron	Potassium hydroxide solution	Nickel oxide	*Jungner type*

The action occurring on discharge at the positive plate is the same in both cells, being a reduction of the nickel oxide to a lower oxide, with the reverse changes on charge.

At the negative plate of the Edison cell the iron is oxidised to ferrous oxide on discharge, while at the Jungner cadmium-iron plate the greater part of the discharge is normally contributed by oxidation of the cadmium, but it is probable that some oxidation of the iron also takes place.

An interesting paper on the use of silver as a positive active material in alkaline accumulators has recently appeared. Silver oxide was one of the oxides named in Jungner's patent[1] of 1899, but no further use was made of it. Jirsa and Schneider[2] have experimented with a positive plate made by pressing spongy silver on to iron or nickel gauze ; this is combined with a negative iron electrode and the cell completed with a caustic soda electrolyte. Apart from its cost, which is in itself almost prohibitive, there appear to be certain difficulties in utilising silver oxide. It tends on successive charges and discharges to pass into colloidal suspension in the electrolyte and migrate to the negative plate, where it is deposited ; but it is stated that this action can be prevented by the addition of potassium sulphate to the electrolyte.

[1] Brit. Pat. 7892, 1899. *Zeit. Elektrochem.* 33, 129, 1927.

CHAPTER II

DEVELOPMENT, CONSTRUCTION AND MANUFACTURE OF ALKALINE CELLS

ALL the types of alkaline cells which have been produced on a commercial scale differ mechanically in some essentials from the familiar constructional forms of the lead cell.

The theoretically important parts of any accumulator are the active materials of the plates and the electrolyte, but practical troubles in operation, and manufacturing difficulties, are as often due to the means of retaining and supporting the active materials as to these materials themselves.

In alkaline cells the nickel oxide of the positive plate, and the finely divided iron of the negative plate, are contained in very finely perforated pockets of nickelled steel sheet. A number of pockets are clamped in nickelled steel frames to form the complete plate. The cell container is also of steel, and is sometimes electrically connected to one set of plates. There are no continuous or perforated sheet separators, such as are necessary in all lead cells except the heavy stationary types; but thin rods of ebonite, or ebonite studs fixed to the plates, are employed, simply acting as spacing pieces to prevent the plates of opposite polarity from coming into contact. As the materials are held in very finely perforated pockets, there is no possibility of their forming a bridge between the two plates, nor of any considerable loss of active material occurring.

The use of steel throughout the cell, which is possible in a cell with alkaline electrolyte, permits a refinement of detail and a precision of manufacture which is in marked contrast to the comparatively rough and heavy castings which must be used in the lead-acid cell. The steel construction of the alkaline cell also makes it much more robust and durable than the lead cell.

The welded sheet-steel container is a considerable improvement on the containers of lead-acid accumulators, which are always either cumbersome or unsatisfactory.

Early History and Development

The Edison Cell.—This cell was first patented in 1901, but during the next few years many alterations were found to be necessary, and it was only after the adoption and perfection of many new processes that the Edison cell, as it is manufactured to-day, was evolved.

The original form of the cell, manufactured on the basis of the patents of 1901, was withdrawn from sale in 1904, as it had not proved satisfactory, and it was not until 1908 that the present type of cell was produced commercially. In the period of seven years thus elapsing between the first production of the cell and its final manufacture many radical alterations were made in the methods of preparation of the materials and in the construction of the cell. It is of interest to trace briefly the historical development of this cell, which affords a notable example of the difficulties which are encountered in accumulator work.

Construction of the Plates.—According to the original patent,[1] the plates were made by wrapping a perforated sheet of nickel or nickelled iron, 0·125 mm. thick, round a frame to which the sheet was riveted, forming a hollow plate with pockets to contain the active material. This type of plate construction was soon abandoned, and in a later patent [2] a plate is described which was built up of separate rectangular pockets clamped into a metal frame. This form of plate was used for both positives and negatives in the early type of Edison cell. It is still used in essentially the same form for the modern negative plate, and will be described in detail later.

Negative Active Material.—The active material for the negative plate was at first prepared from a mixture of four parts by weight of finely-ground ferrous sulphide, and one part of flake graphite, the latter being added to improve the electrical conductivity of the mass. Some such addition was found to be essential, as the conductivity of the iron oxides is

---

[1] Brit. Pat. 2490, 1901.

[2] Brit. Pat. 10,505, 1901.

poor, and the electrolytic processes only occur in close contact with a conducting surface. The mixture was moistened with a 20 per cent. solution of potassium hydroxide, pressed into the pockets, and then subjected to a series of alternate oxidations and reductions in a potassium hydroxide solution. The sulphur was eliminated by this process, and ultimately finely-divided iron was obtained, and the plate was ready for use.

Ferrous sulphide was used owing to the difficulty of reducing electrolytically the dried oxides or hydroxides of iron. The hydroxides were difficult to handle without drying, which rendered them very inert to electrolytic reduction. After boiling in water for many hours ferric hydroxide was electrolytically reducible, but the material obtained was so bulky that only a much smaller weight could be packed into the pockets. The iron prepared from the sulphide was compact and reactive.

In the later patent of 1901 [1] a method of preparation of the negative active material by the reduction of dried ferric oxide in hydrogen at 260° C. was described. The resulting mixture of iron, ferrous oxide, and magnetic oxide, was cooled in hydrogen, to render it non-pyrophoric, and was then ready for use.

The preparation was further modified in 1903.[2] The finely-divided oxide was reduced in hydrogen at 480° C., cooled in hydrogen, and water admitted to cover the mass and prevent oxidation by the air. This method is substantially the same as that now in use.

Positive Active Material.—The active materials for the positive plate, as described in the original patents, were lower oxides of nickel or cobalt, nickel being preferred on account of cost. Nickel hydroxide was precipitated from a sulphate solution, dried, finely ground, and mixed with graphite in the proportion of seven parts to three by weight. As in the negative plate, the function of the graphite was to improve the conductivity of the mass. The mixture was pressed into the pockets and electrolytically oxidised.

Trouble was experienced owing to the excessive swelling of the nickel hydroxide when immersed in the alkaline electrolyte, straining and bulging the pockets in which it was contained. In addition, the ordinary green nickel

---

[1] Brit. Pat. 10,505, 1901.

[2] Brit. Pat. 322, 1903.

hydroxide, prepared by precipitation from the solution of a nickel salt, was difficult to handle on a large scale. Edison states that it was colloidal and bulky, and took hours to settle. It was difficult to wash and to make cheaply. On drying, it formed a hard, glassy mass, which swelled badly when immersed in the electrolyte. Nickel sesquioxide, prepared by the action of an alkali hypochlorite on a nickel salt, was stated to have the same objectionable properties.

A new method of preparation, which avoided these troubles, was developed.[1] The hydroxide was precipitated from a boiling solution of nickel nitrate with magnesium hydroxide, and after washing and drying was treated with chlorine to form the sesquioxide. Six parts of this oxide and four parts of graphite were used for the active material.

It was claimed in a later patent [2] that the addition of 6 to 9 per cent. of bismuth hydroxide increased the capacity of the positive material by 20 per cent. As this practice does not appear to have been adopted commercially it was probably not found efficacious.

It was not found possible in this cell to bring the capacity of the nickel oxide plate up to that of the iron plate, and it therefore became necessary to use two positive plates, back to back, for each negative plate.

Positive and negative plates were similar, each consisting of 24 pockets of paste.

Early Type of Edison Cell.—This was the final form of the earlier type of Edison cell, known as type E. The E-18 cell, for example, contained twelve positive plates and six negative plates. The total weight of the paste, including the graphite, in the positive plates was 922 gms., and in the negative plates 662 gms. The electrolyte was 3·1 lbs., about 1400 gms., of a solution of potassium hydroxide of density 1·190. The weight of the complete cell was 12·66 lbs., and the capacity, on discharge at 30 amps. to a final voltage of 0·75, was 114 amp. hours, with an average voltage, during the discharge, of about 1·23 volts.

Owing to the development of unexpected faults, this type of cell was withdrawn from the market in 1904, to be replaced in 1908 by the modern type of Edison cell, incorporating several radical alterations and improvements. In the interval

---

[1] Brit. Pat. 10,505, 1901.

[2] Brit. Pat. 26,948, 1904.

Fig. 1. Edison Negative Pocket.

Fig. 2. Edison Negative Plate.

Fig. 3. Edison Positive Tube.

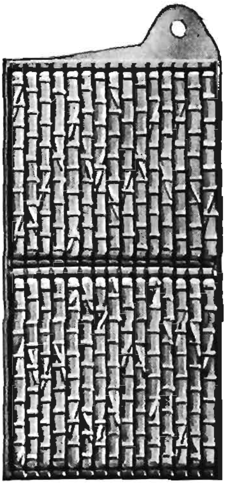

Fig. 4. Edison Positive Plate.

(*Edison Accumulators Ltd.*)

PLATE II.

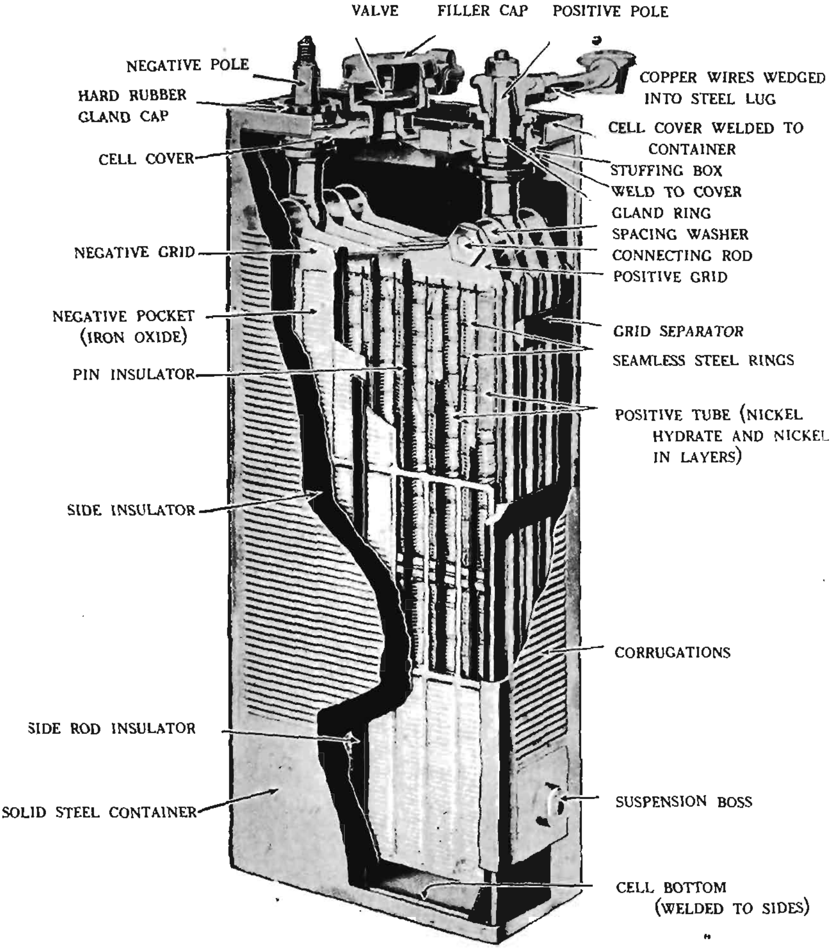

Fig. 5

Edison Cell—Sectional View.

(Edison Accumulators Ltd.)

a number of patents had been taken out, which describe the modifications made in the cell.

The use of graphite in the negative plate had not been found satisfactory. In Brit. Pat. 322, 1903, the addition of mercuric oxide to the negative paste was described, or alternatively, the addition of copper oxide or of a mixture of the two. This change does not appear to have been made in the early type of cell, but in the new cell of 1908 the use of mercuric oxide in the negative plate was adopted. During the first charge this was reduced to metallic mercury, which acted as the agent necessary to improve the conductivity of the negative active material.

The form and materials of the positive plate were also changed. The graphite had been found to cause swelling of the positive plate, and it was also gradually oxidised, causing bad conductivity and a loss of capacity of the plate. In the new cell the conducting agent was very fine flake nickel. The construction of the plate was on entirely different lines, with the object of preventing the troubles which had occurred in the early type of cell owing to loss of contact between the paste and the pockets caused by the changes in volume of the paste. The rectangular pockets were replaced by cylindrical tubes held in a frame, and it was no longer found necessary to use two positive plates for each negative. This practice had not been satisfactory, since the percentage of the positive active material which actually took part in the discharge was in any case small, and was still further reduced by using two plates back to back.

The construction of the present type of Edison cell and the methods of preparing the materials—the culmination of a long and costly period of experimental work—are described in the following section.

The 1908 Type of Edison Cell

NEGATIVE PLATES

Preparation of the Active Material.—Ferrous sulphate is prepared by dissolving pure, finely-divided iron in sulphuric acid. The sulphate is purified by several recrystallisations, separated from the liquid by centrifuging, and dried at 200° C. The salt is then roasted in an oxidising atmosphere, forming ferric oxide, Fe_2O_3. Traces of sulphate are removed by leaching. The finely-divided oxide is reduced by heating in a hydrogen atmosphere at 480° C. in a muffle furnace. The material is allowed to cool in hydrogen, and a solution of sodium hydroxide is then run into the combustion chamber to prevent oxidation by the air. After being dried and ground, the material is mixed with 6 per cent. of yellow oxide of mercury, which, as mentioned above, gives the mass the necessary electrical conductivity.

The mercury also has certain other important effects on the active material, a discussion of which will be found in later chapters.

Construction of Negative Plates.—The active material is contained in rectangular pockets of perforated nickel-plated sheet steel. Each pocket (Fig. 1) is 3 ins. long, $\frac{1}{2}$ in. wide, and $\frac{1}{8}$ in. thick, and is made from two strips of specially prepared steel ribbon. Cold-rolled carbon steel ribbon is passed through rolls which perforate it with 560 holes to the square inch. The burrs are removed by emery wheels, and the ribbon is cleaned by revolving wire brushes, to ensure that the perforations are open and allow free access of the electrolyte to the active material. The ribbon is then passed through a series of tanks containing washing and plating solutions. The first tank contains a solution of potassium hydroxide to remove the grease. This is followed by a tank of hot water to wash off the alkali. The plating tank, containing a solution of nickel ammonium sulphate, is the next, and is followed by tanks of hot and cold water and finally a tank of dilute ammonia to remove any traces of acid solution. After plating, the ribbon is dried and annealed in a hydrogen atmosphere, a process which welds together the nickel plating and the steel, and prevents scaling.

The ribbon thus prepared is cut into lengths and the sides are flanged over, two lengths then being fitted together to form a negative pocket. One end is left open, and the active material is tamped into the pocket, which is afterwards crimped together and completed.

Twenty-four of these pockets are fixed in the negative grid, which is a nickel-plated steel punching having rectangular holes to fit the pockets. By means of a hydraulic press the pockets are made to flange out over the holes of the grid and are thus fixed in position and in good contact with

PLATE III.

Fig. 6

" Ionic " Nickel-Steel Pocket.

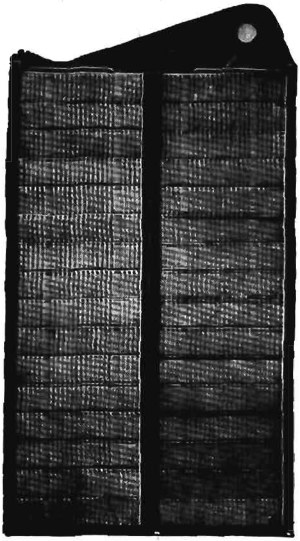

Fig. 7

" Ionic " Positive or Negative Plate.

(Iron and Nickel Battery Co. Ltd.)

PLATE IV.

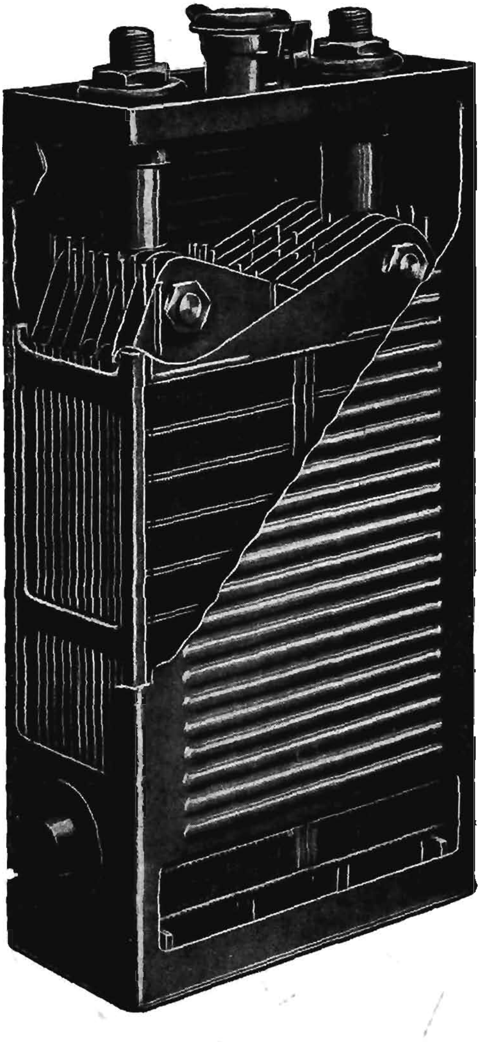

Fig. 8.

" Ionic " Accumulator, Sectional View.

(Iron and Nickel Battery Co. Ltd.)

the grid. In the same process the surfaces of the pockets are corrugated, which strengthens the sides and allows for the volume changes which occur in the active material during working. A complete negative plate of a Type A cell is shown in Fig. 2.

POSITIVE PLATES

Active Material.—Nickel shot is dissolved in sulphuric acid, and the solution is treated to remove certain impurities which are usually present, such as copper, tin, antimony, and iron. The nickel sulphate solution is then sprayed into tanks containing a hot 10 to 15 per cent. solution of sodium hydroxide. The precipitated nickelous hydroxide is collected and dried. Sodium hydroxide, carbonates, and sulphates, are removed by leaching with hot water, and the hydroxide is again dried and its quality tested. If satisfactory, it is ground and sifted, the material used ranging between 30 and 190 mesh.

It is of interest to note that the method finally adopted is one which was originally condemned as yielding an unsatisfactory product (cf. p. 13). Presumably the condition of the precipitate depends on the control of such physical factors as temperature, concentration, and method of mixing the reacting solutions.

Flake Nickel.—The flake nickel for use as a conducting agent in the plates consists of flakes $\frac{1}{16}$ in. square and 0·00004 in. thick. It is prepared by plating layers of nickel and copper on to rotating copper cylinders, which are dipped alternately into nickel- and copper-plating baths for the required time, with intermediate washings by sprays of water. The process is continued until 125 layers of each metal have been deposited, an operation which takes about five hours. The composite sheet is then stripped from the cylinders and cut into $\frac{1}{16}$-in. squares. The copper is dissolved chemically, leaving the separate nickel flakes, which are washed, centrifuged, and dried.

Positive Tubes.—The active material in the positive plates is contained in cylindrical perforated steel tubes. These are made from the same ribbon as is used for the negative pockets, by winding it spirally. The seams are lapped and swaged flat. Tubes are made $\frac{1}{4}$ in. and $\frac{3}{16}$ in. in diameter, and $4\frac{1}{2}$ ins. or $3\frac{1}{8}$ ins. long.

Filling the Tubes.—A cap is placed at the bottom of each tube, and the filling machine drops in a specified amount of nickel hydroxide and then of flake nickel. This is pressed down by a blow of 2000 lbs. per square inch delivered by a ram-rod. The process is repeated 315 times in filling a tube, so that each tube contains 630 alternate layers of nickelous hydroxide and flake nickel. The flake nickel constitutes about 14 per cent. of the contents of the tube. When the tubes are completely filled, a cap is placed at the top, and the ends are pinched together. Eight seamless nickel-plated steel rings are fitted equidistantly round each tube, to prevent any possibility of the tubes bursting when the active material swells in the forming process. A finished tube is shown in Fig. 3.

Construction of Positive Plate.—Two rows of the positive tubes are fixed in a nickel-plated steel frame to form the complete plate (Fig. 4). The ends of the tubes are caught underneath ears on the sides of the frame, and are clamped in place by a hydraulic press. To guard against any possibility of distortion of the plate, adjacent tubes are wound with left- and right-hand spirals alternately.

ASSEMBLY

The plates are mounted on steel rods which pass through the eyes of the frames at the top of the plates. Washers separate the plates to the correct spacing, and they are fixed in position by a lock washer and nut screwed on to the end of the rod. Groups of positive and negative plates thus formed are intermeshed to form the element, and are separated by hard rubber pins. The element is insulated from the container by hard rubber sheets at the sides of the plates and a hard rubber frame or grid at the edges. The element rests on a bridge of hard rubber at the bottom of the container.

The container is of nickel-plated steel, with welded seams. The sides are corrugated to give additional strength.

The terminal pillars from the plate groups pass through holes in the cover, from which they are insulated by rubber bushings.

The gas-valve and filler is in the centre of the cover. There is a hemispherical valve, held down by a spring, and forced open by pressure of gas during charging. The valve is lifted when the cap is opened for filling or "topping up."

Fig. 5 is a sectional view of a complete cell.

ELECTROLYTE

The electrolyte of an Edison cell is a solution of potassium hydroxide, with the addition of a small percentage of lithium hydroxide. An account of the properties and behaviour of the electrolyte is given in Chap. V, p. 68, and VII, p. 101.

The Gouin Cell

A type of cell containing the same couple as the Edison cell, an oxide of nickel as the positive material and iron as the negative material, has been described,[1] but does not appear to have been a commercial success. The positive plate was made in a similar manner to that of the early type of Edison cell. The negative plate, instead of holding pockets filled with the finely-divided active material, was initially filled with fine threads of pure iron, which were treated by a process of electrolytic oxidation and reduction comparable with the classical Planté process in the lead accumulator, the " formation " process resulting in a finely-divided active material.

S.A.F.T., and Ionic Accumulator

The " Ionic " accumulator, manufactured by the Societé des Accumulateurs Fixes et de Traction, and marketed in this country by the Iron and Nickel Battery Co., is another cell using the combination iron, potassium hydroxide, nickel oxide.

It differs from the Edison cell in using graphite as a conducting material in the positive paste, and in the construction of the positive plates which are built up of flat pockets of perforated steel, similarly to the Edison negative plate.

---

[1] Montpellier.
(*a*) *Electrician*, 38, 1909, 209.
(*b*) *Cong. Int. delle App. Elec. Turin*, 3, 1911, 527; *Rev. d' Electrochim.* 6, 1912, 206.

The active material of the negative plate is substantially the same as that of the Edison cell.

The construction of the pockets is shown in Fig. 6. The complete plate is shown in Fig. 7, built up from 32 pockets in vertical steel frames. Fig. 8 gives a sectional view of the complete cell, showing the assembly.

The Jungner Cell

This type of cell was first developed in Sweden at about the same time as the Edison cell, and is the only essentially different type of alkaline cell which has been successfully manufactured. Cells of this type are now being manufactured by several independent companies. The "Nife" accumulator, manufactured by Batteries, Ltd., and the "Alklum" accumulator, manufactured by Worsnop & Co., are examples of cells now being produced on the Jungner system in this country.

Positive Active Material.—The positive active material in all cells of the Jungner type is nickel hydroxide. In order to give the necessary conductivity flake graphite is added to the material. It is stated that in batteries manufactured twenty years ago, impurities in the graphite led to the formation of mellitic acid, which resulted in a loss of graphite from the paste and consequent lowering of the conductivity, but that special processes have been introduced which render the graphite chemically inert.

Negative Active Material.—The essential difference between the Jungner and the Edison types of cell is in the nature of the negative active material. In the Jungner cells a mixture of iron and cadmium is used. The proportions vary with the type of cell, and with the maker. Jungner found that the iron plate had many disadvantages, especially the poor conductivity of the oxide formed during the discharge, and the tendency to become inactive, which necessitated the addition of mercury to the mass. The use of cadmium by itself as the active material was at first proposed, but this proved unsatisfactory owing to the tendency of the material to cake and lose porosity. By the use of a mixture of iron and cadmium, Jungner found that the favourable properties of both materials could be utilised, the

PLATE V.

Fig. 9

Pocket for "NIFE" Electrodes.

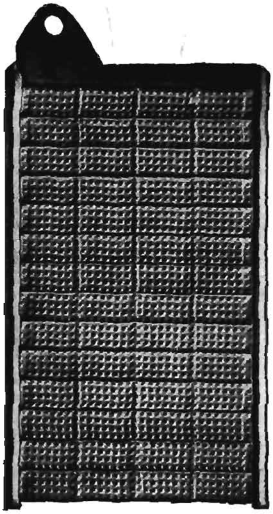

Fig. 10

"NIFE" Plate--Positive or Negative.

(*Batteries Ltd., Redditch*)

PLATE VI.

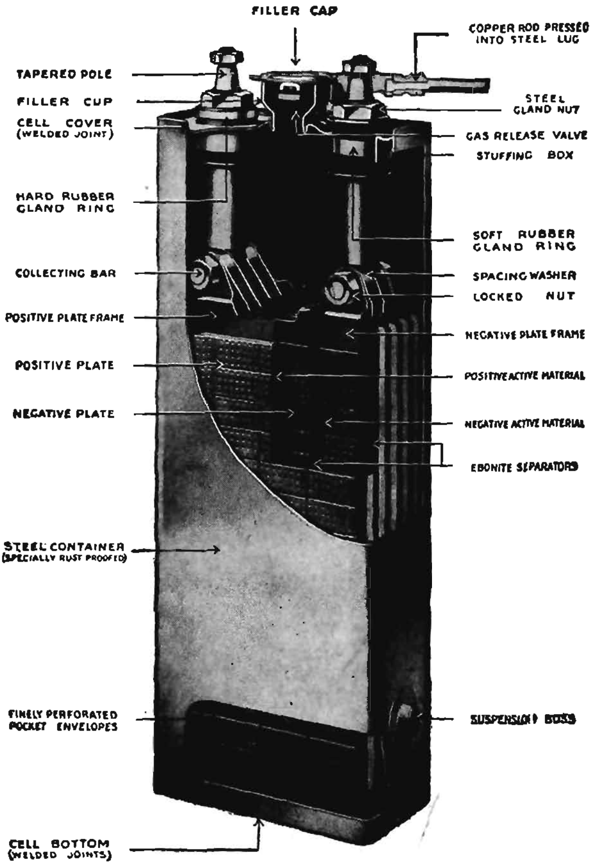

Fig. 11

"NIFE" Cell—Sectional View.

(*Batteries Ltd., Redditch*)

cadmium oxide having a comparatively high conductivity, while the presence of the iron prevented caking.

The cadmium-iron powder is prepared by simultaneous electro-deposition from mixed solutions of cadmium and iron salts. The precise details of this process are closely guarded by the manufacturers, but the general method was described by Jungner.[1] A mixed solution is used, containing the metal sulphates in proportions depending on the ratio of cadmium and iron required in the deposit. Separate anodes of cadmium and iron are employed, whose effective surfaces are proportional to the atomic ratio of the metals required in the cathodic deposit. The current density is 10 amps. per square decimetre.

A pulverent mixture of the two metals is obtained, which is dried at 50–60° C., powdered, and moulded into blocks to fit the plate pockets.

In a later patent[2] the use of nickel or cobalt instead of iron was described. This metal is inactive, and was added solely for the purpose of preventing caking of the cadmium. Various advantages are claimed for the use of these metals rather than of iron, but, as the commercial practice is still to use iron in the negative plates, some further disadvantage was presumably found.

Construction of Plates.—Both positive and negative plates of the well-known makes of Jungner cells are built up of rectangular pockets holding the active material. These are of perforated nickelled steel ribbon, two strips being folded and fixed together to form the complete pocket, containing a pressed briquette of the active material. The completed pockets are fixed in a nickelled steel frame, and the surfaces are ribbed or corrugated to give additional strength and resilience.

In general the constructions of the positive and negative plates are identical except that the positive plate is commonly made thicker than the negative.

Assembly.—The assembly and construction of cells of the Jungner type is illustrated in Figs. 9–13. Welded steel containers are used by all makers. While the containers of the Ionic and Edison cells are insulated from the plate groups by ebonite frames at the sides and ends, in both the Alklum

---

[1] Brit. Pat. 9964, 1910.

[2] Brit. Pat. 5545, 1912.

and Nife cells, the container is "live," and is in electrical contact with the positive plates.

Ebonite rod separators, or spacing pieces, are fitted to keep the plates in position and out of contact with adjacent plates.

In some cells of the Jungner type the plates are welded on to the equaliser bar, while in the Edison and Ionic cells the plates are held on to the bar by nuts and spaced by steel washers.

Electrolyte.—The electrolyte in all the Jungner type cells is a solution of potassium hydroxide, usually a 20–25 per cent. solution. The following specification for the purity of new solid potash for use in Nife cells is given by the makers.

KOH	84–88 per cent.
K_2CO_3	2–2·5 " "
KCl	nil
K_2SO_4	nil
K_2SiO_3	0·075 per cent.

PLATE VII.

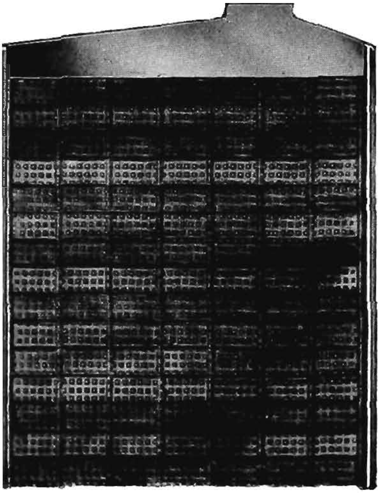

Fig. 12

Alklum Plate—Positive or Negative.

(Worsnop & Co. Ltd., Halifax)

PLATE VIII.

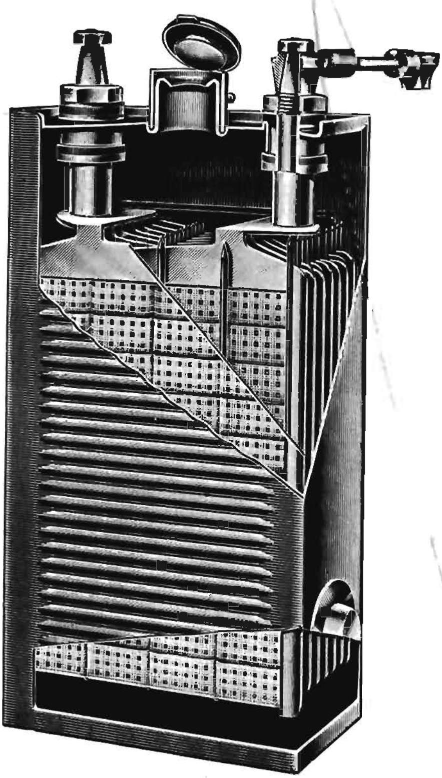

Fig. 13

Alklum Cell—Sectional View.

(*Worsnop & Co. Ltd., Halifax*)

CHAPTER III

ELECTROCHEMICAL THEORY

The Dissociation of Solutes

WHEN a salt, acid, or base, is dissolved in water its molecules split up into two or more parts carrying electric charges. Thus with potassium hydroxide and sodium chloride we get:

$$KOH \rightleftharpoons K^+ + OH^-$$
$$NaCl \rightleftharpoons Na^+ + Cl^-$$

This process is known as electrolytic dissociation, and the charged bodies formed are called *ions*. The positively-charged ion (*e.g.* K^+, Na^+) is called the *cation* and the negatively-charged ion (*e.g.* OH^-, Cl^-) the *anion*. It is convenient to use, generally, a somewhat different notation from the above, positive charges being represented by dots, thus $K^{\cdot}$, and negative charges by dashes, thus OH'. The charge carried by an ion is always a simple multiple of the unit electronic charge. The number of such charges carried by an ion is called its *valency*, thus a $K^{\cdot}$ ion is univalent and a $Zn^{\cdot\cdot}$ or SO_4'' ion is bivalent.

The extent to which electrolytic dissociation takes place differs considerably with different solutes, but for all strong acids and bases and for most salts it proceeds to a very considerable extent. The degree of dissociation is increased as the solution becomes more dilute, though at the same time the actual concentration of ions becomes diminished owing to the smaller number of molecules present in a given volume. A current passing through a solution is carried entirely by these charged ions, the positive ions moving towards the *cathode* and the negative to the *anode*. Thus, in an alkaline cell on charge, the $K^{\cdot}$ ions migrate towards the negative plate and the OH′ ions to the positive plate, these directions being reversed on discharge.

Faraday's Laws of Electrolysis

The passage of the current is also associated with the discharge of ions at the electrodes, although the ions discharged are not necessarily those playing the main part in carrying the current, but may be other ions existing in the neighbourhood of the electrodes. The two laws governing the passage of current through an electrolyte are known as Faraday's Laws of Electrolysis and may be stated as follows :

(1) The amount of electrochemical action, which takes place at an electrode, is proportional to the quantity of electricity which passes, that is, to Ct where C is the current and t the time.

(2) If a current be passed through a number of electrolytic cells in series in which, for example, silver, copper, zinc, etc. are respectively deposited at the cathodes by the current, the amounts of these metals deposited are directly proportional to their chemical equivalent weights. The same law holds equally for the anode.

The weight of an element deposited or released by unit current, 1 coulomb, is known as its electrochemical equivalent. Its value for silver is 0·001118 gms., copper 0·000329 gms., etc., and these values are, in accordance with the second law enunciated above, proportional to the chemical equivalent weights of the elements. Writing the electrochemical equivalent of an element as z, we have :

$$z = \frac{\text{Equivalent Weight}}{F}$$

where F is a constant, being the number of coulombs required to deposit one equivalent weight (in grams) of any element. This constant has the value 96500, and is known as the *Faraday*. Conversely, when the material of the electrode passes into solution the same laws govern the loss of weight of the electrode per coulomb passing through the cell. Faraday's second law thus enables us to calculate the maximum capacity which could be obtained from a given weight of any materials if used in a cell, and hence, by comparison with the actual experimental figure, to calculate the proportion of the material which is "active," *i.e.* which takes part in the discharge.

Transport Numbers

Although, when a current is passed through a cell, equivalent amounts of ions are released at the two electrodes, the current is not carried through the solution in equal proportions by the positive and negative ions, but is shared between them in a ratio which is dependent on the *transport numbers* of the ions involved. It has been found that ions when subject to the same force differ in the rate at which they move, and at a given temperature each ion has its own characteristic migration velocity. It is to this inequality in their migration velocities that the difference in the current-carrying capacities of ions is due.

The transport number of an ionic constituent of a solution is the ratio of the current carried by it to the total current passing, or, in terms of movement of the ions, it is the ratio of the number of equivalents of the ion reaching one electrode to the total number of equivalents of ions transferred to and from that electrode. Now the amount of current carried by each species of ion is proportional to its concentration, its ionic charge (*i.e.* its valency), and its rate of movement. For a binary solute such as KOH, giving rise to two monovalent ions only, the rate of movement is proportional to the *mobility* of the ion, which is its rate of movement under unit force.

Let c_a and c_c be the concentrations of anion and cation, which in this case are equal, and let u_a and u_c be their respective mobilities. Then the transport number of the anion

$$n_a = \frac{c_a u_a}{c_a u_a + c_c u_c} = \frac{u_a}{u_a + u_c}$$

Similarly,

$$n_c = \frac{u_c}{u_a + u_c}$$

From the definition of the transport numbers and the fact that the whole current is carried by these two species of ions, it is obvious that:

$$n_a + n_c = 1.$$

For potassium hydroxide $n_a = 0{\cdot}73$, and the greater part of the current is carried by the hydroxyl ion. For potassium chloride $n_a = 0{\cdot}51$, and the current is divided almost equally between the two ions.

Although the rates at which ions of both types migrate to and from an electrode are not the same, it must not be supposed that an accumulation of ions of one sign occurs. Consider the electrolysis of a solution of a binary salt MX, the electrolyte being assumed divided across the middle into an anode and a cathode compartment. Let n_a be the anion transport number and $n_c = 1 - n_a$ that of the cation. On the passage of one faraday of current the following changes occur:

$(1 - n_a)$ gram equivalents of $M^{\cdot}$ leave the anode compartment and enter the cathode compartment. At the cathode 1 gram equivalent of $M^{\cdot}$ deposits out

$$\text{Total cathode loss of } M^{\cdot} = 1 - (1 - n_a) = n_a$$
$$\text{Total anode loss of } M^{\cdot} = 1 - n_a$$

In addition n_a gram equivalents of X' leave the cathode compartment and enter the anode compartment. Here also at the anode 1 gram equivalent of X' is discharged.

$$\text{Total cathode loss of } X' = n_a$$
$$\text{Total anode loss of } X' = 1 - n_a$$

Hence, in the cathode compartment the loss is $n_a M^{\cdot} + n_a X'$

$$= n_a \text{ gram equivalents MX.}$$

In the anode compartment the loss is $(1 - n_a)M^{\cdot} + (1 - n_a)X'$

$$= (1 - n_a) \text{ gram equivalents MX.}$$

It is seen that there is no excess of one sign of ion in any compartment, but that both ions disappear in equal numbers at any one electrode. The example further shows that different amounts of the salt are lost at anode and cathode, and hence the solution in the neighbourhood of these two points changes in concentration by differing amounts. This factor is of much importance in the consideration of the actions occurring in electrolytic cells and will be met with again later.

Electrode Action

A mental picture of the process by which an electrode sets up an E.M.F. is most easily obtained in terms of the Nernst solution pressure theory which leads directly to some important relations. Nernst assumed that, if a sheet of a metal, *e.g.* silver, be immersed in water, positively-charged ions tend to pass into solution in virtue of what was called the solution pressure of the metal. This leaves a negative charge on the plate and sets up a potential difference between plate and solution. The existence of this electrostatic potential difference renders the passage of further positively-charged silver ions into solution more difficult, and an equilibrium is established when the solution pressure and potential difference balance each other. This normally occurs, owing to the strong electrical forces involved, when only an exceedingly small and undetectable mass of metal has passed into solution. It is obvious at once that the greater the solution pressure of a metal the larger will be the electrical force required to balance it and produce equilibrium, and, hence, the greater the potential difference between solution and metal.

Now consider what happens if the plate is immersed in a solution of one of its salts, *e.g.* silver nitrate. The silver ions have a certain tendency to deposit out on the metal. This tendency is measured by the osmotic pressure of the ions, which, for small concentrations, may be taken as proportional to the ionic concentration ; for a given small ionic concentration it is the same for all ions. If this osmotic pressure (O.P.) were just equal to the solution pressure (S.P.) of the metal, no net transfer of ions would occur and no potential difference between metal and solution would be set up. If, however, the S.P. is greater than the O.P. some silver will pass into solution as ions, setting up a potential difference until the combined effect of this and the O.P. of the solution balances the S.P. This will obviously occur at a lower potential difference than in water since the O.P. is helping to balance the S.P. If, on the other hand, the O.P. is greater than the S.P. some silver ions deposit out, charging the plate positively with respect to the solution. This process will cease and equilibrium be established when the combined potential difference and S.P. forces balance the O.P.

We therefore have :

(1) S.P. $>$ O.P. Plate negatively charged with respect to the solution.
(2) S.P. $=$ O.P. No charge.
(3) S.P. $<$ O.P. Plate positively charged with respect to the solution.

The potential difference between a metal and a solution containing its ions is therefore dependent on the S.P. of the metal and the O.P. of the solution. It may easily be shown that the E.M.F. established is related to these two factors by the following equation :

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

where n is the valency of the ion concerned, F the faraday, R the gas constant, T the absolute temperature, and P and p the S.P. of the metal, and O.P. of the ions respectively. Converting to common logarithms and evaluating R, T, and F we obtain at 18° C.

$$E=\frac{0{\cdot}058}{n}\log\frac{p}{P}$$

$$=\frac{0{\cdot}058}{n}\log\frac{c}{C}$$

on substituting concentration terms, p being proportional to c which is the concentration of the salt in the solution. Since for a given metal C (which bears the same relation to the S.P. as c bears to the O.P. of the ions) is constant, we may write :

$$E=E_0+\frac{0{\cdot}058}{n}\log c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $$E_0=-\frac{0{\cdot}058}{n}\log C$$

E_0 is known as the electrolytic or *normal potential* of the element in question, and, as is seen from equation (1) above, is the potential difference between a metal and a normal solution of its ions ($c=1$).

A potential always corresponds to a process and is a measure of the work which the process is capable of doing. Thus, the normal potential of a metal is a measure of its tendency to send ions into solution, and it allows us to calculate what is known as the " free energy " change attendant on this process. It is not necessary that the process should be occurring continuously for this potential to be set up, but, as we have seen from the Nernst theory of electrode action, an equilibrium is rapidly established and no further transfer of metal into ions occurs.

When a current is taken from the cell the equilibrium is disturbed, as the charge accumulated on the plate flows away, and, in order to re-establish the equilibrium, more metal passes into solution as ions. This process continues as rapidly as the charge leaves the electrode to flow round the circuit, and the rate will be dependent on the resistance of the circuit and the driving force. The circuit must be completed by some second electrode in order to bring the current back into the solution, or into some other solution in contact with it. At this second electrode a process will occur in which the direction of transfer of electrical charge is the reverse of that at the first, *i.e.* if at the first electrode positive ions are going into solution, then at the other electrode positive ions must deposit out or negative ions pass into solution. Thus, if we consider the Daniell cell, which consists of a copper plate immersed in a copper sulphate solution which is in contact with a zinc sulphate solution containing a zinc plate, we have the following action :

$$\begin{array}{ccc} \mathrm{Cu} \mid \mathrm{CuSO_4} & \mid & \mathrm{ZnSO_4} \mid \mathrm{Zn} \\ \mathrm{Cu} \leftarrow \mathrm{Cu^{\cdot\cdot}} & & \mathrm{Zn^{\cdot\cdot}} \leftarrow \mathrm{Zn} \\ & \longleftarrow\!\!-\!\!-\!\!-\!\!-\!\!-\!\!- & \end{array}$$

Direction of flow of positive ions in the solution.

The zinc ions pass into solution leaving a negative charge on the zinc plate, while at the copper plate copper ions deposit out leaving a positive charge on the plate. The negative charge from the zinc plate flows round the external circuit and neutralises the excess positive charges at the copper plate, and the circuit is completed by the movement in solution of positive ions from zinc to copper and negative ions in the reverse direction. The driving force, or E.M.F. of the cell, is the algebraic sum of the two electrode potentials.

We may compare the E_0 values for various elements, since from these the E.M.F. of a complete cell can be calculated. The list which is shown in Table 1 is known as the potential series of the elements. The absolute potential difference, as defined above, of a single electrode cannot be measured directly since two electrodes have always to be combined to form a complete cell. All electrode potentials are therefore referred to an arbitrary standard, and for this purpose the potential difference between a hydrogen electrode at atmospheric pressure and a normal solution of hydrogen ions is assigned the value zero.[1]

TABLE I

Normal Potentials of the Elements

Metal.	Process.	Potential (ϵ_h).
Potassium	$K \rightarrow K^{\cdot}$	−2·92
Sodium	$Na \rightarrow Na^{\cdot}$	−2·71
Zinc	$Zn \rightarrow Zn^{\cdot\cdot}$	−0·76
Iron	$Fe \rightarrow Fe^{\cdot\cdot}$	−0·44
Cadmium	$Cd \rightarrow Cd^{\cdot\cdot}$	−0·40
Nickel	$Ni \rightarrow Ni^{\cdot\cdot}$	−0·22
Tin	$Sn \rightarrow Sn^{\cdot\cdot}$	−0·136
Lead	$Pb \rightarrow Pb^{\cdot\cdot}$	−0·12
Hydrogen	$H_2 \rightarrow 2H^{\cdot}$	0·00
Copper	$Cu \rightarrow Cu^{\cdot\cdot}$	0·34
Silver	$Ag \rightarrow Ag^{\cdot}$	0·80
Mercury	$2Hg \rightarrow Hg_2^{\cdot\cdot}$	0·80
Platinum	$Pt \rightarrow Pt^{\cdot\cdot\cdot\cdot}$	0·86 (?)
Gold	$Au \rightarrow Au^{\cdot}$	1·50

It will be observed that the alkali metals, which are the most easily oxidised elements, are the most electronegative, *i.e.* have the largest solution pressures, while the noble metals, gold, platinum, etc., fall at the electropositive end of the series. In general, any metal in the above table will displace one below it from solution and pass into solution in its place, *e.g.* if iron is placed in a copper sulphate solution copper deposits out and iron goes into solution. This table only compares the potentials which would be obtained if each of the elements were immersed in a normal solution of its own ions; in many cases such a solution cannot be obtained, and this is the case for many elements in alkaline solutions. Thus, in potassium hydroxide solution many metals form insoluble hydroxides which only give rise to minute ionic concentrations. It is nevertheless of interest for our purpose to compare the potentials exhibited by the metals in alkaline solution, though these correspond to varying ionic concentrations which are dependent on the solubility of the metal oxide or hydroxide concerned. The potentials given in the following table are, in most cases, those

---

[1] Another scale based on an assumed value of +0·56 volt for the normal calomel electrode is also in use. The value of the normal hydrogen electrode on this scale is +0·277.

shown in a normal potassium hydroxide solution, and are referred, as before, to the normal hydrogen electrode as zero.

TABLE 2

Potentials in Alkaline solutions

Metal.	Oxide formed.	Potential (ϵ_h).
Zinc	ZnO	−1·18
Iron	FeO	−0·87 *
Hydrogen	H_2O	−0·82
Ferrous oxide	Fe_2O_3	−0·75
Cadmium	CdO	−0·71 (?)
Lead	PbO	−0·56
Copper	Cu_2O	−0·35
Copper	CuO	−0·21
Lead	PbO_2	−0·16
Mercury	HgO	+0·11
Silver	Ag_2O	+0·35
Nickelous oxide	Ni_2O_3	+0·48 *

* 2·85 N.KOH solution.

We may now consider the E.M.F. of a complete cell. If we have two metals, for instance, copper and zinc, as in the Daniell cell, immersed in solutions of their own ions of concentrations, c_{Cu} and c_{Zn} respectively, the E.M.F. at each electrode is :

$$E_{\text{Cu}} = E_{o_{\text{Cu}}} + \frac{0\cdot058}{2} \log c_{\text{Cu}}$$

$$E_{\text{Zn}} = E_{o_{\text{Zn}}} + \frac{0\cdot058}{2} \log c_{\text{Zn}}$$

(NOTE, $n=2$ since we are dealing with bivalent ions.)

The total E.M.F. of the cell

$$\text{Cu} \mid \text{CuSO}_4 \mid \text{ZnSO}_4 \mid \text{Zn}$$

is then

$$E = E_{\text{Cu}} - E_{\text{Zn}} = E_{o_{\text{Cu}}} - E_{o_{\text{Zn}}} + \frac{0\cdot058}{2} \log \frac{c_{\text{Cu}}}{c_{\text{Zn}}}.$$

The E.M.F. of the cell is hence dependent on the normal potentials of the metals forming the electrodes and on the concentrations of the solutions in which they are immersed.

If, instead of zinc, we substitute a second copper electrode, and a second copper sulphate solution of concentration c'_{Cu}. we have the cell

$$\begin{matrix} Cu \mid CuSO_4 \mid CuSO_4 \mid Cu \\ E_1 c_{Cu} \qquad c'_{Cu} E_2 \end{matrix}$$

which is known as a *concentration cell.*

$$\begin{aligned} E &= E_1 - E_2 \\ &= E_{o_{Cu}} + \frac{0{\cdot}058}{2} \log c_{Cu} - E_{o_{Cu}} - \frac{0{\cdot}058}{2} \log c'_{Cu} \\ &= 0{\cdot}029 \log \frac{c_{Cu}}{c'_{Cu}} \end{aligned}$$

and it is seen that the E.M.F. of such a cell is dependent on the ratio of the two solution concentrations and is independent of the electrode metal. This equation is not strictly accurate, for it neglects the potential difference at the boundary between the two copper sulphate solutions of differing concentrations. The potential set up at a liquid junction is dependent on the mobility of the ions meeting at that junction and would be zero in such a case as the above, if the positive and negative ions had the same mobility. Actually this is never the case, and a correction is necessary.

The Reactions in Alkaline Accumulators

The actions occurring in alkaline accumulators are not as definitely established as the corresponding actions in the lead cell. For this reason it is necessary to discuss rather fully the evidence which is available, in order that the degree of validity of the present theories may be properly appreciated. This discussion will be found in Chapter VI, and in this section only an outline of the general conclusions can be given.

The active material of the positive plates of the Edison or Jungner type cell consists of nickel oxides. On charge, the two oxides, NiO_2 nickel peroxide, and Ni_2O_3 nickel sesquioxide are formed, but the proportion of the former is small, never amounting to more than about 10 per cent. On discharge, nickelous oxide (NiO) is formed, and the reactions occurring may be written

$$2NiO_2 + H_2O \rightarrow Ni_2O_3 + 2OH' \quad . \quad . \quad . \quad (1)$$

$$Ni_2O_3 + H_2O \rightarrow 2NiO + 2OH' \quad . \quad . \quad . \quad (2)$$

Nickel peroxide is an unstable substance and decomposes rapidly after charge, evolving oxygen and being converted to nickel sesquioxide. The rate at which this occurs increases with rise of temperature. If a charged cell is left for about a week at ordinary temperatures all the nickel peroxide will have disappeared and nickel sesquioxide remains. The capacity of a nickel oxide plate therefore drops comparatively rapidly for the first 24 hours after charge, more slowly for the next few days, and finally when only nickel sesquioxide remains the rate of loss becomes small.

A nickel oxide plate discharged soon after charge, or at any time while some nickel peroxide remains undecomposed, shows two stages in its discharge curve because the potentials corresponding to reactions (1) and (2) differ. A discharge curve for such a nickel oxide plate is curve 1, Fig. 14. The initial descending portion AB of the curve 1 corresponds to discharge according to equation (1) and comes to an end when all the nickel peroxide has reacted and disappeared. The discharge is then carried on, according to equation (2), by the nickel sesquioxide which provides the major part of the discharge curve and gives the horizontal portion BC. When all the effective nickel sesquioxide has been utilised (*i.e.* all that actually exposed to the electrolyte and in

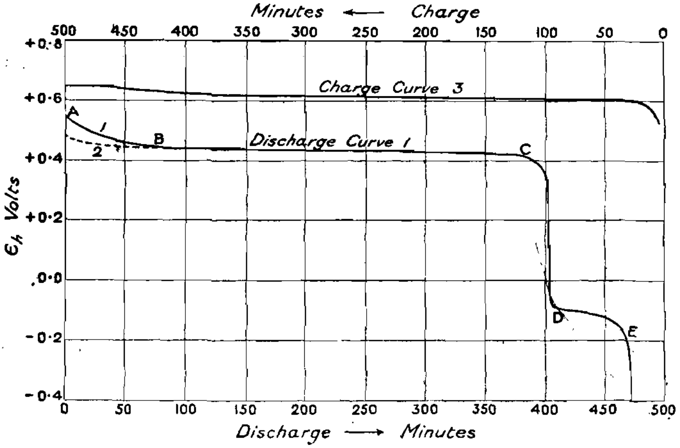

FIG. 14.—Discharge and charge curves of nickel oxide plate.

electrical contact with the conducting frame, but not necessarily all that existing in the plate) the discharge curve drops away steeply and no further useful discharge can be obtained. A small halt DE is seen in the discharge curve and has been attributed to a further discharge reaction which is discussed in Chapter VI.

In practice, cells are not discharged beyond the point C, owing to the large voltage drop occurring there, and the section DE has therefore little practical interest. This stage is further only found in those commercial cells whose positive plates contain graphite. If a nickel oxide plate is allowed to stand 24 hours before discharge, the initial high potential section of the discharge curve is shortened and we obtain a curve 2 consisting almost entirely of the horizontal portion corresponding to equation (2). On further standing no initial high potential portion of the curve is obtained, but only the nickel sesquioxide curve.

On charge (curve 3) the potential of a nickelous oxide plate rapidly rises past that corresponding to nickel sesquioxide formation and formation of nickel peroxide occurs as the primary reaction. Nickel sesquioxide is subsequently formed by reaction with nickelous oxide,

$$NiO_2+NiO=Ni_2O_3 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The cell reactions are therefore not strictly reversible, as the charge curve corresponds to a process which is different from that of the main portion of the discharge curve. This higher charge voltage necessitates a greater theoretical input of energy to the cell than can be obtained on discharge, the difference between these, neglecting heat loss due to internal resistance of the cell, being made up of the heat liberated and lost in reaction (3), and of the energy loss due to subsequent decomposition of nickel peroxide to nickel sesquioxide with evolution of oxygen.

At the iron electrode of the Edison type cell the main discharge reaction is:

$$Fe+2OH' \rightarrow FeO+H_2O \quad . \quad . \quad . \quad . \quad (4)$$

but on prolonged discharge the action

$$2FeO+2OH' \rightarrow Fe_2O_3+H_2O \quad . \quad . \quad . \quad (5)$$

sets in. Discharge and charge curves for an iron plate are shown in Fig. 15.

The portion AB of the discharge curves 1 and 2 corresponds to reaction (4); it is followed by a rapid drop in potential to C where reaction (5) commences to control the discharge and occupies the remainder of the discharge curve except possibly for a small final portion. On charge a curve of type 3 is obtained. The final portion GH corresponds to the reduction of ferrous oxide (or hydroxide) to iron, but it occurs at a potential much higher than that of the corresponding discharge reaction. A high polarisation is necessary for this charge action, and hydrogen evolution occurs simultaneously during the whole of this stage, rendering the charge efficiency far from theoretical. The initial portion of the curve EF probably corresponds to the direct reduction of ferric oxide (or hydroxide) to the metallic state. In practice cells are not discharged beyond the first stage AB, as a considerable drop in voltage is experienced here. Any discharge in the second stage is also undesirable since the subsequent direct

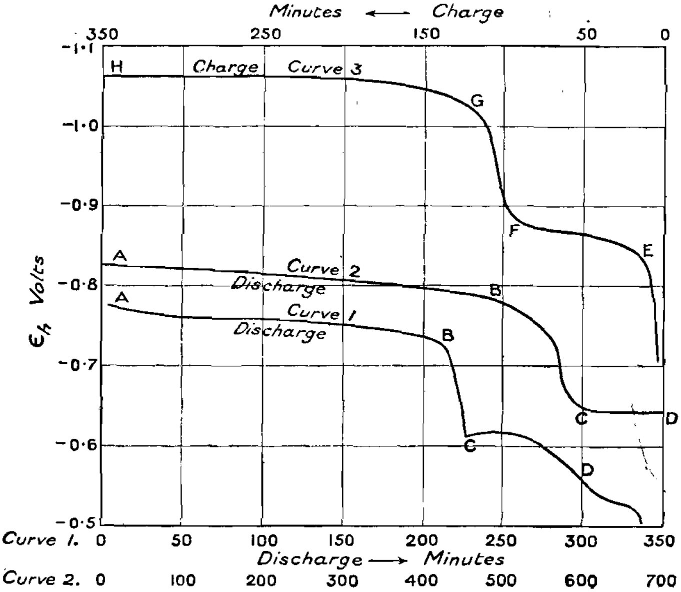

FIG. 15.—Discharge and charge curves of iron plate.

primary reduction of ferric oxide to iron covers the underlying ferrous oxide with a metal film and renders it to a considerable extent inactive. It is usual in Edison type cells to provide a considerable excess negative plate capacity and thus prevent any discharge of the iron electrode beyond the point B. Under such conditions, when no discharge beyond B occurs, the charge falls entirely, or almost entirely, along GH, and the portion EF is not observed. The above curves refer to iron electrodes which do not contain mercury. In commercial iron plates in which mercury is present the discharge curves are similar, but the charge curve shows a rise to a maximum on the initial portion of GH followed by a drop corresponding to the similar maximum shown in the cell charge curves (see Fig. 19, p. 54).

It will be observed that, according to equations 1, 2, 3, and 5, no change in total alkali concentration occurs, the same number of OH′ ions being produced at one electrode as are used up at the other. This is not entirely correct as the degrees of hydration of the various oxides involved are not the same, and a small change in the total free water, and hence in the alkali concentration, occurs. This effect is, however, small, and in the above equations the reacting oxides have been written for convenience without the water of hydration attached. The complete cell equations for the normal discharge reactions can be formulated as follows, again neglecting all water of hydration,

$$Fe+2NiO_2 \rightarrow FeO+Ni_2O_3 \quad . \quad . \quad . \quad (6)$$

$$Fe+Ni_2O_3 \rightarrow FeO+NiO \quad . \quad . \quad . \quad . \quad (7)$$

The more complete equations will be found in Chapter VI.

In the Jungner type cell the positive plate is the same as in the Edison, but the negative plate is a mixture of cadmium and iron. Owing to the scanty information available, it is not possible to give the actions in the form of definite equations, and the matter must be left until Chapter VIII, where such evidence as is available is discussed. It may nevertheless be noted here that the cadmium-iron plate has a lower charge potential than the iron plate, while both plates have almost identical discharge curves. The energy efficiency of the charging process is therefore considerably higher for the cadmium-iron plate than for the iron plate.

The small variation of the electrolyte concentration during the operation of alkaline cells is an important feature, contrasting as it does with the steady fall in concentration which occurs during the discharge of the lead accumulator.

The E.M.F. of alkaline cells is almost independent of the electrolyte concentration, while that of a lead cell varies considerably with concentration. Thus the E.M.F. of a lead cell decreases by about 0·13 volt when the acid density drops from 1·250 to 1·100. In actual practice this does not, however, confer an advantage on alkaline cells as the voltage drop on discharge is proportionately greater in these than in the lead cell owing to the operation of other causes.

The action in alkaline cells does lead to *local* changes in electrolyte concentration at the two plates, the electrolyte becoming more concentrated at the positive plate and diluted at the negative plate on discharge; the combination of the two results in a slight rise in the mean density. Local concentration changes occur also in the lead cell, the acid at the positive plate becoming more diluted than that at the negative plate on discharge.

Polarisation

It is a general physico-chemical principle that if a system in equilibrium be acted upon by a force it changes in such a way as to neutralise the effect of that force as far as possible. If such a system be subject to an applied E.M.F. a current passes and the system changes in such a way as to oppose the applied E.M.F., or in other words a "back" E.M.F. is set up, that is, an E.M.F. in a direction opposed to the original one. This general principle may be used to illustrate many polarisation effects.

When two platinum electrodes are immersed in a sulphuric acid solution, and a current from an external source is passed through the cell, the action consists in the evolution of hydrogen and oxygen at anode and cathode respectively. On cutting off the source of current, but keeping the circuit closed, it is found that a current flows in an opposite direction for a short time, decreasing rapidly in intensity, showing that an opposing E.M.F. has been set up. It is further found with such a cell that a certain minimum voltage is necessary to cause an appreciable current to flow, this minimum voltage being not less than the back E.M.F. set up. This back

E.M.F. is usually known as the polarisation E.M.F. and is equal to the "decomposition potential" of the solution, which is the algebraic sum of the single potentials of the two electrodes formed by the reaction products, in this case the electrodes $Pt(H_2)$ and $Pt(O_2)$. Such electrodes as platinum in sulphuric acid solution are known as polarisable electrodes.

If now the electrodes are coated with, or are in contact with, some substance which removes the reaction products, *i.e.* the hydrogen or oxygen, the electrodes become more or less non-polarisable: the substances effecting this are known as depolarisers. Manganese dioxide in the Leclanché cell provides a familiar example of a depolariser.

On passing a current in such a direction as to discharge hydrogen ions at a nickel oxide (peroxide or sesquioxide) electrode, evolution of hydrogen does not occur, but reduction of the oxide takes place preferentially. Similarly oxygen is not evolved at a finely-divided iron electrode, and formation of ferrous oxide, or hydroxide, occurs. Hence the materials of these electrodes are sometimes described as depolarisers, but it must not be supposed because they are so described that they are not sources of energy. In general, the presence of a depolariser causes, at an electrode, the replacement of one action involving the consumption of energy by another action which either liberates energy or involves the consumption of a smaller amount. They therefore cause an increase in the cell E.M.F.

There is another type of polarisation known as *concentration polarisation.* This is caused by the accumulation in the solution round an electrode of the products of the electrode action, or alternatively, to a diminution in concentration of any one of the reactants taking part in the cell action. Thus in a Daniell cell

$$Zn \mid ZnSO_4 \mid \underset{\longrightarrow}{CuSO_4} \mid Cu$$

the current flows in the direction shown, zinc goes into solution and copper deposits out. This leads to an increased concentration of zinc sulphate in the neighbourhood of the zinc electrode, and a decreased copper sulphate concentration in immediate contact with the copper electrode. This causes a decreased cell E.M.F. In this particular case the concentration polarisation is small since liquid diffusion, convection, and ionic migration, all tend to maintain the salt concentration uniform. In the lead accumulator, on the other hand, concentration polarisation becomes very large, because acid is used up in the pores of the plate on discharge and its replacement by diffusion and convection is much slower.

A further example of polarisation may be quoted, though it is covered already by the first type. It is a familiar fact that if an excessive current be taken from a Leclanché cell the E.M.F. rapidly drops. This is due to the current discharging hydrogen ions at the manganese dioxide electrode more rapidly than the solid manganese dioxide can oxidise it, and hence free hydrogen appears setting up a back, or polarisation, E.M.F.

It is desirable that the electrodes in an accumulator should be non-polarisable, since otherwise a drop in voltage will occur during discharge. In practice it is known that accumulators are not completely non-polarisable and a drop in E.M.F. occurs during the discharge, but this is sufficiently small for the utility of the cells not to be seriously impaired. In the lead accumulator concentration polarisation is mainly responsible for the fall in E.M.F. on discharge, but in alkaline accumulators this factor is probably of less importance, and, neglecting the drop due to disappearance of nickel peroxide, the cause of the fall in E.M.F. is attributable to certain more complex changes occurring at the iron electrode.

The iron electrode of the Edison type alkaline accumulator affords an example of a polarisation phenomenon which is essentially different from those referred to above. This iron plate, as shown in Fig. 15, requires a charge potential which is considerably more negative than the equilibrium potential before the reaction $Fe \rightarrow FeO$ can be reversed. This plate, indeed, cannot satisfactorily be charged at low current densities as the potential established at the electrode is insufficient and hydrogen evolution occurs instead. On increasing the current density the potential necessary for hydrogen evolution becomes more electronegative, and a point is reached at which the action $Fe \rightarrow FeO$ can be reversed. It follows, therefore, that an iron electrode can only be charged with concomitant hydrogen evolution. This charge polarisation is due to the partial irreversibility of the discharge reaction, a considerably greater amount of energy being required on charge than can be obtained on discharge even at very low discharge rates. The mechanism of this is discussed in more detail in Chapter VI.

OVERVOLTAGE

When an electrode reaction involves the discharge of a gas at an electrode surface the phenomenon of *overvoltage* (sometimes called polarisation-overvoltage) appears. It is found that at a platinised platinum electrode the potential required to discharge hydrogen from an acid electrolyte is the same as the potential set up by a platinised platinum electrode in contact with hydrogen and the same solution. This electrode is thus a reversible electrode. If, however, a plain unplatinised electrode is employed a higher potential is required to discharge hydrogen than at the platinised electrode, and the difference between the two potentials is known as the overvoltage to hydrogen discharge at the smooth platinum surface. Other metal electrodes also require an overvoltage for hydrogen discharge, and the same phenomenon occurs with other gases.

Overvoltage is dependent on the material of the electrode, the physical state of its surface, the nature of the gas discharged, and other factors. It is measured by the difference between the potential of the reversible gas electrode under the given conditions and that of the electrode at which the gas is being released by discharge of ions on the passage of a current.

In the following table the overvoltages of electrodes composed of various materials to hydrogen and oxygen discharge are given.

TABLE 3

Metal.	Overvoltage to Hydrogen.		Overvoltage to Oxygen.	
	N.H_2SO_4	N.NaOH	N.H_2SO_4	N.NaOH
Lead	0·9	0·64	1·0	0·8
Nickel	0·25	0·23	0·5	0·54
Cadmium	0·70	*circa* 0·5	—	*circa* 0·6
Copper	0·35	0·50	0·5	—
Iron	0·28	0·33	0·7	0·5
Platinum	0·00	0·24	0·7	0·7
Silver	0·25	—		
Zinc	0·7	—		
Mercury	0·7	—		

The above data are taken for the most part from the results of Newbery and were obtained either by the commutator method or by his more recent method using the cathode ray oscillograph. The latter method appears to be the most reliable and yields results which are generally rather higher than those given by the commutator, but below those given by the "direct" method. The overvoltage as measured by the cathode ray oscillograph varies little with current density. Current densities are therefore omitted in the above table.

Overvoltage is a most important factor in the working of accumulators, and did it not exist, the present accumulators would be impossible. In the lead cell neither positive nor negative plate would be stable but for the high overvoltages of lead to hydrogen and of lead peroxide to oxygen discharge. Lead, as will be seen from the table of normal potentials on p. 30, comes above hydrogen in the potential series and therefore tends to displace hydrogen ions from solution as hydrogen gas, lead ions going into solution in their place.

$$Pb + 2H^{\cdot} \rightarrow Pb^{\cdot\cdot} + H_2$$

This process would discharge the negative plate. The overvoltage of lead to hydrogen discharge is, however, greater than the E.M.F. of the couple $Pb \mid H_2SO_4 \mid H_2$, except possibly for very small current densities, and hence gas evolution can only occur at a very slow rate. A similar state exists at the positive plate. Except for this high overvoltage of lead, charging of the cell would not be possible, as gas evolution would occur in preference to the charge reaction, and if prepared materials, lead and lead peroxide, were made up into cells they would self-discharge, evolving hydrogen and oxygen respectively.

Similar considerations apply to alkaline accumulators. The iron electrode is electro-negative to hydrogen in alkaline solution and would evolve hydrogen on open circuit and be incapable of being charged. The overvoltage to hydrogen evolution is sufficient to stop this open circuit action at ordinary temperatures, but the charge potential required is much more electronegative to hydrogen, and much hydrogen evolution occurs, making the charge efficiency far from theoretical. With the cadmium-iron plate the charge potential required is less electronegative and the charge efficiency is more nearly theoretical.

PASSIVITY

If a sheet of iron is dipped into strong nitric acid solution and then placed in a dilute acid solution it is found to remain unattacked, while iron which has not been so treated dissolves. The strong nitric acid solution has rendered the metal *passive*, and the general phenomenon of such changes occurring in metal surfaces is known as *passivity*.

Passivity may also in some cases be induced by making a metal anode in a suitable solution and passing a current, when it is found that oxygen evolution occurs instead of the metal going into solution. Further, if passive iron is placed in a solution of copper sulphate no action occurs, while with active iron copper is deposited on the metal and iron passes into solution, as is to be expected from their relative positions in the electropotential series. The effect of passivity is therefore to displace a metal downwards in the potential series and render it more noble. No attempt can be made here to discuss the theories of this action, beyond mentioning that it has often been attributed to the formation of a surface skin, but its occurrence in alkaline accumulators is of interest and pertinent.

Iron in alkaline solution tends to adopt the passive state and oxygen evolution occurs at its surface in preference to oxidation of the metal. Iron in a very finely-divided state, as used in the negative plates, is also passive after immersion in the alkaline electrolyte, but on cathodic polarisation for a short time (discharge of hydrogen at its surface) it becomes active and can be anodically oxidised, and hence the normal plate discharge reaction can occur. On discharge, iron oxide is formed, and it might appear that passification would again set in. This actually occurs slowly and has an important influence on the discharge of the iron electrode. The effect of this slow passification, and the influence of the mercury, added to the negative active material of the Edison cell, in preventing it, is discussed in Chapter VI.

Relation between Heat of Reaction and E.M.F. of Galvanic Cells

We have to consider here the relation between the heat evolved in a chemical reaction and the external work which can be done when the action is made to take place under such conditions as to give rise to electrical energy.

The first law of thermodynamics, which expresses the principle of the conservation of energy, gives us

$$U=A+Q$$

where Q is the heat given out, A the external work done, and U the total diminution of internal energy of the system during the process. If no external work is done, $U=Q$, or the heat of reaction measures the diminution in internal energy. It might be anticipated that in a galvanic cell, which is an arrangement for converting chemical into electrical energy, the electrical energy obtained would be equivalent to the total diminution of internal energy, *i.e.* to the heat of reaction as determined by calorimetric methods, and hence that

$$A=U.$$

The electrical energy obtained is equal to Eq volt-coulombs, where E is the E.M.F., and q the number of coulombs passed.

Now 1 volt-coulomb=0·239 calorie, and the electrical energy is thus equivalent to 0·239 Eq calories. If we now compare this with the heat of reaction for any given process we can test whether the assumption that $A=U$ is correct.

In the Daniell cell the reaction occurring on passing two faradays (or 2×96,500 coulombs) is

$$Zn+CuSO_4=ZnSO_4+Cu$$

The E.M.F. of this cell is 1·09 volts.

$$\begin{aligned}\text{Electrical energy} &= 0{\cdot}239\ Eq\\ &= 0{\cdot}239\times1{\cdot}09\times2\times96{,}500\\ &= 50{,}270 \text{ cals.}\end{aligned}$$

The heat of reaction, as measured by calorimetric means, is 50,130 cals., in close agreement. It thus appeared that the thermochemical and electrical energies were equivalent and that $A=U$, a relation known as *Thomson's law* which was first put forward over seventy years ago. Despite the agreement obtained in the case of the Daniell cell, it was later found that this law was only an approximation, and the correct relation was provided by the *Gibbs-Helmholtz equation.* This equation is derived directly from the second law of thermodynamics, and is

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

in which U represents the total change of energy in a reaction, A is the free energy change, T the absolute temperature, and $\frac{dA}{dT}$ the rate of change of free energy with temperature. The free energy is a direct measure of the maximum work which can be done by the reaction. U, the total change in energy, is measured by the heat of reaction Q when no external work is done.

For A we can substitute nFE, where n is the number of faradays involved in the process (*e.g.* 2 in the Daniell cell). Substituting Q, the heat of reaction, for U, we have

$$nFE-Q=nFT\frac{dE}{dT}$$

This expression gives the correct relation between heat of reaction and electrical energy. It contains Thomson's law as a special case, viz. when $\frac{dE}{dT}=0$. For the Daniell cell the temperature coefficient of E.M.F. is very small, and hence in this case the application of Thomson's law shows a good agreement. In cells in which $\frac{dE}{dT}$ is large, Thomson's law breaks down entirely.

An important deduction from the Gibbs-Helmholtz equation is that when $\frac{dE}{dT}$ is positive $nFE>Q$, and hence the cell absorbs heat while discharging and therefore tends to drop in temperature, lowering its E.M.F. When $\frac{dE}{dT}$ is negative, $nFE<Q$ and heat is evolved in the cell, which rises in temperature, again decreasing its E.M.F. Except when $\frac{dE}{dT}$ is zero, the discharge of a cell always tends to change its temperature in such a way that its E.M.F. drops.[1]

This equation may now be applied to alkaline accumulators.

---

[1] In practice the heat evolved owing to the internal resistance of the cell, may reverse the above effect in the case when $\frac{dE}{dT}$ is positive.

We have

$$E=\frac{Q}{nF}+T\frac{dE}{dT}$$

The thermochemical heats of reaction for the following possible reactions are :

(1) $Fe \rightarrow Fe(OH)_2+68{,}280$ cals.

(2) $Fe \rightarrow Fe(OH)_3+97{,}570$ cals.

(3) $Ni(OH)_3 \rightarrow Ni(OH)_2+650$ cals.

The temperature coefficient of E.M.F. of the iron-nickel oxide cell is unfortunately in much doubt. For the purpose of calculation a value derived from data of Thompson and Richardson (see p. 58) of 0·00024 in 23·8 per cent. KOH will be used. At 18° C. this gives $T\frac{dE}{dT}=0{\cdot}07$ volt.

For the following cell reactions we have :

(4) $Fe+2Ni(OH)_3 \rightarrow Fe(OH)_2+2Ni(OH)_2+69{,}580$ cals.

The value of Q must be expressed in volt-coulombs since these are the terms in which E and F are expressed : 1 calorie =4·183 volt-coulombs, and $n=2$ since two faradays are involved in the above equation.

Substituting, we have :

$$E=\frac{69{,}580\times 4{\cdot}183}{96{,}500\times 2}+0{\cdot}07$$

$$=1{\cdot}51\times 0{\cdot}07=1{\cdot}58 \text{ volts.}$$

(5) $Fe+3Ni(OH)_3=Fe(OH)_3+3Ni(OH)_2+97{,}520.$

Here $n=3$, and we get

$$E=1{\cdot}41+0{\cdot}07=1{\cdot}48 \text{ volts.}$$

(6) $Fe(OH)_2+Ni(OH)_3=Fe(OH)_3+Ni(OH)_2+27{,}940.$

Here $n=1$,

$$\therefore\ E=1{\cdot}21+0{\cdot}07=1{\cdot}28 \text{ volts.}$$

The E.M.F. of a freshly-charged iron-nickel oxide cell is about 1·48, while the steady value reached on standing is 1·35.

It might appear that the 1·48 corresponds to reaction (5) and the 1·35 to reaction (6), but other evidence shows definitely that such a deduction would be incorrect, and that the initial value of 1·48 corresponds to a higher nickel oxide than Ni_2O_3, while the iron undoubtedly discharges according to equation (1), except in the second stage of the discharge. The discrepancy is clearly due to two causes. In the first place the degrees of hydration of the oxides probably do not correspond to those used here, and an unknown correction has therefore to be applied to the heats of reaction, and in the second place little reliance can be placed on the value of $\frac{dE}{dT}$ used. Owing to the lack of accurate data, the application of the Gibbs-Helmholtz equation does not provide the definite test that might have been anticipated of the mechanism of the discharge reactions.

CHAPTER IV

ELECTRICAL CHARACTERISTICS

Capacity.—The capacities of various types of alkaline cells, together with weights, dimensions, and other relevant data, will be found in the Appendix, Tables 11 and 12. The corresponding data for lead cells of similar capacity are included in Table 11 for comparative purposes. The values given in this table are the capacities quoted by the manufacturers, and may be taken as typical figures.

Factors determining Capacity.—The capacity of any cell is, of course, limited primarily by the amounts of the active materials present and their " coefficients of utilisation," that is, the percentage of the total weight of active material which is capable of reacting during the discharge before the limiting voltage is reached.

The final voltage is fixed empirically, from a consideration of the characteristics of the cell. As a rule the discharge curve of any cell (voltage plotted against time) slopes gradually for the main period of the discharge and then becomes steeper, and finally falls abruptly. This last steep part of the curve represents a part of the discharge which is of no value in practice, and the final voltage is usually fixed at the point where the voltage begins to fall rapidly—sometimes called the " knee " of the discharge curve.

The actual physical conditions in the cell which cause this rapid fall in voltage at the end of the discharge are of quite a different nature in alkaline and lead cells.

In the lead cell the controlling factor in limiting the capacity at normal rates is not the exhaustion of the available active materials in the plates, but the reduction of acid density in the pores of the plates. When the discharge has proceeded for some time, the rate of diffusion of acid from the bulk of the electrolyte into the inner parts of the active material is not sufficient to balance the rate of removal of acid by the discharge reaction. Thus the acid becomes very dilute, the E.M.F. is lowered, and the internal resistance and concentration polarisation are increased, causing the voltage of the cell to fall.

In the alkaline cell, the limiting factors are entirely different. Since the change in electrolyte concentration at both plates is extremely small, diffusion effects and change in electrolyte resistance have practically no part in limiting the discharge. The exhaustion of the available active material in the plates determines the capacity. This does not mean that all the nickel oxide and iron or cadmium respectively have reacted. The discharge reactions can only take place on the surface of a particle of the material, in contact with the electrolyte, and in electrical contact with the conducting grid or frame. The physical factors which limit the discharge are thus the porosity, or available surface, of the materials, their conductivity, and the efficiency of contact between them and the metal pockets containing them. It is well known that the oxide of iron formed during the discharge of the Edison cell has a low electrical conductivity, necessitating the addition of mercury as a conducting agent. During the discharge of the cell considerable changes in volume of the active materials occur, and the electrical contact between the paste and pockets is reduced. These factors cause an increase in the internal resistance of the cell, and result in the fall of voltage. This essential difference between the physical behaviour of lead and alkaline cells is reflected in the relation between capacity and rate of discharge.

In the lead cell the reduction of acid concentration in the pores proceeds much more rapidly at high rates of discharge, and in consequence the limiting fall in voltage occurs much more rapidly. For example, the capacity when discharged at the 1-hour rate is little more than half of that obtained at the 10-hour rate. Since the resistance of the pastes, and of the electrolyte between the plates, is so low as to have little effect on the available voltage, the terminal voltage of the cell at the beginning of the discharge is only slightly lower at high than at low rates, but the curve of voltage against ampere hours drops much more steeply.

In the alkaline cell, owing to its higher internal resistance, the cell-voltage is lower at the beginning of the discharge at high rates; but if voltage is plotted against ampere hours at different rates, the curves are almost parallel. Thus it is frequently stated that an alkaline cell is capable of giving almost its full capacity at high rates of discharge. It must be remembered, however, that the voltage at the end of such a discharge may be so low as to be of little value for many purposes.

Curves are given in Figs. 16 and 17 showing the discharges of Edison and Nife cells at normal and higher rates of discharge. These curves have been drawn from data and curves published by the manufacturers of the cells. The curves of Fig. 18 show the discharge of a lead cell, plotted in the same way, at the normal and higher rates, which may be compared with the curves for the alkaline cells. The voltage of the lead cell falls rapidly if the discharge is continued beyond the normal end-point, and it is not possible to obtain the normal capacity, when discharging at high rates, by continuing the discharge to a low final cell-voltage, as may be done with alkaline cells.

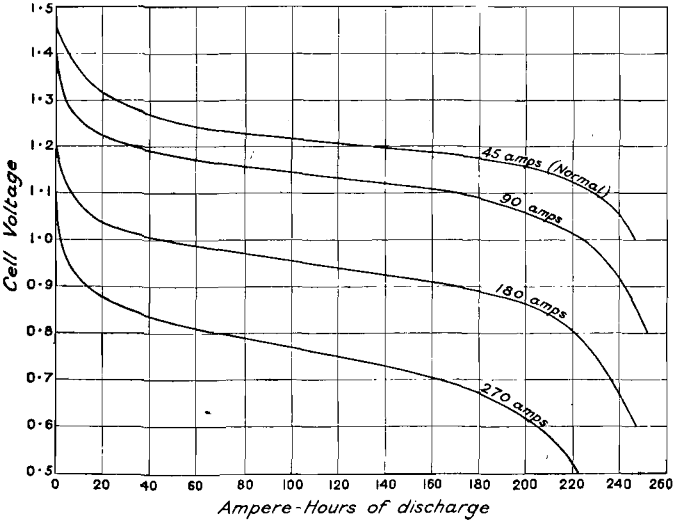

FIG. 16.—Discharge of Edison cell at different rates.

Other factors must be considered, which make the capacity/rate relationship less simple. The internal resistance of the alkaline cell increases during the course of the discharge, and, as this causes a fall in terminal voltage proportional to the current passing, the loss is greater at the

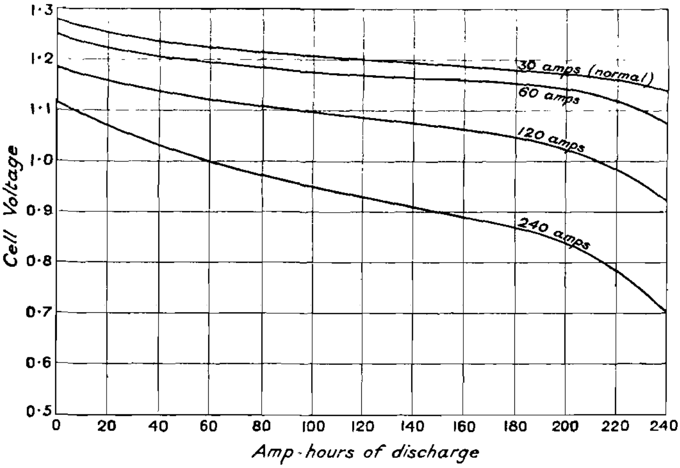

FIG. 17.—Discharge of Nife cell at different rates.

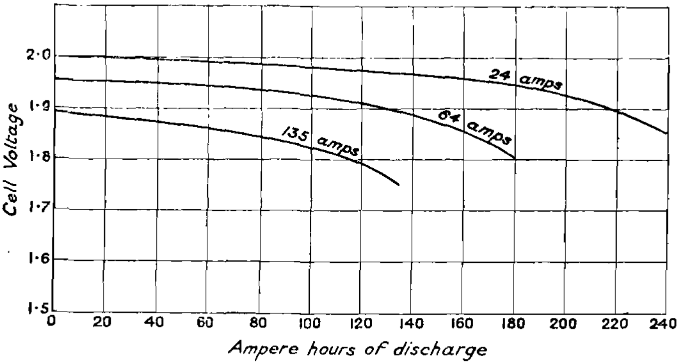

FIG. 18.—Discharge of lead accumulator at different rates.

end of a high rate discharge, and is represented by a steeper slope in the high-rate than in the low-rate discharge curve.

At excessively high rates the iron negative plate tends to become "passive"—especially at low temperatures. This factor is probably not of importance at any but exceptionally high rates of discharge at ordinary operating temperatures.

Coefficients of Utilisation of Active Materials.—If the theoretical weight of active material required for each ampere hour of discharge is calculated, and compared with the actual weight of material necessary to give a capacity of 1 amp. hour, it is found that in all secondary cells the material must be present in much greater amounts than the theoretical minimum. The fraction of the weight of material actually taking part in the discharge is called the "coefficient of utilisation."

In the Edison cell[1] the coefficients are: for the positive material 0·215, and for the negative material 0·173.

The Nife positive plate has a coefficient of 0·23, and the negative 0·42. These values are calculated from weights of material stated by the manufacturers, and the coefficient for the negative plate is determined on the assumption that 75 per cent. of the discharge is given by the cadmium and 25 per cent. by the iron.

Comparative values for lead cells are of interest. The positive plate coefficient[2] may vary from 0·43 for a soft paste, to 0·20 for a very hard paste.

Measurements made on a small cell give a value 0·19 for the negative plate. This cell, however, had a considerable excess of capacity in the negative plates, and a complete discharge of the negatives gave a coefficient of 0·33.

Change of Capacity with Temperature.—It is generally agreed that there is a critical minimum temperature below which a cell of the iron-nickel type will not give any useful discharge capacity. This is attributed to the passivity of the iron at low temperatures, which is particularly marked at high rates of discharge. With the cadmium-iron negative plate, the reduction in capacity at low temperatures, though still very considerable, is less serious.

At normal rates of discharge the Edison cell loses about 2 per cent. of its capacity for a reduction in temperature of

---

[1] Vinal: *Storage Batteries*, p. 207.

[2] *Ibid.*, p. 183.

1° C., between 20° and 10°, the final voltage being fixed at 1·0 volt; the loss in the cadmium-iron type is somewhat less. At about 5° C., at high rates of discharge, no capacity can be obtained from the iron-nickel cell above the normal end-point of 1·0 volt, while the cell with cadmium-iron negative gives only about one-third of the capacity measured at 25° C. at the same rate of discharge, to the same final voltage.

The temperature coefficient of capacity of an Edison cell is given by Turnock[1] as about 1·6 per cent. per 1° C. between 20° and 30°, and about 2·3 per cent. per 1° C. between 30° and 40°. A further small increase of capacity is obtained at 50° C., but above this temperature the capacity decreases. This decrease is attributed to the inefficiency of the charging process at the positive plate at high temperatures, and to the fact that the iron negative material is attacked by the potassium hydroxide solution at such temperatures.

Bennett and Gilbert[2] state that they obtained a discharge of 233 amp. hours at a temperature of 4° C. from an Edison cell whose normal capacity was 350 amp. hours. The cell was discharged to 0·7 volt in all cases. This figure was obtained in a single discharge, and no corroborating capacity measurements were made. As pointed out by Holland in discussing the paper, the loss in capacity at low temperatures is normally much greater than the value given by Bennett and Gilbert, and not much weight can be attached to the result of a single measurement.

Herold[3] states that an Ionic battery has a capacity 25 per cent. smaller at 0° C. than at 50°, when the final voltage is 1·0 volt, the average voltage during discharge being 7 per cent. lower. As the characteristics of this type of cell are, in general, very similar to those of the Edison cell, it is probable that this figure seriously underestimates the loss in capacity as the temperature is reduced.

The following table, which is derived from curves supplied by the makers, gives the capacity of Nife cells of two types: Type I, low resistance type, 125 amp. hour cell; Type II, normal type, 120 amp. hour cell, to final voltages between

---

[1] *Trans. Amer. Electrochem. Soc.*, 30, 1916, 273.

[2] *Journ. Phys. Chem.*, 17, 1913, 322.

[3] *Bull. Soc. Belge. Ing. et. Indust.* V., 1924, No. 2.

1·20 volts and 0·5 volt, when discharged at 70 amps. in room temperatures of 20° C. and −16° C. respectively.

TABLE 4

Capacities (A.H.) of Nife Cells at 20° C. and −16° C.

Final cell voltage.	Type I. Room Temperature.		Type II. Room Temperature.	
	20°.	−16°.	20°.	−16°.
1·20	32·0	—	—	—
1·10	81·7	3·0	24·7	—
1·00	98·0	28·3	76·0	0·7
0·90	103·7	43·8	103·3	3·6
0·80	106·8	49·2	112·5	22·2
0·70	108·1	50·3	116·0	43·2
0·60	108·9	52·0	119·0	54·2
0·50	109·5	54·5	120·0	60·1

It should be noted that although the capacity of an alkaline cell is considerably reduced at low temperatures, particularly in the case of Edison cells, such cells can be, and frequently are, used in conditions where the external temperature is excessively low. When they are in continuous use, the working of the cells maintains their temperature well above that of the surroundings, and the cells can be usefully employed (cf. Fox [1] and Smith [2]).

Discharge Curves.—Typical charge and discharge curves of alkaline cells are given in Fig. 19. A comparison of any of the discharge curves with the typical form of discharge curve for the lead cell (Fig. 20) shows that the most striking difference is the greater proportional fall in voltage in the alkaline cell during the discharge. The alkaline cells fall from about 1·25 to 1·00 volts, 20 per cent., while the lead cell falls from 1·95 to 1·75 volts, approximately 10 per cent. This voltage variation has an important bearing on the methods of operation of alkaline cells and will be discussed further under that heading (Chapter V).

Charge Curves.—The charge curves of the two different types of alkaline cell are very instructive. The iron-nickel (Edison or Ionic) cell rises on charge at the normal rate to a voltage of 1·60–1·65 volts almost immediately. This is frequently followed, in the Edison cell, by a slight fall in

---

[1] *Electrician*, 72, 1914, 580.

[2] *Trans. Amer. Elec. Chem. Soc.*, 31, 1917, 339 (discussion).

voltage, due probably to changes in temperature and internal resistance, which is not of theoretical or practical importance.

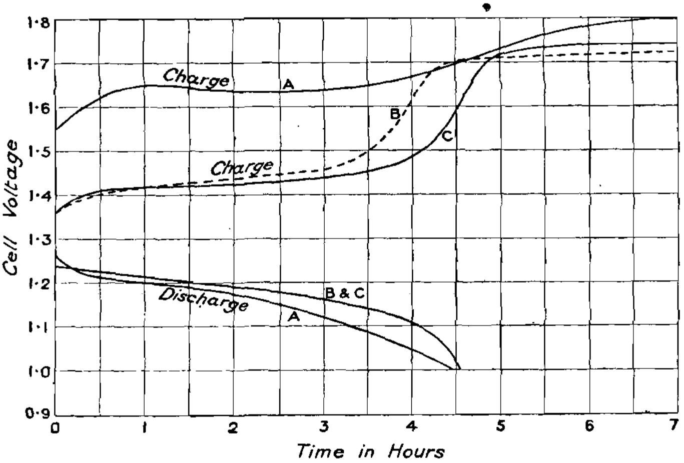

FIG. 19.—Discharge and charge curves: A. Edison cell. B and C, Jungner cells.

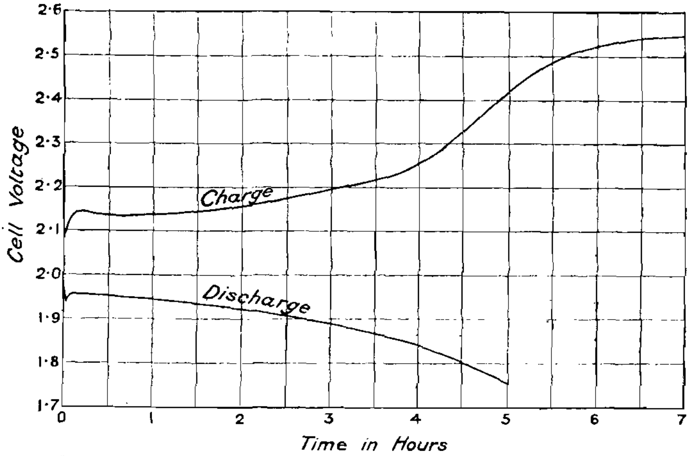

FIG. 20.—Discharge and charge curves of lead accumulator.

The voltage then rises gradually throughout the whole of the charge, more steeply when the charge is nearing completion, and reaches an approximately steady value between 1·80 volts and 1·85 volts.

The Jungner type of cell, with cadmium-iron negative plate, rises at first to a voltage of about 1·4 or 1·5 volts, and the greater part of the charge is carried out at this voltage. After about two-thirds of the total time of charge, the voltage rises to about 1·7 or 1·8 volts, and only a slight further rise occurs during the remainder of the charge.

This difference in the behaviours of the two types of cell is of considerable theoretical and practical interest. From the practical point of view, it means that the watt-hour efficiency of the Jungner type of cell is appreciably higher than that of the Edison type, since the average charging voltage of the former is about 0·15 volt (or about 10 per cent.) lower.

The high voltage throughout the charge of a cell with iron alone as the negative material is due to the fact that the iron oxide formed on discharge cannot be charged "reversibly," but only when a considerable excess of voltage is available. As a result of this, a very low charging rate is ineffective, since hydrogen can be evolved, with a low current density, at a lower voltage than is required to reduce the iron oxide. At higher current densities the two reactions proceed simultaneously, hydrogen being evolved during the whole of the charge. This means, of course, a waste of current, and a reduction of the ampere-hour efficiency of the cell, in addition to the reduction in watt-hour efficiency noted above.

The fact that the charge proceeds at a lower voltage in cells of the Jungner type must be attributed to the presence of the cadmium in the negative plates. The charging potential of the iron plate is not reached until the "step" after about two-thirds of the charge is complete. Further, there is no appreciable evolution of hydrogen during the first stage of the charge, and the ampere-hour efficiency is therefore higher in this type of cell. This point is further discussed in Chapter VI, p. 89, and Chapter VIII, pp. 113 *et seq.*

Efficiency.—It will be seen from the form of the charge curves (Figs. 19 and 20) that the watt-hour efficiency of both types of alkaline cell is distinctly lower than that of the lead-acid cell owing to the higher ratio of average charging voltage to average discharge voltage.

The reactions of the alkaline nickel-iron cell are not strictly reversible at either plate. According to Thompson and Richardson[1] the efficiency of the nickel-oxide plate is lower than that of the iron plate. Their measurements were made on the early type of Edison cell, and may therefore not be applicable to present-day types. Fox[2] gives the normal ampere-hour and watt-hour efficiencies as 80 per cent. and 58·5 per cent. respectively for the later type of Edison cell. The manufacturers of this cell state that in normal conditions the ampere-hour efficiency is 75–80 per cent., and the watt-hour efficiency 55–60 per cent., while the Jungner type of cell is stated by the makers to give an ampere-hour efficiency of 75–80 per cent. and watt-hour efficiency of 60–65 per cent.

These figures may be compared with the normal values for a lead cell, viz. ampere-hour efficiency about 90 per cent., watt-hour efficiency 75 per cent.

The figures quoted all refer to a battery working normally with complete charge and discharge. If a shorter charge is given, a higher value of efficiency is obtained, but, of course, a smaller capacity.

Thompson and Byrne[3] state that the efficiency of both plates in the Edison cell is lower at lower temperatures.

Effect of Overcharging.—After a considerable excess over the normal charge has been given to an alkaline cell, the capacity of the positive (nickel-oxide) plate is appreciably higher than normal. In the Edison cell, and some types of Jungner cell, the positive plate has a smaller capacity than the negative, and therefore controls the capacity of the cell. In these conditions an additional capacity can be obtained from the cell by excessive charging. At least one type of Jungner cell, having a greater capacity in the positive plate than in the negative, does not show this effect, since the negative plate, and not the positive, controls the discharge.

Loss of Capacity when Standing Idle.—The fully

[1] *Trans. Amer. Elec. Chem. Soc.*, **7**, 1905, 97.

[2] *Electrician*, **72**, 1914, 580.

[3] *Trans. Amer. Elec. Chem. Soc.*, **31**, 1917, 339.

charged nickel-oxide positive plate contains a percentage of unstable nickel peroxide. If the cell is immediately discharged, the first reaction is the discharge of the nickel peroxide to nickelic oxide, after which the usual reaction continues at a lower potential. If the cell is allowed to stand idle in the fully charged condition, the peroxide is decomposed, and a corresponding loss in the capacity of the positive plate results. When all the nickel peroxide has been decomposed, either by standing or by a partial discharge of the cell, the loss of capacity is very slow.

The following data are taken from curves given by Holland.[1]

Time of Standing (hours).		1.	3.	6.	12.	24.
Percentage loss.	Fully charged cell	3·5	5·5	7·0	8·5	11·0
	One-third discharged cell	0·5	1·0	1·5	1·5	1·5

The above figures refer to cells at 75° F.

The loss of capacity when standing at 35° F. was found to be rather less than half that occurring at 75° F.

Thompson[2] gives a curve showing the loss of capacity of Edison cells at 22° C. During the first day the cells lost 8 per cent. and in four days about 15 per cent. of their capacity, after which the loss was almost constant, and equal to about 0·5 per cent. per day.

Loss of capacity due to this cause will not, of course, be observed in cells with an excess of capacity in the positive plate. The high initial voltage due to the presence of nickel peroxide will be observed in the discharge of such a cell immediately after charge, but after a period of standing following the completion of charge, the initial voltage on discharge will be lower, while the capacity will remain practically unaltered.

The rate of loss of capacity of the negative plate at ordinary temperatures should be practically negligible, but at high temperatures the attack of the alkali on the iron

[1] *Electrician*, 66, 1910, 47 and 83.

[2] *Theoretical and Applied Electrochemistry*, 1925, p. 326.

causes a loss of capacity which cannot be recovered by overcharging. This effect is considered in more detail elsewhere (see Chapter VII).

Effect of Temperature on E.M.F.—The available data do not give consistent values for the temperature coefficient of E.M.F. Thompson and Richardson[1] quote Foerster as giving the value 0·0007 volt per degree, between 0° and 30° C., independent of the concentration of the electrolyte. These authors themselves found the following values :

Concentration of Electrolyte (per cent.).	Range.	Temperature Coefficient of E.M.F. (volts).
6·25	4·6°—17·7°	+0·00069
23·8	1·3°—32·6°	+0·00026
23·8	4·18°—20·11°	+0·00022
50·0	4·9°—17·9°	+0·00008

Schoop[2] gives a value of 0·00035 volt per degree between 0° and 60° C.

Internal Resistance.—In general, the internal resistance of an alkaline cell is higher than that of a lead cell of similar capacity. In discussing the internal resistance of a cell it is important to define what is meant by the term, as different values are obtained by different methods of measurement. In a lead cell at the beginning of a discharge, the voltage across the cell terminals is lower than the open circuit voltage by an amount depending on the rate of discharge. The loss of voltage is due to a combination of the true ohmic resistance of the cell and the polarisation of the electrodes due to the passage of the current. If the resistance of the cell is measured by an A.C. bridge method, the polarisation effect is excluded, and the true resistance may be determined. In practice, however, the important factor is the fall in voltage when a discharge current is delivered by the cell, and the ratio of fall in voltage to current passing, may be called the " effective " resistance of the cell.

Vinal[3] gives the value of the internal resistance of a lead cell of capacity 140 amp. hours, as 0·0016 ohm. This may be compared with the values given by Lyon[4] in a curve

---

[1] *Loc. cit.*

[2] *E.T.Z.*, **26**, 1905, 769.

[3] *Storage Batteries*, p. 293.

[4] *Jour. Ind. and Eng. Chem.*, **3**, 1911, 922.

showing the change in resistance of Edison cells during a normal discharge. For the A–4 cell, capacity 150 amp. hours, the resistance is approximately 0·003 ohm at the beginning of discharge, and remains almost constant until near the end of the discharge when it rises rapidly, reaching 0·0075 ohm when the discharge was stopped. Similar results are given by Holland.[1]

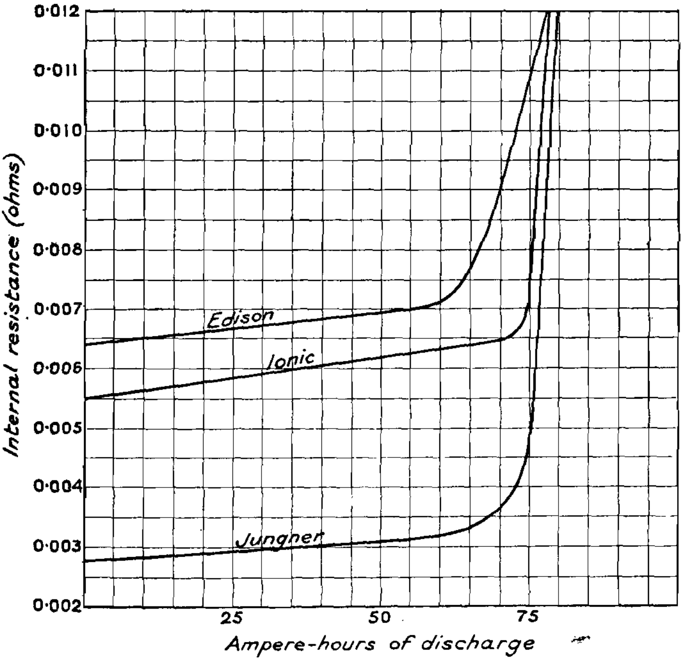

FIG. 21.—Internal resistance during discharge.

Curves are given in Fig. 21 showing the change in internal resistance of Edison, Ionic, and Jungner cells of 75 ampere-hour capacity throughout the discharge. These curves are reproduced from a paper by Herold.[2] The much

---

[1] *Electrician*, 66, 1910, 47 and 83.

[2] *Bull. Soc. Belge Ing. et Indust.*, V., 1924, No. 2.

lower internal resistance of a cell of the Jungner type is noteworthy.

In normal operation the internal resistance of an accumulator is so small a factor as to be of little importance ; but when very high rates of discharge are required, the available voltage of the cell is correspondingly reduced, and the rise of temperature in the cell may be serious (cf. p. 66, Chapter V).

Life.—The mechanical strength of the alkaline type of cell and its freedom from serious ailments are possibly the most striking features in a comparison between this and the lead-acid accumulator. While no definite figures can be given for the normal life of a cell, since operating conditions are not always alike, there is no doubt that the alkaline cell is capable of giving a satisfactory performance for a much longer life than the lead cell. This feature is particularly valuable under severe operating conditions, such as traction and vehicle lighting batteries undergo, where the cells are subject to serious vibration.

An independent observer has recorded a useful life of fourteen years for a battery of Edison traction cells. This cannot be taken as an average life, but it indicates the remarkable permanence of alkaline cells, due mainly to their strong mechanical construction.

CHAPTER V

OPERATION AND MAINTENANCE

It is important to emphasise the differences between the treatment required by alkaline cells and that given to lead cells. In the previous chapter, the electrical characteristics of alkaline cells have been described, and the operation of a battery must be modified to suit the peculiarities of the cells employed.

Voltage Regulation.—As is seen in the discharge curves of Fig. 19, p. 54, there is a considerable fall in voltage during the discharge of an alkaline cell. If it is required to maintain a constant difference of potential between the bus-bars during a complete discharge, some means of varying the number of cells in series in the battery is necessary.

The usual practice is to compensate for the fall in voltage by switching into circuit a number of "end-cells." These are connected in series with the main battery, and a tapping is taken from between each two end-cells to a switch so arranged that any number of the end-cells can be included in the battery as required. If, for example, it is required to maintain a voltage of 100 volts from a battery of Edison cells, throughout a complete discharge at the normal rate, the total number of cells required will be 100, of which 30 must be connected as end-cells. At the beginning of the discharge, with a voltage of 1·40 volts per cell, only the 70 permanently-connected cells will be in circuit, while at the end of the discharge, with a voltage of 1·00 volt per cell, almost all the end-cells will be required. Since the end-cells are only partly discharged, their average voltage will be rather higher than 1·00 volt at the end of the discharge, and the arrangement described will leave a margin of safety in case of weak cells or excessive discharge.

Using cells of the nickel oxide—cadmium-iron type, with a voltage range from 1·25 to 1·0 volts during the discharge, a battery of 100 cells, of which 20 are connected as "end-cells," will be necessary for a constant battery voltage of 100 volts.

On charge it is, of course, desirable to cut out the end-cells gradually, so that each cell receives a charge proportional to its discharge. This practice can readily be adopted with the regulating cells of a battery of lead accumulators, each cell being cut out of circuit when its charge is complete. With an alkaline battery, however, the difficulty of determining the state of charge of the cells makes this treatment impracticable, and it is better practice to include all the end cells in the complete charge of the battery. A lower efficiency is obtained from the battery, but this is justified by the simplicity of operation.

Indications of the State of Charge of a Cell.—In the operation of a lead cell there are three distinct indications of the completion of a charge. The *voltage* of the cell, charging with a constant current, rises to a steady figure; the *density* of the electrolyte rises during the charge to a constant value; and free *evolution of gas* occurs from both positive and negative plates when the charge is complete.

In the alkaline cell there are no such definite criteria of the state of charge. As will be observed from the curves of Fig. 19, the voltage rises comparatively slowly over a long period of the charge, and if the charge is prolonged beyond the normal period, the voltage continues to rise slowly.

The electrolyte, which undergoes little or no change with the reactions of the cell, does not alter appreciably in density during charge or discharge, and cannot therefore be used as an index of the state of charge.

Gas evolution occurs during the whole time of charge, particularly in Edison type cells, and the rate of evolution increases gradually towards the completion of the charge. The construction of alkaline cells also makes it difficult to observe the rate of gassing.

Similarly, when the cell is discharging, the acid density in a lead cell indicates the state of the cell, and the amount of capacity still available, whereas in the alkaline cell no such indication is given.

It is clear, then, that the operation of a battery of alkaline cells cannot be controlled by means of occasional observations of " pilot " cells, as is usual with a lead battery.

The state of charge of an alkaline cell can only be satisfactorily determined by a knowledge of its previous treatment.

During a continuous discharge at constant current, the voltage of a cell or battery is an indication of its state. Curves of discharge voltage at various rates are usually issued by the manufacturers and recommended for this purpose. On an intermittent discharge, however, the indication given by the cell voltage and the use of a discharge curve cannot be considered a trustworthy guide.

For this reason it is necessary, in many installations, to measure the amount of discharge taken from a battery, and the amount of charge given to it, by means of an ampere-hour meter, or recording ammeter. The capacity taken from a battery since the last full charge and the capacity remaining available are then known.

At least one firm of alkaline cell manufacturers make it a condition of their guarantee for road vehicle and locomotive batteries that an ampere-hour meter shall be mounted in the charge and discharge circuit of the battery, and that the meter shall be adjusted to read either 25 per cent. slow on discharge or 33½ per cent. fast on charge, in order that the battery may be worked to an average ampere-hour efficiency of 75 per cent.

This may seem a simpler operation than the observation of specific gravities in a lead battery, but it is difficult to obtain ampere-hour meters capable of recording accurately the input and output of a battery under loads which vary from hundreds of amperes to very small currents, as commonly occurs with stationary batteries.

The amount of charge required by a battery is determined by multiplying the output measured during discharge by a factor depending on the ampere-hour efficiency of the battery. An excess of about 30 per cent. over the discharge capacity is necessary.

Alternatively, the charge may be continued until the voltage has remained constant for one hour at the normal charging rate. Where practicable, the former method of charging is preferable.

The absence of clear indications of the state of charge must be considered a definite disadvantage of the alkaline cell, as it leads to difficulties in operational routine.

The practice of taking regular readings of the acid density of lead cells is, however, not adopted merely as a means of controlling the operation of the battery. It is necessary to take periodical readings, in order to guard against failures caused, for example, by under-charging, excessive charging, or self-discharge due to impurities or internal short circuits. The alkaline cell, on the other hand, does not require any constant care necessitating regular observations of the individual cells. As it is little affected by standing idle in any state of charge, by over discharge, or by excessive charging, the trouble is limited to one of operation, and against it must be weighed the fact that no routine of regular observations of individual cells is required.

Rates of Charge.—Owing to the nature of the reactions in the iron-nickel (Edison type) cell, which are not completely reversible, it is not possible to charge an alkaline cell of this type at less than a certain minimum current density. The iron negative plate can only be charged when a definite polarisation is exceeded, and the charging potential of this plate is actually higher than the potential required for the evolution of hydrogen. Consequently, at very low current densities, where the polarisation is small, current is wasted in evolution of hydrogen. As the current is increased, the polarisation increases until the charging potential of the iron oxide is reached ; above this current density the reactions proceed concurrently, part of the current being usefully employed in charging the plate, while part is still wasted in gassing.

The result of this characteristic of the cell is, of course, to reduce the ampere-hour efficiency, and also to make cells of this type unsuitable for certain applications. It is not possible, for example, to operate a nickel-iron alkaline battery by the method known as "floating on the line." In this arrangement, the battery, usually about three-quarters charged, is connected across the terminals of a generator which is at the same time supplying current to an external circuit. The battery has thus a small charging current or a small discharging current according to the load, and in the lead accumulator the voltage is almost unchanged with change in direction of the current.

Cells of the Jungner type, with a mixed cadmium-iron negative material, can be efficiently charged at low rates, except when the cell is completely discharged, since the charging potential of the cadmium oxide does not exceed that required for hydrogen evolution. As with the nickel-iron cell, however, the difference in cell voltage when charging and discharging, even at low rates, makes this type of cell unsuitable for use as a battery " floating on the line."

The *maximum charging rate* of an alkaline cell is limited principally by the rise in temperature. A definite maximum temperature may not be exceeded without damage to the cells. The time required for a cell charging at a given rate to reach this limiting temperature will, of course, depend on the external temperature, and definite figures cannot be given for the maximum rates of charge. In average conditions the following charge rates may be used for Edison cells:

5 times the normal rate for 5 minutes.
4 " " " 15 "
3 " " " 30 "
2 " " " 60 "

Certain makers of cells of the Jungner type allow a maximum temperature of about 140° F., as compared with a limit of 115° F. for Edison cells and for others of the Jungner type, and higher rates, or longer periods, will therefore be permissible with these cells. In general, however, such excessive temperatures should be avoided.

In tall cells the rise of electrolyte and frothing through the filler may limit the charging rate.

The *normal rate of charge* is the same current as the 5-hour rate discharge. This is approximately the rate specified by all makers of alkaline cells.

Boosting charges, or freshening charges at a high rate for short periods, may be given, at a rate determined by the amount of discharge which has been taken from the cell and the time available for boosting, up to the maximum rates of charge quoted above. A temporary idleness of a battery may thus be utilised to give a supplementary charge and obtain additional service from the battery before the regular normal charge.

Constant potential charging of a battery is a method in which a constant potential is maintained across the battery terminals throughout the whole charge. The current initially is much above the normal charge rate, but falls as the battery potential rises to a value nearly equal to the impressed voltage. By the introduction of a suitable series resistance in the battery circuit, a modified or " semi-constant potential " system may be employed. The potential across the battery and resistance is then kept constant, and, as the current decreases, the potential across the battery terminals will automatically increase.

This method has the further advantage that small variations in the impressed voltage will not cause such large fluctuations of the current as in the absence of the series resistance.

The constant current method of charging is preferable, especially as alkaline cells rapidly rise in temperature at high rates of charge. If the constant potential method is adopted, special care must be taken that the permissible limit of temperature is not exceeded.

Rates of Discharge.—The permissible rate of discharge of a battery, like the rate of charge, is limited by the rise of temperature. Normally the one-hour rate is the maximum rate at which a continuous discharge can be taken. Higher rates are, of course, allowable for short periods ; and the external temperature will have an important bearing on the permissible rates.

Maintenance.—One of the most striking of the advantages of the alkaline cell is its freedom from ailments. A lead battery requires constant skilled attention to guard against, and when possible to cure, such faults as sulphation, buckling, and loss of active material, all of which are liable to occur if the operation of the battery is not very carefully controlled. It is necessary to make frequent routine examinations of every cell in the battery to detect such faults.

In the alkaline battery, on the other hand, it is not necessary, for the health of the cells, to control the operation exactly, since faulty operation (insufficient or excessive charging, etc.) does no damage.

For similar reasons, the maintaining or refreshing charges which must be given to a lead battery which is standing idle are unnecessary with an alkaline battery. After a *long* period of idleness it is usually found that an alkaline cell gives a low capacity. The treatment recommended by the Edison Company is to discharge the battery to zero voltage, short circuit for six hours, and give an extended charge. This treatment should be repeated up to six times if the results justify. A manufacturer of the Jungner type of cell states that only a temporary sluggishness is caused by a long period of idleness, and that this may be rectified by charging the cells at the normal rate for double the normal time. One such treatment is stated to restore the cells to full activity.

As a general rule it is desirable to overcharge rather than undercharge an alkaline battery.

Periodical Discharges.—In a battery which is not normally working in cycles of complete discharge and charge, it is recommended that a discharge down to 1·0 volt per cell should be taken once a month, and that this discharge should be followed by a charge at the normal rate for double the normal time.

" Topping Up."—The level of electrolyte must be maintained by the addition of pure distilled water, at intervals which will depend on the working conditions. High temperatures and large amounts of charging will, of course, accelerate the loss of water from the cells. Owing to the difficulty of observing the level of electrolyte in alkaline cells, of which the containers are of steel, a special apparatus is sometimes used for topping-up, which indicates when the correct level has been reached by completing an electric bell circuit through the electrolyte.

It is essential that the electrolyte level should not be allowed to fall below the tops of the plates, as there is a liability of permanent damage being done to the active materials; the iron of the negative plate, in particular, is damaged by oxidation when exposed to the air, and loss of capacity results.

Insulation and Cleaning.—All alkaline cells have metal containers, which necessitates the provision and maintenance of efficient insulation between adjacent cells, and between each cell and earth, in order to avoid leakage currents. The cells are normally provided with insulating supports, and with studs for the separation of the containers.

Care must be taken to keep the outsides of containers clean and free from splashes or leakage of electrolyte. With metal containers, supported and separated by insulating blocks, comparatively short leakage paths, with correspondingly low resistance, may result from the lack of this precaution. Leakages of current between cells, or from a section of the battery through an accidental earth, may cause considerable trouble.

It is desirable to keep the tops of the containers slightly oily, as this reduces the probability of leakage-paths being formed by splashes or creeping of electrolyte. A regular brushing with mineral jelly is recommended.

Impurities in Electrolyte.—While little definite information is available about the effects of various impurities on the performance of alkaline cells, it is generally stated that the presence of carbonate in the electrolyte leads to a reduction in capacity. A potassium hydroxide solution, such as is used for electrolyte, very readily absorbs carbon dioxide, forming potassium carbonate. Special precautions must therefore be taken to exclude the air—which normally contains a small percentage of carbon dioxide—from the cells. Alkaline cells are always constructed with sealed containers, the only openings being the necessary gas vent and filling cap. The gas vent is, as a rule, provided with a valve, or in larger cells a water seal, which prevents the entry of air into the cell. It is important that these valves should be kept closed and in working condition. A further source of contamination is the distilled water used for topping up, which contains carbon dioxide in solution, unless kept in sealed vessels. This source of impurity does not appear to be generally recognised, but it is certainly desirable to keep distilled water for topping-up out of contact with air as far as possible.

The effect of carbonate and other impurities is discussed more fully in Chapter VII.

It is usual for manufacturers to issue instructions that the electrolyte must be changed at intervals of about 12 or 14 months. The determining factor in deciding when the electrolyte should be changed is the fall in specific gravity. For Edison cells a limit of 1·160 is given, while the manufacturers of the Nife (Jungner type) cell state that 1·170 is the minimum allowable specific gravity. The latter firm also state that the electrolyte should not be used after the potassium carbonate in the solution has reached a concentration of 30 gms. per litre.

The available data do not show clearly that any permanent improvement results when the carbonate content is reduced by changing the electrolyte. Curves published by the Edison Co. indicate that a gain in capacity of about 5 per cent. was observed after the electrolyte was changed, but this gain appears to have been lost in the course of a few cycles, and the rate of loss of capacity of the cell then continued at the same rate as before the renewal. No analyses are given showing the percentages of carbonate present in the electrolyte when the various changes were made, so that no definite conclusions can be drawn from the curves.

The presence of carbonate causes a " sluggishness " of the cell, that is, a poor output, especially at high rates of discharge.

A number of causes help in the reduction of the specific gravity of the electrolyte, of which the loss of alkali carried over by the gas during charge, and accidental spilling, are the most important.

Renewal of Electrolyte.—For the Edison cell special renewal electrolytes are supplied, differing in composition from that used for a new cell. The " First Fill Electrolyte " is a 21 per cent. solution of potassium hydroxide containing 50 gms. of lithia per litre. The " Refill Electrolyte " is used for cells which have been " formed " by the manufacturers and dried off for transport. It is a 21 per cent. solution of potassium hydroxide, containing as much lithium hydroxide as is normally found in the original electrolyte after formation; its purpose is, of course, to reproduce in the cell the same conditions as existed before the original electrolyte was removed. It is also used to replace spilt electrolyte.

The " Renewal Electrolyte " is used for cells in which the specific gravity of the electrolyte has fallen to the lower limit permitted, viz. 1·160. It is a 25-per cent. solution of potassium hydroxide and contains 15 gms. of lithium hydroxide per litre. The stronger solution is necessary, in order that, after it has mixed with the weaker electrolyte held in the pores of plate, the same concentration shall be reached as in the original electrolyte. Less lithium is used because during the working of the cell this becomes bound in some way in the active material of the positive plate, and the concentration of lithium in the electrolyte is thus normally lower than in the new electrolyte.

In alkaline cells of the Jungner type, which do not use lithia in the electrolyte, the only difference between the original and the refill electrolyte is that the density of the solution is increased, to allow for the weaker electrolyte retained by the plates and for water used in washing. Thus, with a normal working density of 1·19, one maker recommends that the electrolyte should be renewed when the density has fallen to 1·17, and the renewal electrolyte has a density of 1·21.

It is stated that in a cell in daily use this limit is reached after about 12–18 months, and therefore annual renewal of the electrolyte is considered necessary.

In renewing the electrolyte, the instructions issued by the makers must be followed closely. Edison cells are discharged and short-circuited. Nife cells are discharged to 0·8 volt, and after emptying are washed out with distilled water and drained.

Ventilation.—It is essential that efficient ventilation be provided in battery rooms and charging rooms, to prevent the accumulation of an explosive percentage of hydrogen, and also to carry away any fine spray from the electrolyte suspended in the air.

Potassium hydroxide is not so injurious to the common metals as the acid spray from lead accumulators, but may do damage to instruments, and may cause trouble by spoiling the insulation between various electrical circuits.

The total amount of gas evolved from an alkaline cell during charge is greater than from a lead cell charging at the same rate, because gassing occurs during the whole of the charge of the alkaline cell. The maximum rate of gas evolution at the completion of charge, when the whole of the current is spent in gassing, is, of course, the same in both types of cell, being dependent only on the current passing, and determined by the laws of electrolysis.

The same precautions are necessary as in a lead battery room against the use of naked flames during charging.

Single Plate Potentials.—It is often desirable, especially in a weak cell, to determine which of the two plates, positive or negative, is controlling the capacity. The potential of each plate separately must be measured against an unchanging auxiliary electrode placed in the cell during the discharge, and for this purpose a strip of zinc is most commonly used. A high resistance voltmeter should be used, to avoid polarising the auxiliary electrode by taking an appreciable current from it, and the strip should be suitably insulated with rubber or ebonite to prevent electrical contact with the case or the tops of the plates.

On open circuit, the potential difference between the zinc strip and a charged negative plate is about 0·35 volt in the Edison cell; in the Jungner type, with iron-cadmium negative plate, the open circuit value is about 0·40 volt. Readings of the positive plate potential should not be taken with a zinc strip, but should be obtained by adding the cell potential to the reading of the negative plate against the zinc strip. The high E.M.F. between the positive plate and the zinc increases the danger of polarisation vitiating the readings. (The resistance of a good cell-testing voltmeter is between 200 and 400 ohms; this is suitable for the procedure described above.)

From readings taken at intervals during the discharge of a cell, curves can be plotted of the voltage variations of the separate plates throughout the discharge. A comparatively rapid change in voltage is observed at the end of the discharge in the plate which has the smaller capacity. In order to determine which plate of a weak cell is responsible for the loss in capacity, the result so obtained must be compared with the curves given by a cell in normal condition. In the Edison cell there should be an excess of capacity in the negative plate, and consequently the rapid drop at the end of discharge should occur in the positive plate. The makers of Jungner type cells differ in their practice, some normally providing excess capacity in the positive, others in the negative plates.

Operation of Cells at Low Temperatures.—While it is true that at low temperatures the capacity of alkaline cells —especially of the Edison type—is much reduced, it is by no means impossible to use the cells for many purposes when the atmospheric temperature is low. The actual operation of the cells maintains the temperature at a point which allows of useful working, though the external temperature may be below the freezing-point of the electrolyte.

In order to take advantage of this property it is very desirable to surround the cells with a heat insulating enclosure. This can readily be done, for example, in train-lighting or traction batteries, and will be found to improve the performance of the cells during periods of low temperature.

The electrolyte of an alkaline cell freezes at about —24° C., as compared with about —40° to —50° C. for the electrolyte of a fully charged lead accumulator. The acid in a discharged lead accumulator may have a freezing-point of —15° C. or higher, whereas the state of charge of the alkaline cell has little effect on the concentration, and hence makes no serious change in the freezing-point, of the electrolyte.

The effect of freezing of the electrolyte is first that no capacity can be obtained from, nor charge given to, the battery while frozen. In an alkaline cell, however, no permanent damage appears to be done by freezing, while in a lead cell, especially if frozen in the discharged condition, damage to the plates is liable to result.

Repairs.—Owing to the enclosure of the alkaline cell in a welded steel container, it is generally impracticable to dismantle the cells for any repair work. Alkaline cells should not, however, develop any faults in service which require the removal of the plates from the container. There is no rapid accumulation of "sludge" from the plates in the bottom of the cell, a factor often necessitating the dismantling and clearing out of a lead cell. Only in exceptional cases can a short-circuit occur in the cell.

Short circuits have been known to occur, owing to the buckling or distortion of a plate or pocket until contact was made with the opposite plate. This is so extremely rare an occurrence that it need not be regarded as a risk. Accidental introduction of any metallic object into the cell may cause the same trouble.

There is no normal weakness or source of trouble in the cell which requires the removal of the plates from the container, and it is not intended that this should be done as maintenance work by the user of a battery.

If any occasion should necessitate the opening and examination of a cell, it is preferable to return the cell to the manufacturer for treatment.

Storing of Batteries.—Batteries for use abroad are normally exported dry. They should not be stored for more than one or two months in the dry condition, and while stored dry should be kept air-tight by plugging the apertures.

Cells to be stored should be filled with electrolyte. Edison cells to be stored should be discharged and short circuited for some hours. Jungner cells should be stored half-discharged.

CHAPTER VI

THEORY OF THE REACTIONS IN ALKALINE CELLS

THE mechanism of the processes occurring during the operation of alkaline cells was the subject of considerable speculation from the time of their introduction, but for some years no very definite evidence in favour of the various hypotheses was produced. The name of Foerster must always remain associated with the alkaline cell, for it is to the series of researches published by him during the years 1909–10 that the major part of our present knowledge is due. The views put forward by Foerster have been generally accepted as giving a correct interpretation of the processes occurring, but in certain respects the results of other workers are not in complete agreement with his theories. It will appear, from the considerations developed in this chapter, that while Foerster's theory is correct in general outline it may require some modification in points of detail. The discussion will be limited to the nickel-oxide electrode, which is common to both Edison and Jungner type cells, and to the Edison type negative plate. No detailed investigations on the cadmium-iron plate comparable with that of Foerster and Herold on the iron plate have appeared, and the discussion of the problems presented by the Jungner type plate is more conveniently dealt with in a later chapter.

1. The Positive Plate

In the earlier publications on the Edison type cell, it is common to find the positive plate action written indiscriminately as $NiO_2 \rightarrow Ni_2O_3$, $Ni_2O_3 \rightarrow NiO$, or other similar equations. This was due to the insufficient evidence available at that time, but the practice has survived to the present day and is to be attributed to the absence of any detailed account in the English language of the work of Foerster, Zedner, and others.

The complete discharge of the nickel-oxide electrode shows, apart from the initial peak, two distinct stages at potentials of about $\epsilon_h = +0{\cdot}45$ volt and $-0{\cdot}1$ volt respectively (see Fig. 14, p. 33). The second stage does not, however, occur in electrodes not containing graphite. Jouast[1] found that only about 10 per cent. of the total discharge capacity was obtained in the second stage, and that if the discharge was stopped during this stage, and the cell left on open circuit, the plate potential rose to $+0{\cdot}5$, the potential of the first stage. An attempt to associate these potentials with those shown by known oxides of nickel was made by Thompson and Richardson,[2] who measured the potentials shown by such oxides in 25 per cent. potassium hydroxide solution, without, however, reaching any very definite conclusions.

During the years 1900–05 various equations purporting to represent the cell reactions were suggested by Elbs, Hibbert, Jouast, Hospitalier, Marsh, and others, but none was supported by adequate experimental evidence. It was generally considered that an oxide of nickel with a higher oxygen content than nickel sesquioxide, Ni_2O_3, existed in the positive plate, and various formulæ such as Ni_3O_5, Ni_4O_7, NiO_2, etc., were given to it. Dufau[3] had shown that an oxide of the formula NiO_2 existed in a combined form, but it was the work of Belluci and Clavari[4] which first clearly demonstrated the existence of this oxide. These two investigators studied the action of a number of oxidising agents on nickel sulphate in alkaline solution, and found that an oxide was obtained at 0° C. with a higher proportion of oxygen than could be obtained at any higher temperature. The oxide obtained at 0° C. had the composition NiO_2, but readily lost oxygen, yielding compounds whose composition varied between NiO_2 and NiO, of which they were regarded as mixtures. While the existence of nickel sesquioxide, Ni_2O_3, as a definite compound is now

---

[1] *Eclairage Elect.*, 38, 201, 1904.
[2] *Trans. Amer. Electrochem. Soc.*, 7, 97, 1905.
[3] *Compt. rend.*, **123**, 495, 1896.
[4] *Atti. R. Accad. Sincei.* V., **14**, ii, 234, 1905.

established, we may regard the other intermediate oxides as mixtures of the three simple oxides, NiO, Ni_2O_3, and NiO_2.

To Zedner[1] must be allotted the credit for carrying out the first comprehensive investigations on the action at the nickel oxide electrode. Zedner found that deposits of nickel oxide could be prepared electrolytically which gave a potential $\epsilon_h = 0{\cdot}44$ in a 25 per cent. potassium hydroxide solution; this was identical with the potential reached on open circuit by a partially discharged accumulator plate. Analysis showed that the composition of the material after drying was Ni_2O_3, yH_2O, from which Zedner concluded that the charged plate contained simply a hydrated nickel sesquioxide. Two hydrated nickel sesquioxides were found to exist—$Ni_2O_3,3H_2O$, which was stable at aqueous vapour pressures below 3 mm., and $Ni_2O_3,6H_2O$, stable at all higher pressures. Reisenfeld[2] had previously concluded that the compositions of these hydrated oxides were $Ni_2O_3,2H_2O$ and $Ni_2O_3,4H_2O$, but, as these merely represented compositions after drying, Zedner's results are to be preferred.

In 1907 Foerster[3] published a paper on the nickel-oxide electrode, the first of a series of papers dealing with the reactions of alkaline accumulators. Analysis of a positive plate immediately after charge showed that 0·53–0·56 atoms of active oxygen per atom of nickel were present, whereas Ni_2O_3 requires only 0·50 (the active oxygen being that in excess of the amount required to form NiO). It was thus evident that a small percentage of nickel peroxide must be present in the freshly charged electrode material. Foerster found that the charged electrode liberated oxygen on standing, indicating that the peroxide was unstable, and that a simultaneous fall in potential occurred. The instability of the nickel peroxide was also shown by the change in composition after drying. Its composition then corresponded to $Ni_2O_3, 1{\cdot}1-1{\cdot}3H_2O$, the nickel peroxide having decomposed.

On open circuit a charged plate tends towards a constant potential, which is reached when the decomposition of the nickel peroxide is complete. The gradual fall in potential

---

[1] *Z. Elektrochem.*, **11**, 809, 1905; **12**, 463, 1906; **13**, 752, 1907.

[2] *Ibid.*, **12**, 621, 1906.

[3] *Ibid.*, **13**, 414, 1907.

of a charged positive plate is shown by the following data:

Time after charge:	4 min.	2 hours.	1 day.	4 days.	12 days.
Potential ϵ_h	0·607	0·573	0·552	0·530	0·508

The final steady value which is reached after 20–30 days varied between 0·48 and 0·49, and the composition of the active material then corresponded to the formula Ni_2O_3. It will be noted that this steady value of the potential is in good agreement with the value obtained by Zedner if allowance is made for the difference in electrolyte concentration. Foerster[1] has given the following values for the potential of a nickel sesquioxide electrode in potassium hydroxide solution at 25° C.:

KOH Normality:	0·4	1·0	1·9	2·8
ϵ_h	0·576	0·545	0·52	0·485

Extrapolating these data to 5·5N (25 per cent. KOH), which is the concentration of the electrolyte used by Zedner, a value of about 0·43–0·45 is obtained compared with Zedner's measured value 0·44.

Foerster concluded that the initial high potential of a freshly charged nickel-oxide electrode must be due to a solid solution of nickel peroxide in the sesquioxide. The potential falls as the proportion of nickel peroxide in the solid solution decreases, until finally the material is solely sesquioxide and the steady potential corresponding to this is reached. The assumption of a solid solution rather than the existence of the peroxide as an independent phase is necessitated by the gradual fall in potential. If the nickel peroxide existed as a separate phase, the potential would be constant as long as any appreciable quantity of the peroxide existed, and, when it had all decomposed, would drop more or less abruptly to the nickel sesquioxide potential.

The initial high potential might be attributed to the decreased concentration of the electrolyte in the plate pores as a result of charging, since this process leads to dilution of the electrolyte at the positive plate. This explanation was favoured by Zedner; but, if this were correct, a rapid fall of potential would occur as diffusion processes equalised the solution concentration. Such a fall actually occurs at the iron plate, whose high potential disappears within an hour,

---

[1] *Elektrochemie Wassëriger Losungen*, 1st edition, p. 133.

in marked contrast to that of the nickel oxide plate which requires twenty or thirty days.

In order to formulate the plate actions completely a knowledge of the amount of water released or bound by the oxides during operation is required. Zedner has estimated the water consumption during the discharge of the nickel sesquioxide by measurements of the change of E.M.F. of the cell

$$Ni_2O_3 \mid KOH \mid H_2$$

with alteration of electrolyte concentration. On passing two faradays of current through this cell the reaction is

$$Ni_2O_3,xH_2O+H_2+(m-1)H_2O=2NiO,(x+m)H_2O$$

where Ni_2O_3,xH_2O represents the initial oxide and x is 3 or 6. If two such cells with different potassium hydroxide concentrations are placed back to back (*i.e.* in series, but with opposing E.M.F.'s), and a quantity of electricity 2F is passed through the pair, the net effect on the electrolyte is the transfer of $(m-1)$ mols water from the cell in which the nickel oxide plate is discharged to that in which this plate is charged. The work done in this process is equal to that of evaporating $(m-1)$ mols water from cell 1 and condensing it again in cell 2. If p_1 and p_2 are the aqueous vapour pressures over the two electrolytes, the work done is

$$(m-1)RT\log\frac{p_1}{p_2}=(E_1-E_2)2F$$

where E_1 and E_2 are the E.M.F.'s of the two cells, and the right-hand side of the equation is the equivalent electrical work. Let v_1 and v_2 be the concentrations of electrolyte in the two cells expressed in mols potassium hydroxide per mol water. For values of $v > 0{\cdot}1$ (about 5·2N) $d\log p/dv$ is approximately constant, the curve obtained by plotting $\log p$ against v being almost a straight line in this concentration region. Following Zedner, we may utilise this approximation and write

$$\frac{d\log p}{dv}=-a$$

whence $$\log p=k-av$$

Hence $$\log\frac{p_1}{p_2}=-a(v_1-v_2)$$

and the equation becomes

$$E_1-E_2=(m-1)\frac{RT}{2F}(v_2-v_1)a$$

For potassium hydroxide solutions of concentrations above $v=0{\cdot}1$, the value of a is 3·9, and $(m-1)$ can be calculated, if E is known for any two values of v. Evaluating the constants, we obtain at 11° C.

$$E_1-E_2=(m-1)(0{\cdot}048)(v_2-v_1)$$

Zedner obtained the following results at 11° C.:

v	E.M.F.	E_1-E_2
0·1	1·314	0·011
0·2	1·303	
0·3	1·293	0·010

Then for $v_2-v_1=0{\cdot}1$, $E_1-E_2=0{\cdot}0105$, whence $m=3{\cdot}2$, or approximately 3.

The equation for this hydrogen-nickel oxide cell thus becomes

$$Ni_2O_3,xH_2O+H_2+2H_2O=2NiO,(x+3)H_2O$$

Now at $v=0{\cdot}3$ the vapour pressure of a potassium hydroxide solution at 11° C. is 3·8 mm.[1] and at $v=0{\cdot}1$ (about 23·7 per cent.) it is 7·8 mm., and therefore over the whole range of electrolyte concentrations up to a maximum of $v=0{\cdot}36$,

---

[1] Zedner (*Zeit. f. Elektrochem.*, **12**, 463, 1906) stated that the vapour pressure of a potassium hydroxide solution of concentration $v=0{\cdot}3$ was 2 mm. at 11° C., and concluded that the hydrate existing must be $Ni_2O_3,3H_2O$. This, as Zedner realised, necessitated a change in the hydrate between $v=0{\cdot}3$ and $v=0{\cdot}1$, and, since the above E.M.F. data did not suggest any such change, Zedner considered that $Ni_2O_3,3H_2O$ must persist at the lower concentrations. Zedner's vapour pressure value is, however, inaccurate. At 11·7° C. the vapour pressure at $v=0{\cdot}3$ may be calculated from Wullner's data (*Pogg. Ann.*, 1860, **110**, 564) to be 3·8 mm., using the value of $d\log p/dv=-3{\cdot}9$ to extrapolate beyond Wullner's highest concentration, which was $v=0{\cdot}158$. At 0° C. and $v=0{\cdot}3$ we have from Dieterici's data (*Landolt. Börnstein Phys. Chem. Tab.*, 1923, p. 1382) a vapour pressure of 1·8 mm. Applying the Clausius equation in the form $\log p=-\frac{\lambda}{RT}+\text{constant}$, an approximate value of 3·6 mm. at 11° C. may be calculated. The stable sesquioxide at 11° C. is therefore $Ni_2O_3,6H_2O$ over the range considered. The original equations given by Zedner on the assumption that $Ni_2O_3,3H_2O$ was the formula of the hydrated sesquioxide have been modified accordingly.

where the vapour pressure falls to 3 mm., the stable sesquioxide hydrate is $Ni_2O_3,6H_2O$ in accordance with Zedner's other results (p. 76).

We therefore have for all potassium hydroxide concentrations below about 52 per cent.

$$Ni_2O_3,6H_2O+H_2+2H_2O=2NiO,9H_2O$$

and the nickel oxide plate reaction can be written

$$(1)\quad Ni_2O_3,6H_2O+4H_2O=2NiO,9H_2O+2OH'+2\oplus$$

Although the foregoing equation gives a fair representation of the action, it is probable that it is an "average" equation rather than an exact stoichiometric relationship. The nickelous oxide exists as an amorphous colloidal solid, and the water of hydration is probably present in part as adsorbed water, the amount of which will vary continuously with temperature, electrolyte concentration, and conditions of formation, *e.g.* rate of discharge. It is therefore improbable that the equation can be regarded as an exact relation, and it is to be considered more as a mean of reactions which may vary somewhat in the proportions of water involved.

The amount of water combined with the nickel peroxide is not known, but we may write the general equation for the discharge of this oxide as

$$(2)\quad 2NiO_2,xH_2O+(7-2x)H_2O=Ni_2O_3,6H_2O+2OH'+2\oplus$$

The type of charge and discharge curves obtained by Foerster has already been shown in Fig. 14, p. 33. Considering these discharge curves, it can be concluded that the initial portion ($\epsilon_h=0{\cdot}55$ to $0{\cdot}44$) is caused by discharge of nickel peroxide according to equation (2), while the steady portion (about $\epsilon_h=0{\cdot}44$) is due to discharge of nickelic oxide in accordance with equation (1).[1] As already mentioned in Chapter III, the portion of the curve above $\epsilon_h=0{\cdot}44$ to $0{\cdot}48$ decreases if the plate is allowed to stand on open circuit before discharging, and finally vanishes when all the nickel peroxide has decomposed. This decomposition of nickel peroxide leads to a loss of energy from the plate since the capacity is diminished and the initial high voltage is lost.

---

[1] Foerster writes the formula representing the composition of the hydrated nickel sesquioxide as $Ni_2O_3,1{\cdot}2H_2O$, because this was the composition of the oxide after drying. A composition so obtained does not, however, give any indication of the state of the oxide when in the cell.

The following values from some data due to Foerster may be quoted :

Energy obtained on discharge immediately after charge, 107·5 W.H.

Energy obtained on discharge 18 hours after charge, 95·6 W.H.

The energy lost was 11·9 per cent., while the capacity (A.H.) loss was 8·5 per cent.

Even apart from this loss of energy on standing, the electrode cannot be regarded as completely reversible. It is seen that the charge curve starts at about $\epsilon_h = 0{\cdot}48$, the nickel sesquioxide potential, but at once ascends to a considerably higher value and one which is greater than that obtained by the subsequent discharge of the NiO_2—Ni_2O_3 solid solution. The primary process on charge is formation of nickel peroxide, and not of sesquioxide. The nickel peroxide formed reacts with unchanged nickelous oxide to form the sesquioxide with a concomitant loss of energy. The energy lost throughout the charge, apart from gassing, is equivalent to the difference in the energies required for the formation of NiO_2 and Ni_2O_3 respectively, since the charge is entirely to NiO_2 as primary reaction, and the main part of the discharge is from Ni_2O_3 to NiO and not from NiO_2 to NiO.

At ordinary temperatures nickel sesquioxide shows practically no tendency to decompose, and, after it had stood for one week in 2·8N potassium hydroxide solution, Foerster found that its active oxygen had only decreased from 0·49 to 0·48 atom per atom nickel. At higher temperatures nickelic oxide is unstable, and at 75° C. the active oxygen content fell to 0·28 in 22 hours and to 0·22 in 48 hours.

We may now consider briefly the second discharge stage, which is of little but theoretical interest since, except in an over-discharge, it is never used. Zedner found that this stage occurred at a potential about 0·40–0·55 volt below the nickel sesquioxide potential, the difference becoming greater as the discharge rate was increased. The capacity obtained in this stage also decreased with increasing discharge rate and finally vanished. Zedner stated that this second discharge stage is only found in electrodes containing graphite and attributed it to oxygen occluded by the graphite. He observed, in favour of this theory, that if the discharge is carried out under diminished pressure the capacity of the second stage was decreased, and that heating produced the same effect.

These results were confirmed by Herold,[1] who found that the second stage does not occur in the discharge of Edison positive plates, which contain no graphite, but that it is present in the discharge of positive plates of other manufacturers in which graphite is present.

Foerster obtained this second discharge stage at a potential of $\epsilon_h = -0{\cdot}1$ to $-0{\cdot}2$ (see Fig. 14), and its capacity, in one case recorded, reached about one-sixth of the total capacity of the plate. He rejected the absorbed oxygen theory and suggested that this stage was due to an intermediate oxide such as Ni_3O_4 or Ni_4O_5. In support of this he found that at the end of the first discharge stage the composition of the active material corresponded to an active oxygen content of 0·115 per atom nickel, while after complete discharge a value 0·03 was obtained.

On the whole, Zedner's theory is to be preferred

2. The Iron Negative Plate

The iron electrode attracted the attention of a number of investigators within a few years of the introduction of the Edison cell. Schoop,[2] who was the first to carry out any detailed studies, found that the complete discharge occurred in two stages; this was confirmed by Elbs,[3] Grafenburg,[4] and Jumau [5] amongst others. Roloff,[6] on the other hand, considered that three stages were present in a complete discharge. Little definite evidence concerning the reactions was obtained in these studies, though ferrous oxide was usually regarded as a product of the discharge.

More extensive investigations were carried out by Faust,[7] who also found the two separate discharge stages. Faust considered that the active agent in the first stage was hydrogen

---

[1] *Bull. Soc. Belge. Ing. et Indust.*, V., No. 2, 1924.

[2] *Elektrotech. Zeit.*, **26**, 769, 1905.

[3] *Z. Elektrochem.*, **11**, 734, 1905.

[4] *Ibid.*, **11**, 736, 1905.

[5] *Rev. Elec.*, **6**, 297, 1906.

[6] *Z. Elektrochem.*, **11**, 950, 1905.

[7] *Ibid.*, **13**, 161, 1907.

adsorbed at the iron surface, a theory which he later modified in favour of an iron-hydrogen layer in which both constituents oxidised simultaneously. Pure iron was thought to be the active agent in the second stage and to form ferric oxide on discharge.

Some further experiments were carried out by Krassa,[1] who showed that a massive iron electrode could be " formed " by alternate oxidation and reduction in hot alkaline solutions. This process, it may be noted, was the method employed in the Gouin cell (p. 19).

It had long been known that iron became passive on immersion in alkaline solutions, but Schoop had found that the iron was activated again when hydrogen was discharged at its surface by cathodic polarisation. The full significance of this observation escaped the attention of the earlier workers except Faust, who, however, had looked upon hydrogen as an active agent providing in itself a considerable share of the discharge capacity. It was not until the work of Foerster and Herold that the true rôle of the hydrogen became apparent.

Foerster and Herold [2] found that the amount of current required to activate the electrode by cathodic polarisation was only 1 per cent., or less, of the capacity obtained from the electrode on subsequent discharge. It is clear that the hydrogen discharged during this treatment can serve only to activate the iron and cannot itself provide any appreciable discharge. This action is now generally attributed to the removal of oxygen by the discharged hydrogen and not to any specific effect of the hydrogen. Oxygen is regarded as a negative catalyst retarding the process $Fe \rightarrow Fe^{\cdot\cdot}$, but there is still some controversy over the mechanism of its action.

The Discharge Curve.—The general form of the discharge curve of an iron electrode is shown in curves 1 and 2, Fig. 15 (p. 35). These curves show two distinct stages, AB and CD, while an indication of a small third stage is provided by the break occurring below D. For convenience, these stages will be referred to as I, II, and III. Curve 1 shows a peculiar transition from Stage I to Stage II, the potential sinking to a minimum during the change. This behaviour is found in commercial negative plates only when

---

[1] *Z. Elektrochem.*, 15, 490, 1909.

[2] *Ibid.*, 16, 461, 1910.

they are discharged at very low rates, but it becomes marked if plates containing iron in a less finely divided state are used. The normal curve for commercial plates is (2).

The degree of subdivision of the iron active material has a great effect on the discharge capacity also. Foerster and Herold found that, with an iron powder which was of such coarseness that the individual grains could be felt on rubbing between the fingers, the maximum total capacity obtained in Stages I and II corresponded to a coefficient of utilisation of 19 per cent., of which 13 per cent. occurred in Stage I. With an impalpable iron powder the average total value was about 75 per cent., of which 33 per cent. occurred in Stage I.

Schoop had observed that, when an iron electrode is completely discharged for the first time, the capacity yielded is considerably greater than that given on any subsequent discharge. This fall in capacity was found by Foerster and Herold to be characteristic of pure iron electrodes. It indicates that, on charging a completely discharged electrode, the electrolytic reduction is less efficient than the reduction methods employed in the initial preparation of the iron powder used in the electrode. For coarse iron powders the fall amounted to about 33 per cent. of the initial capacity.

The Charge Curve.—The form of the charge curve is dependent on the extent of the previous discharge. After a complete discharge through Stages I and II, a charge curve of type 3, Fig. 15, is obtained. The product of reaction (2) is reduced with almost quantitative current consumption along EF at a potential slightly more electronegative than that of the first discharge reaction, but, before the full capacity yielded by the second stage has been restored to the plate, the potential rises to G, and all further reduction along GH is accompanied by hydrogen evolution.[1] An electrode which has only been discharged to the end of Stage I shows but one stage on charge, the portion GH of curve 3. If, on the other hand, a fully discharged electrode is charged only to the point F, and then discharged, the discharge occurs for the most part in Stage II.

The Plate Reactions.—Foerster and Herold carried out

---

[1] As mentioned on p. 36, the potential of iron electrodes containing mercury does not proceed smoothly along GH, but shows an initial maximum and then reverts to the curve GH. This maximum has no significance from the standpoint of the cell reactions.

a detailed investigation of the composition of charged and discharged iron electrodes, and their results throw much light on the nature of the plate reactions. The average composition before discharge of some experimental plates used by these authors was

Metallic Iron (Fe) 90·7 per cent.
Ferrous Iron (Fe^{II}) 4–5 per cent.
Ferric Iron (Fe^{III}) 5–6 per cent.

After discharging through Stage I only, to a potential $\epsilon_h = -0{\cdot}65$, it was found that the average composition of a number of plates had become

Fe 65 per cent.
Fe^{II} 22 per cent.
Fe^{III} 12 per cent.

while the capacity obtained from the discharge was slightly less than that calculated on the assumption that the reaction was $Fe \rightarrow Fe^{II}$. It is seen that the ferrous iron content had risen by about 17 per cent. and the ferric iron content by 6–7 per cent. Part of the rise in the latter was attributed to air oxidation while taking samples from the plates, and Foerster and Herold concluded that the discharge product of reaction (1) was $Fe(OH)_2$, the reaction being

$$Fe + 2OH' \rightarrow Fe(OH)_2 + 2\ominus$$

The actual degree of hydration of the ferrous oxide produced was not definitely determined, but the product was thought to be the normal hydroxide.

The average composition of plates discharged to the end of Stage II, to a potential $\epsilon_h = -0{\cdot}55$, was as follows:

Fe 41·5 per cent.
Fe^{II} 16·5 per cent.
Fe^{III} 42 per cent.

The main change in Stage II was obviously, from comparison with the previous compositions at the end of Stage I, the disappearance of metallic iron and the formation of ferric iron, though at the same time a slight fall in the ferrous iron content occurred. The capacities obtained in this stage were in general agreement with those calculated on the assumption that the reaction occurring was $Fe \rightarrow Fe^{III}$. It is clear that this is the main reaction, but the ferrous iron plays some part in addition.

Effect of Discharge in Stage II.—It was found by Foerster and Herold that a plate which had been completely discharged and then charged to the end of the first charge stage, *i.e.* to the point F, curve 3, Fig. 13, showed a metallic iron content of only 51 per cent.; this is much below the 65 per cent. found at the beginning of Stage II on discharge. On charging this plate, after the complete discharge, the point F, at which the potential rises and hydrogen evolution sets in, was reached when only about one-third of the capacity which the plate had previously yielded in the Stage II discharge had been restored to it. Since the completely discharged electrode contained about 39–43 per cent. of metallic iron, the two sets of data are in agreement, and, further, it is clear that, during charge, reduction of ferric iron to the metallic state occurs direct without intermediate formation of ferrous iron.

These results are of considerable practical significance. Hydrogen evolution occurred in the above case when only a minor proportion of the ferric iron had been reduced, and although the reduction of ferric iron proceeded quantitatively along EF the current efficiency eventually became low. The reduction of the ferric iron to metallic iron covered the underlying layers of material and shut them off from contact with the electrolyte. The reduction became more difficult and hydrogen evolution at the covering film of reduced iron took its place.

The capacity drop which occurs after an iron plate has been completely discharged for the first time is due to this cause. Some of the underlying iron oxides become coated over with iron and remain unreduced. After this initial fall in capacity the output of an iron plate remains steady if the subsequent discharges are confined to Stage I, but further losses occur if the plate is discharged beyond this stage. It is therefore important that iron negative plates should not be allowed to discharge in the second stage; this is assured in practice by a careful adjustment of the ratio of the plate capacities, that of the iron plate being made considerably greater than that of the positive plate. Under normal working conditions no discharge of the iron plate beyond the first stage can therefore occur. If, however, a cell is left idle for a period of some months and then discharged, the iron plate potential soon drops and the discharge passes over into the second stage. On a subsequent discharge following a normal charge the cell is found to have lost capacity, but a charge of about double the normal usually restores it. Although occasional discharges of the iron plate in Stage II do not very seriously affect it, repeated over-discharges lead to a loss of capacity which is difficult to restore completely. Except by deliberate reverse charge, it is unlikely that this could take place.

The Reaction in Stage II.—The theory of this reaction needs some further consideration.

If no arrest occurred in the emission of ferrous ions during discharge, ferric ion formation could only occur when the potential of the process $Fe \rightarrow Fe^{II}$ had dropped and become equal to that of the processes $Fe \rightarrow Fe^{III}$, and $Fe^{II} \rightarrow Fe^{III}$. These three potentials will reach one common value simultaneously since they are connected by the relation

$$E_2 = \frac{2E_1 + E_3}{3}$$

where E_1, E_2 and E_3 represent the potentials of the processes $Fe \rightarrow Fe^{II}$, $Fe \rightarrow Fe^{III}$ and $Fe^{II} \rightarrow Fe^{III}$ respectively for any given ferrous and ferric iron concentrations.

In 2·85 N potassium hydroxide $E_1 = -0{\cdot}86$, and E_3 was found by Foerster to have the value $-0{\cdot}76$ while Faust obtained the value $-0{\cdot}75$. We thus derive $E_2 = -0{\cdot}83$. The potential E_1 would fall and become equal to E_3 only if the solution became supersaturated with ferrous hydroxide. If such a process occurred, the transition between Stage I and Stage II would be gradual and not abrupt, because the potential E_1 would gradually fall as the ferrous iron concentration rose, while E_3 would rise. These two potentials would eventually become equal and E_2 would simultaneously reach the same common value. Any further rise in the concentration of ferrous iron in solution would cause E_1 to fall below E_2 and E_3. The process corresponding to the potential E_2 or E_3 would then take over the discharge without any definite break in the discharge curve.

It seems, therefore, that the ferrous iron must play some intermediary role in the reaction of Stage II. The value of the potential E_3 is sufficiently high to make it possible to regard the action $Fe^{II} \rightarrow Fe^{III}$ as responsible for the potential shown in Stage II.

As the discharge in Stage I of an iron plate proceeds, the iron becomes coated with ferrous hydroxide and gradually shut off from direct contact with the electrolyte. The current density at the remaining iron surface rises and the exposed metal eventually becomes passive. The potential E_1 then rapidly falls below E_2 and oxidation of ferrous hydroxide to the ferric state occurs. Foerster and Herold found that solid ferrous hydroxide electrodes were very inert and would only supply a small current at a potential commencing about that of the end of Stage II, $\epsilon_h = -0{\cdot}55$, and rapidly dropping still lower. If the discharge of the iron electrode in Stage II were due to solid ferrous hydroxide a similar behaviour would be anticipated. When, however, the *ferrous* hydroxide layer is oxidised, the film coating the iron is broken, and contact between the *ferric* hydroxide formed, initially in solution, and metallic iron can occur. This ferric hydroxide is reduced by the iron, forming ferrous ions which momentarily exist in solution,

$$2Fe^{III} + Fe = 3Fe^{II}$$

and these can discharge again to ferric hydroxide unhindered by the inertness shown by solid ferrous hydroxide. In practice some slow oxidation of the solid ferrous hydroxide must also take place, since during Stage II, the content of this in the plate falls. As the discharge in Stage II proceeds the metallic iron content of the plate falls, while the covering layer of iron hydroxide becomes thicker. The rate at which the reduction of ferric hydroxide to the ferrous state can occur therefore gradually falls until ultimately little reduction is possible owing to the remaining unoxidised iron becoming too thickly coated. The potential must then drop as the supply of ferrous ions in solution ceases, and Stage II comes to an end. It has been suggested that Stage III may represent the discharge of solid ferrous hydroxide alone. The net result of Stage II is thus the disappearance of metallic iron and the formation of ferric iron, while some reduction of the ferrous iron content also occurs.

The peculiar retrograde manner in which the transition from Stage I to Stage II (see curve 1, Fig. 15) may occur can also be explained by this theory. If the fall of potential at the end of Stage I occurs suddenly, as at low discharge rates, the ferrous iron available in solution on the sudden cessation of reaction (1) is small, and is rapidly consumed, leaving the solid ferrous hydroxide to take over the discharge. The potential then falls excessively. As the discharge of this solid ferrous hydroxide occurs, the film covering the iron commences to break, and the ferric iron produced by the discharge becomes reduced again to the ferrous state. The solution concentration of ferrous iron is raised, and with it the potential, until an equilibrium between the rates of supply and consumption of ferrous ions is reached.

At higher discharge rates the fall from Stage I to II commences earlier in the discharge, but proceeds more steadily. Under such conditions a more gradual transition from Stage I to II takes place and the minimum potential point does not appear, for no rapid diminution of the ferrous iron in solution occurs.

The Charge Polarisation and the Iron Potential.—Attention has already been drawn to the high electronegative potential required for the charge of the iron plate. This potential is considerably more electronegative than the discharge or open circuit potential, and cannot be explained on grounds of changed electrolyte concentration. It is to the iron itself that we must look for the cause of this behaviour.

The potential of the iron electrode has long been known to be dependent on the state of division of the metal and to be affected by the presence of oxygen or hydrogen. The potential, $\epsilon_h = -0{\cdot}88$, of an iron powder electrode had never been observed with massive (*e.g.* sheet) iron, which showed a somewhat lower potential.

It was found by Haber and Maitland[1] that if massive iron were plunged into boiling 11 N potassium hydroxide a potential $\epsilon_h = -1{\cdot}02$ was observed, and it was attributed to the action of the hot alkali in dissolving the iron oxide film from the surface of the metal. The presence of free oxygen renders the iron potential more electropositive, and Richards and Behr[2] found that the potential of porous iron, which is more electronegative than that of massive iron, gradually dropped on exposure to air.

Richards and Behr also observed that finely-divided iron

---

[1] *Z. Elektrochem.*, **13**, 309, 1907.

[2] *Z. Physikal. Chem.*, **58**, 301, 1907.

prepared by reduction at low temperatures has the power of absorbing hydrogen. This lowered the potential slightly. Iron heated in hydrogen and plunged into water showed a potential about 0·15 volt higher than the normal value for porous iron, and this was supposed to be due to the absorption of hydrogen in a specially active form.

The charge potential required to reverse the action $Fe \rightarrow Fe^{II}$ is about $\epsilon_h = -1{\cdot}02$ to $-1{\cdot}07$ (see curve 3, Fig. 15), and is 0·14 to 0·19 volt more electronegative than the open circuit potential. This charge potential approximates closely to Haber and Maitland's potential for massive iron in hot concentrated potassium hydroxide solution, and the charge polarisation to the difference found by Richards and Behr between the usual porous iron potential and that of an electrode supposedly charged with "active" hydrogen.

The theory that the raised deposition potential of iron is due to a specially active form of hydrogen has found little support, but several theories have been suggested in which hydrogen is regarded as the causative agent. Thus Foerster[1] considers that hydrogen is a negative catalyst for the process

$$M^{\cdot\cdot} + 2\ominus \rightarrow M_{\text{deposited}}$$

and that it is the retardation of this process which leads to the charge polarisation. When the potential is made more electronegative, the driving force behind the above process is increased, and hence the velocity.

Another point of view is expressed in a recent paper by Hevrovsky and Soucek.[2] These authors observed that when metals are deposited electrolytically at a mercury cathode the potential of the dilute amalgam which is formed is more electropositive than that of the pure metal, but that iron is a remarkable exception. Iron deposited on a mercury cathode at a potential $\epsilon_h = -0{\cdot}87$ from tenth-normal ferrous sulphate solution, but, on interruption of the depositing current, the potential of the iron-mercury electrode at once dropped to $\epsilon_h = -0{\cdot}47$. The potential shown by this iron-mercury electrode when no current was passing was identical with that of pure iron immersed in the same solution. On measuring the iron-mercury potential 0·05 second after interrupting the depositing current the higher value (—0·87)

---

[1] *Z. Elektrochem.*, **22**, 85, 1916.

[2] *Compt. rend.*, **183**, 125, 1926.

was observed, showing that this potential was momentarily reversible. If the electrode was left for a longer period a rapid drop to the lower potential (−0·47) occurred, and no stable values intermediate between these two end potentials were found. The lower stable potential is close to the value $\epsilon_h = -0{\cdot}45$ to $-0{\cdot}47$ obtained by Richards and Behr for iron in normal ferrous sulphate solution, and to the value $\epsilon_h = -0{\cdot}441$ recently found by Hampden[1] for the normal potential of iron. The higher potential was attributed by Hevrovsky and Soucek to iron in an atomic state, and the drop to the lower stable value to the rapid combination of this atomic iron to form minute crystals. The lower value represents the potential of crystalline iron.

This hypothesis may be applied directly to the negative iron plate. The charge potential represents the back E.M.F. set up by the released iron which, momentarily after deposition, is in an atomic condition, while the electrode discharge potential corresponds to iron present as finely crystalline aggregates. The combination of the iron atoms to form crystalline aggregates results in the evolution of the extra charge energy as heat. It may be noted that Hevrovsky and Soucek specifically reject any hydrogen absorption hypothesis.

Kohlschütter[2] also adopts a theory which is similar in principle since it assumes the deposition of the iron in a highly dispersed form with a high free energy and a more electronegative potential. He invokes, however, the presence of hydrogen to explain the formation of this dispersed form.

Glasstone[3] found that the iron deposition potential approached the equilibrium potential more closely as the temperature was raised, and obtained the results shown in Table 5.

TABLE 5

Deposition Potential of Iron from 1$N.FeSO_4$ *Solution*

Temp. ° C.	15°	36°	55°	70°	90°
Potential ϵ_h	−0·68	−0·55	−0·49	−0·46	−0·46

The open circuit potential of iron in $N.FeSO_4$ is −0·46.

This author also has proposed a theory of the deposition

---

[1] *J. Physical. Chem.*, **30**, 980, 1926.

[2] *Trans. Amer. Electrochem. Soc.*, **45**, 229, 1924.

[3] *Jour. Chem. Soc.*, 1926, 2894.

of iron in a metastable form, though of a different type from those considered above.

For a general discussion of other theories, notably Smit's allotropic theory, the hydrate theory, etc., reference must be made to the appropriate literature.[1]

Effect of Temperature on the Discharge of the Iron Plate.—The capacity of an iron electrode is markedly increased with rise of temperature. In Fig. 22 discharge curves for iron electrodes at 25°, 50° and 75° C. are shown.

The increase of capacity with temperature is large, and the ratio of Stage I to II is greater at 50° than at 25°; at 75° the second stage vanishes altogether and the discharge takes place entirely in Stage I. This effect was first observed by Krassa and later by Foerster and Herold, who suggested an explanation which, in a somewhat modified form, is as follows. The increased solubility of ferrous hydroxide at higher temperatures tends to produce a thicker, but more porous, coating over the iron, since it allows of some increased movement of the ferrous ions after formation, before they are precipitated on the plate. At the same time, the activity of iron increases with temperature and favours the continuation of the process $Fe \rightarrow Fe^{II}$. When finally the exposed iron surface has become so small that Stage II would set in, the coating of ferrous hydroxide has become so thick that the ferric iron produced cannot come into contact with metallic iron, and the stage is therefore suppressed.

The curves in Fig. 22 were obtained by Foerster and Herold with plates that contained a rather coarse iron powder; with the impalpable powder which is employed in commercial plates the increase of capacity with temperature is less marked.

Although these results suggest that an iron plate may be operated at high temperatures with favourable results, it is not practicable, for reasons which are discussed in Chapter VII, to operate iron plates at temperatures above 50° C.

The Influence of Mercury on the Iron Plate.—In the early form of Edison cell, with iron-graphite negative plates, it was found that, at high rates of discharge, the potential

---

[1] A useful summary may be found in Smit's *Theory of Allotropy*, p. 337, English translation by J. Smeath Thomas; Longmans, Green & Co., 1922.

dropped rapidly and the discharge soon passed into the second stage. Such plates also suffered a gradual decrease in capacity if insufficiently charged, owing to the slow accumulation of ferric oxide in the active material. It was found by Edison that the addition of a small percentage of mercury to the active material had a remarkable effect in stabilising the plate capacity, and in enabling high-rate discharges to be taken from the plate without any transition to the second discharge stage occurring. But for this discovery it is doubtful whether the Edison cell would have achieved its present technical success.

The influence of mercury on iron electrodes is clearly demonstrated in Fig. 23 where discharge curves for electrodes free from, and containing, mercury are shown.

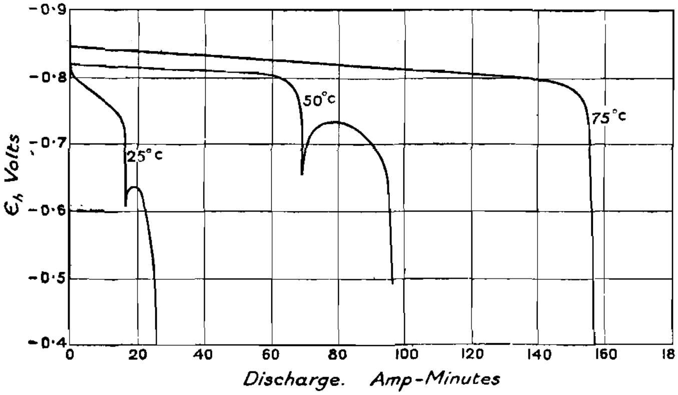

Fig. 22.—Discharge curves of iron negative plates.

In contrast to the mercury-free plates, those containing mercury give almost equal capacities at high and low discharge rates, and no tendency for the discharge to pass into the second stage is observed.

The reason is not clear, but it has been suggested that the mercury may act as a catalyst for the reaction Fe → $Fe^{\cdot\cdot}$, an explanation which throws no definite light on the problem. Alternatively there may be some change in the physical condition of the covering skin of ferrous hydroxide formed during the discharge.

The action of mercury is almost entirely limited to the discharge, and the efficiency of the charge process is not appreciably changed. There is, however, a slight effect on the form of the charge curve. The initial rise of the charge potential of Edison type cells to a maximum (see Fig. 19, p. 54) followed by a fall to a lower value is due to the presence of mercury, as this behaviour is not exhibited by cells whose negative plates are free from mercury.

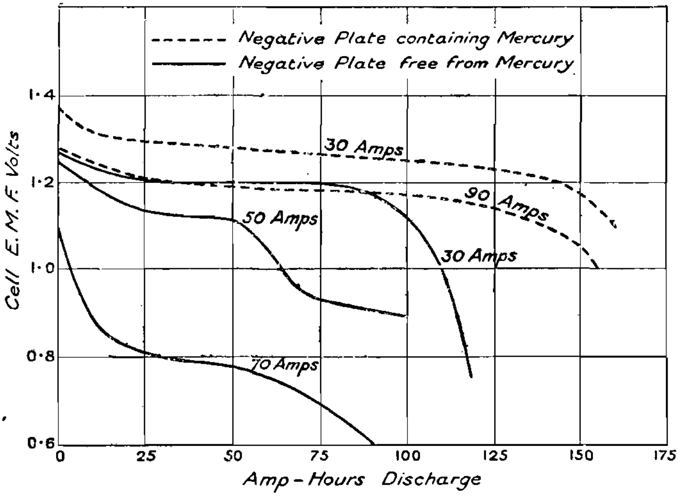

FIG. 23.—Discharge curves of negative plates, with and without mercury.

3. The Electrolyte

In the previous sections the actions at the two plates have been considered independently, and it has been seen that while the initial reaction at the positive plate is

(3) $2NiO_2,xH_2O+(7-2x)H_2O=Ni_2O_3,6H_2O+2OH'+2\oplus$

the main part of the discharge is provided by the action

(4) $Ni_2O_3,6H_2O+4H_2O=2NiO,9H_2O+2OH'+2\oplus$

At the negative plate the reaction for normal discharge is

(5) $Fe+2OH'+yH_2O+2\oplus=Fe(OH)_2,yH_2O$

where the value of y remains uncertain. A more complete picture of the reactions can be obtained by considering the changes occurring in the electrolyte of the cell taken as a whole.

Alkaline cells, in general, belong to a class which is marked by little variation of the electrolyte concentration during operation, and ideally they may be regarded as conforming in their actions to equations of the following type.

(6) . . . . . $M+RO=MO+R$

(7) . . . . . $M+R_2O_3=MO+2RO$

The only change involved in these reactions is the transfer of oxygen from one plate to the other, and, for this reason, such cells have sometimes been called "oxygen-lift" cells. Cells with an action of this type would exhibit no total change of electrolyte concentration on discharge, though local changes would occur at the electrodes and subsequently be equalised by diffusion processes. In practice, however, the products of the charge and discharge reactions are hydrated to different degrees and, as a result, real changes in electrolyte concentration take place during operation of the cells, apart from the local changes which also occur temporarily.

The E.M.F. of alkaline cells is, therefore, not independent of the electrolyte concentration, as would be the case if no change in total electrolyte concentration occurred.

In 1902, Roeber[1] published the first thermodynamical paper on alkaline accumulators. The reaction was assumed to be of the ideal type of equation (7). On discharging such a cell with a potassium hydroxide electrolyte, we have at the two plates

$$M+2OH'=MO+H_2O$$

$$R_2O_3+H_2O=2RO+2OH'$$

and for the complete cell reaction

$$M+R_2O_3=MO+2RO$$

while in addition $2n_c$ potassium ions migrate from the M to the R_2O_3 plate and $2(1-n_c)$ hydroxyl ions in the reverse direction. The net effect is, therefore, the production of $2-2(1-n_c)=2n_c$KOH at the R_2O_3 electrode and the removal of the same amount from the M electrode, while, in addition,

---

[1] *Trans. Amer. Electrochem. Soc.*, 1, 195, 1902.

$1H_2O$ is transferred from the R_2O_3 to the M electrode. These local changes cause a reduction in the cell E.M.F. until equalised by diffusion processes.

Roeber calculated, from vapour pressure data on potassium hydroxide solutions, that if the potassium hydroxide concentration at the M electrode decreased to 9·1 per cent., and at the R_2O_3 electrode rose to 32·9 per cent., the cell E.M.F. would be decreased by about 37 millivolts. Although this calculation could not be applied to alkaline accumulators without some modification, it suggested that the fall in E.M.F. of an Edison cell on discharge was far from accounted for by such polarisation effects.

Zedner,[1] who favoured the theory that the potential fall on discharge was due to concentration polarisation, calculated the value of this polarisation at a nickel oxide electrode. As is shown by equation 4, two hydroxyl ions are formed and four mols water removed on the passage of two faradays through this electrode. In addition, $2n_c$ potassium ions reach the electrode by migration through the electrolyte and $2(1-n_c)$ hydroxyl ions leave it. The total change per faraday is therefore the removal of 2 mols H_2O and the production of n_c mols KOH. The difference in the potential of two nickel oxide electrodes in potassium hydroxide solutions of concentrations c_1 and c_2 is then given by the equation

$$\Delta E = n_c \frac{RT}{F} \log \frac{P_2}{P_1} + \frac{2RT}{F} \log \frac{p_1}{p_2}$$

where P_1 and P_2 are the potassium hydroxide vapour pressures and p_1 and p_2 the aqueous vapour pressures over the two solutions. Expressing, as before (p. 78), concentrations as v mols potassium hydroxide per mol water, and writing $-\frac{d \log p}{dv}$ as a constant a, the above equation may be expressed in the form [2]

$$\Delta E = n_c a \frac{RT}{F} \log \frac{v_2}{v_1} + 2a \frac{RT}{F}(v_2 - v_1)$$

As before, $a=3·9$, and n_c, the transport number of the cation

---

[1] *Z. Elektrochem.*, **12**, 463, 1906.

[2] Cf. Dolezalek : *Ber. d. Deutsch. Physik. Ges.*, 1903, **5**, 90.

in the electrolyte, has the value 0·26. Evaluating the other constants we obtain the expression

$$\Delta E = 0{\cdot}059 \log_{10} \frac{v_2}{v_1} + 0{\cdot}195(v_2 - v_1)$$

For nickel oxide electrodes immersed in solutions of concentration 40 per cent. ($v=0{\cdot}21$) and 24 per cent. ($v=0{\cdot}1$) respectively the difference in potential calculated from this equation is 0·04 volt; for 49 per cent. ($v=0{\cdot}31$) and 24 per cent., 0·07 volt. Hence, for the nickel oxide electrode to drop in potential by 0·07 volt, the potassium hydroxide concentration would need to rise to twice its initial value round that electrode. Despite Zedner's advocacy of the theory, it is therefore improbable that concentration polarisation is responsible for the fall in voltage of alkaline accumulators during discharge; and, as we have seen earlier, the fall in potential of a freshly-charged nickel oxide electrode is due to an entirely different cause.

It is again to Foerster[1] that we are indebted for our knowledge of the total concentration changes occurring in the Edison accumulator on discharge. For two commercial cells the following data may be quoted:

	I	II
Electrolyte density before discharge	1·2133	1·2170
Electrolyte density 2 days after discharge	1·2354	1·2385
Electrolyte density 9 days after discharge	1·2400	1·2428

The rise in density produced on discharge is definite, and its slow increase on standing is to be attributed to the gradual equalisation of concentration by the diffusion of more concentrated solution from the nickel oxide electrode. By measurement of this density change on discharge Foerster found 30·9 gms. water, or 1·7 mols, disappeared per faraday. A similar measurement on charge gave 1·2 mols per faraday. Although these values are not in particularly good agreement, the mean value of 1·45 mols per faraday may be taken as the net result of the discharge reaction at both plates.

The influence of the electrolyte concentration on the E.M.F. of an Edison type cell is shown in the following table.

---

[1] *Z. Elektrochem*, 14, 285, 1908.

TABLE 6

	Potassium Hydroxide Concentration.	E.M.F. Volts, 25° C.
Series 1	2·82 N	1·3377
	5·3 N	1·3348
Series 2 . . .	2·76 N	1·3440
	1·0 N	1·3498
	4·7 N	1·3417
Series 3	1·10 N	1·3409
	2·75 N	1·3320
	1·15 N	1·3368

These three series differ rather much one from another in the absolute value of the E.M.F. at a given concentration, but the changes of E.M.F. with concentration within each series are in fair agreement.

If we place two accumulators, differing in their electrolyte concentration, back to back and pass one faraday through them, the net result is the transfer of m mols water from one cell to the other. The value of m may be obtained from the following equation for the difference in E.M.F. of the two cells:

$$\Delta E = m \frac{RT}{F} \cdot \log \frac{p_1}{p_2}$$

where p_1 and p_2 are the aqueous vapour pressures over the two solutions. We thus obtain at 25° C.

$$\Delta E = 0{\cdot}059 m \log \frac{p_1}{p_2}$$

Using the E.M.F. data in Table 6 and vapour pressure data for potassium hydroxide solutions, and putting $m = 0{\cdot}9$, the results obtained are as follows:

Electrolyte Concentrations	. . . Cell 1	2·8 N	2·75 N	1·0 N
	. . . Cell 2	5·3 N	4·7 N	2·7 N
ΔE Calculated		0·0030	0·0023	0·0017
ΔE Observed		0·0028	0·0023	0·005

Good agreement is obtained in the stronger solutions ($>$2·7 N) by putting $m = 0{\cdot}9$, but the calculated value is much too low in the weaker solutions. At the concentrations used in accumulators, about 20 per cent. or 4·2 N, m is therefore approximately equal to unity, which may be compared with the value 1·45 obtained by Foerster from the density measurements. The agreement between the various data on the amount of water involved in the cell action is not very good.

For the complete cell we have the value 1·0 to 1·5 mols water consumed per faraday passed on discharge, while for the nickel oxide electrode alone we have Zedner's value of 2 mols consumed per faraday. Taking the lower value (1 mol per faraday) for the total water consumption in the cell, we have on passing two faradays :

$$\begin{array}{lll} (8) & \text{Complete Cell : } & Ni_2O_3,6H_2O+Fe,xH_2O+2H_2O \\ & & =2NiO,9H_2O+Fe(OH)_2,(x-2)H_2O \\ & & \\ (9) & \text{Positive Plate : } & Ni_2O_3,6H_2O+4H_2O \\ & & =2NiO,9H_2O+2OH'+2\oplus \\ \hline (10) & \text{Negative Plate : } & Fe,xH_2O+2OH'+2\oplus \\ & & =Fe(OH)_2,(x-2)H_2O+2H_2O \end{array}$$

If, with Foerster, we assume that the ferrous iron is formed as $Fe(OH)_2$, the cell equation becomes

$$\begin{array}{ll} (11) & Ni_2O_3,6H_2O+Fe,2H_2O+2H_2O \\ & =2NiO,9H_2O+Fe(OH)_2 \end{array}$$

If we assume that the ferrous iron exists as FeO and take the higher of the two values (1·5 mol per faraday) for the total water consumption, the equation becomes

$$\begin{array}{ll} (12) & Ni_2O_3,6H_2O+Fe+3H_2O \\ & =2NiO,9H_2O+FeO \end{array}$$

The first series of equations leading to (11) necessitates that the active iron is itself " hydrated," or, more probably, holds adsorbed water at its surface. This, if correct, provides a probable cause for the discrepancies in the various results obtained by Foerster. As with the nickelous oxide, the amount of water so adsorbed is likely to vary somewhat with the previous history of the electrode, and with temperature and electrolyte concentration.

It is clear that the equation for the complete cell reaction still remains in some doubt in as far as the water transfer is concerned, and it is probable that no definite equation can be formulated, but only an approximate equation representing average conditions. Foerster writes the complete cell equation, neglecting the initial reaction „due to NiO_2, as

$$Fe+Ni_2O_3,1{\cdot}2H_2O+1{\cdot}8H_2O=Fe(OH)_2+2Ni(OH)_2$$

but there is little justification for the degrees of hydration employed, and equation (11) or (12) is to be preferred.

CHAPTER VII

FACTORS AFFECTING THE PERFORMANCE OF ALKALINE CELLS

1. The Electrolyte Composition

POTASSIUM hydroxide is always employed in alkaline accumulators, since, although its cost is higher than that of sodium hydroxide, it has a considerably higher maximum conductivity, as is seen from the data in the following table :

TABLE 7

Percentage.	Specific Conductivity * $\times 10^4$ at 15° C.		Temperature Coefficient.	
	KOH	NaOH	KOH	NaOH
5	1750	1969	0·0186	0·0201
10	3140	3125	0·0188	0·0217
15	4230	3465	0·0191	0·0249
20	5040	3270	0·0198	0·0299
25	5400	2715	0·0209	0·0368
30	5390	2020	0·0222	0·0450

* Values interpolated from data of Kohlrausch. (Landolt Börnstein : *Phys. Chem. Tab.*, 1923, 1077.)

The relations at 17·5° C. between the density, percentage, and other modes of expressing the concentration of potassium hydroxide solutions are shown in Table 8.

TABLE 8

Percentage. KOH	Density.	Normality.	$\frac{\text{Mols KOH}}{\text{Mol } H_2O}$
5	1·046	0·95	0·0171
10	1·0895	1·95	0·0354
15	1·136	3·05	0·0568
20	1·1845	4·23	0·0809
25	1·232	5·48	0·1073
30	1·281	6·85	0·1376
35	—	8·40	0·172

Calculated from data by Jones. (Landolt Börnstein : *Phys. Chem Tab.*, 1923, 421.)

Choice of Electrolyte Concentration.—The concentration of the electrolyte used in alkaline accumulators is conditioned by two main factors, apart from the question of cost. If too weak a solution is used the internal resistance is increased and the cell becomes sluggish in its action, this being probably due to a decreased activity of the negative plate. With high concentrations the dangers due to the increased solubility of the iron in the electrolyte, particularly at high temperatures, become prominent, and in practice, therefore, a slightly lower concentration than that which yields the maximum conductivity is employed. In effect, the density selected is the lowest which is satisfactory as regards both the internal resistance of the cell and the activity of the plates.

Vertical Variations in Density.—It has been observed that in practice there is a difference in the electrolyte densities at the top and bottom of a cell. Schoop and Liagre [1] attributed this to gravitational effects and differences in the migration velocities of the two ions. It is probable that the true explanation is the same as that which applies to the lead accumulator, where a similar effect is found. In that case the difference is due to the process of charging, which produces sulphuric acid in the plate pores. Owing to the insufficient rapidity with which it mixes with the main bulk of the electrolyte, this strong acid tends to sink to the bottom of the cell. Diffusion processes slowly equalise this difference, but it is renewed on every charge, and in lead accumulators which are in frequent operation the difference in density is often of considerable magnitude. In alkaline accumulators the electrolyte becomes more concentrated at the nickel oxide plate on discharge and some downward movement is likely to occur, though the effect is of a smaller magnitude than in the lead cell.

Effect of Lithia.—The influence of lithium hydroxide added to the electrolyte is of considerable importance. In the Edison cell the electrolyte contains about 50 gms. LiOH per litre. This has the effect of increasing the cell capacity by about 10 per cent., and, what is even more important, it is claimed that it extends the period during which the capacity of the cell is maintained at its full value. There is unfortunately little definite evidence on the mechanism of

---

[1] *Eclairage Elect.*, 43, 21, 1905.

this action of lithia, but, since in the Edison cell the capacity is limited by the positive plate, it must be this plate whose capacity is increased by the addition of lithium hydroxide to the electrolyte. There may, of course, be an additional effect on the negative plate. Turnock[1] obtained some interesting data on the effect of lithia on the capacity of Edison cells. Lithium hydroxide was added to the electrolyte in amounts up to 50 gms. per litre, which in 20 per cent. potassium hydroxide is practically a saturated solution, and the following results were obtained. The time of discharge was about 2¼ hours.

LiOH gms. per litre	0	10	20	30	40	50
Per cent. increase in capacity	0	5·27	7·14	9·39	10·53	12·03

This increased capacity is not due to a decreased electrolyte resistance, since the addition of lithia actually increases the electrolyte resistance.

LiOH gms. per litre	0	10	20	30	40	50
Per cent. increase in electrolyte resistance	0	7·05	11·7	15·4	18·4	21

The presence of lithia was also found to increase the charge voltage, as would be anticipated from the increased electrolyte resistance. According to Turnock, there is a gradual loss of lithia from the solution owing to some reaction with the plates on discharge which is not completely reversed on charge. Edison, on the other hand, states that in the charged cell the lithia is in some obscure combination at the positive plate and that on discharge this combination is broken up and the lithia released. In the Edison cell more lithia is added initially than is required for a saturated solution, and the excess is usually sufficient to maintain the capacity for about a year. After this the electrolyte should be renewed, and details of the renewal electrolytes have already been given (p. 69).

Foerster[2] has suggested that the effect of lithia is to maintain the fineness of division and high surface area of the nickel oxide active material. This active material has a tendency to diminish in capacity, especially at high temperatures, owing probably to shrinkage of the surface. The

---

[1] *Trans. Amer. Electrochem. Soc.*, **32**, 405, 1917.

[2] *Electrochemie Wasseriger Lösungen*, 3rd edition, 1922, p. 267.

presence of lithia appears to prevent this, and it may actually cause a swelling of the active material.

Many suspensions are maintained in a fine state of division in alkaline solutions by adsorption of the ions, and, further, the alkali metal ions are the better adsorbed the lower their atomic weight. Hence, Foerster suggests, lithium hydroxide, being the lowest member of the series, is strongly adsorbed by the nickelic oxide and maintains it in a finely divided condition, thus raising and maintaining the capacity of the plate.

Effects of Impurities.—The influence of impurities in the electrolyte is of importance. Of the acid radicles the commonest and most important impurity is carbonate. This slowly accumulates in the electrolyte of a cell, being introduced in solution in the distilled water added for topping-up. It may also find its way into the cell through air leakage at the gas-escape vent. Definite quantitative evidence on the effect of carbonates is unfortunately lacking, but qualitatively its presence is stated to cause a loss in capacity and a decrease in voltage. The evidence, however, is not very definite.

Alkaline cell manufacturers state that carbonates lead to sluggishness of the cell, which is particularly marked at high discharge rates, and fix the maximum allowable limit of potassium carbonate at 30 gms. per litre of electrolyte. It is usually stated by the manufacturers that the replacement of carbonated electrolyte by fresh electrolyte results in partial, or complete, recovery of any lost capacity, provided the cell has not been worked too long in a heavily carbonated condition.

It is, of course, obvious that apart from any specific effect on the plates the presence of carbonate must, since it causes an increased electrolyte resistance, lead to a decreased cell voltage at any given discharge rate and a decreased capacity when discharging to a given end voltage.

Other acid radicles, such as sulphate, also have an adverse effect on the positive plate, though again this conclusion is based on general experience and is at present unsupported by quantitative data. Such an action, however, seems likely, since we may assume that any radicle which causes a change in the state of division of the positive active material will affect the capacity of that plate. Now, in general, any substance in solution which lowers the surface tension at the interface between the solid and the electrolyte may be expected to favour a more finely divided condition of the solid. A substance which, in solution, lowers the solid-liquid surface tension should raise the surface tension of the liquid against air and *vice versa*. If we compare the surface tensions of solutions of the same percentage content of the hydroxides, carbonates, and sulphates of any one alkali metal, it will be found that the hydroxide has considerably more effect than the carbonate or sulphate in raising the surface tension of a water-air interface. It is therefore likely that the presence of sulphates and carbonates tends to increase the surface tension between the solid nickel oxides and the electrolyte, and thereby to decrease the fineness of division of the active material and with it the plate capacity. Such effects are not likely to be of much importance unless the sulphate or carbonate is present in comparatively large amounts, say, several per cent., and, in the case of carbonates at least, this is confirmed by experience.

In the Edison cell electrolyte, contamination with carbonate must also decrease the amount of lithia in solution owing to the solubility of lithium carbonate being less than that of lithium hydroxide. In water at 20° C. the solubility of lithium hydroxide is 128 gms. per litre, while that of lithium carbonate is only 13·3 gms. per litre. In 20 per cent. potassium hydroxide solution the solubility of lithium hydroxide is only about 50 gms. per litre, and the solubility of the carbonate is probably reduced also. Hence, absorption of carbon dioxide by the electrolyte must eventually result in precipitation of lithium carbonate.

Metallic impurities in alkaline cells act in a manner which is quite different from the action of acidic impurities. Any metal which is electropositive to iron in alkaline solutions will, if introduced into the electrolyte, deposit out on the iron plate and set up "local action" cells, or couples. If a metal M deposits out, the couple

$$M \mid KOH \mid Fe$$

is set up, and iron is oxidised while hydrogen is discharged at the M surface, provided that the overvoltage to hydrogen discharge at the M surface is not greater than the E.M.F. of the couple $Fe \mid KOH \mid H_2$. This leads to a continuous self-discharge of the plate. Since many metals form insoluble hydroxides in alkaline solution they will not cause damage in this way, as the amount which can be held in solution, and so deposit out on the iron plate, is very small. Tin, however, is soluble in alkali hydroxide solutions, and, if it is introduced into the electrolyte by any means (*e.g.* storage of electrolyte in tinned cans, a not unknown occurrence), will act in the above manner. There are few metallic impurities which affect the positive plate, but iron itself, when present in solution, is stated by Edison to be damaging to this plate. At ordinary temperatures the iron oxides of the negative plate are almost entirely insoluble in the electrolyte, but the solubility increases considerably at higher temperatures (see p. 108). Jungner has stated that iron in solution combines with the nickel oxides at the positive plate forming a nickel-iron compound, and that the nickel oxide so combined is rendered inactive, thus causing a loss in capacity of the positive plate.

2. Temperature Effects

TEMPERATURE AND CAPACITY

The very considerable effect of low temperatures on alkaline cells has already been indicated in Chapter IV. In both Jungner and Edison type cells the decrease in capacity at low temperatures is to be attributed to the lower capacity of the plates and only in a minor degree to increased electrolyte resistance. The resistance of a 20 per cent. potassium hydroxide solution increases by about 2 per cent. for every degree (C.) the temperature is lowered, while the corresponding value for a 1·24 sp. gr. sulphuric acid solution is about 1·7 per cent. In the Edison cell the serious loss of capacity at low temperatures is due to the increased passivity of the iron. The cause of the loss of capacity in the Jungner type cell is not clear, but it appears probable that it is due to the negative rather than to the positive plate. Low temperatures have no permanent effect on either type of cell, but only lead to an inertness which is removed when the temperature is raised again. Freezing of the electrolyte can only occur under very severe conditions, as is shown by the following table:

Freezing-points of KOH Solutions

Per cent. KOH	5	10	15	20	25	30
F.P. (° C.)	−3°	−8°	−14°	−24°	−38°	−59°

Freezing of the electrolyte does not damage the plates of alkaline cells although in the lead accumulator it is often disastrous to the plates.

At high temperatures the internal resistance of the cells is lowered owing to the decrease of electrolyte resistance which, from 20° to 50° C., falls to about one-half. Moreover, a rise in temperature, by increasing diffusion rates, reduces any concentration polarisation which may lower the available discharge E.M.F. Up to a certain point increase of the operating temperature is generally favourable to the working of the cell, since the activity of the iron is increased and also the capacity obtainable from the nickel oxide plate. Beyond that point, however, any further increase of temperature has serious disadvantages which far outweigh the advantages. This critical temperature may be taken as about 50° C. (122° F.), and in practice a cell should not be allowed to exceed it. In the following discussion on the effects of high temperature the deleterious actions occurring beyond this critical point will first be considered.

DAMAGING EFFECTS OF EXCESSIVELY HIGH TEMPERATURE

1. The Negative Plate.—The active iron of the negative plate is, even at normal operating temperatures, slowly attacked by the electrolyte according to the equation

$$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2$$

The loss of capacity so produced is only slight, and is comparable with that caused by the rather similar action of the acid electrolyte on the negative plate of a lead cell

$$Pb + H_2SO_4 = PbSO_4 + H_2$$

Both these actions are accelerated at higher temperatures; in the case of the lead cell an increase of temperature from 22° to 30° C. increases the rate by about 50 per cent., but for the iron plate no quantitative data are available. There is little information concerning the effect of high temperatures on the cadmium-iron plate, but, as cadmium is less attacked by alkali solutions than iron, the cadmium portion of this plate is likely to be more resistant to electrolyte attack.

The discharge of an iron electrode at high temperatures in a strong alkali solution is characterised by the formation of soluble iron compounds in which the iron is present in the acidic radicle. On anodic oxidation in alkali solutions the iron passes into solution in either the bivalent or sexavalent conditions, forming, for example, in potassium hydroxide the salts K_2FeO_2 and K_2FeO_4 in which ferrous oxide, FeO, and a hypothetical acidic oxide, FeO_3 respectively, are combined with a molecule of potassium oxide (K_2O). Iron does not pass into solution in alkalies by anodic oxidation in the tervalent condition to form salts of ferric oxide such as $K_2Fe_2O_4$. Such compounds are, however, formed by the direct solution of ferric oxide in strong potassium hydroxide solutions.

$$(1) \quad . \quad . \quad Fe_2O_3+2KOH=K_2Fe_2O_4+H_2O$$

The ferrates, the salts of the hypothetical FeO_3, are unstable and decompose, evolving oxygen and precipitating ferric hydroxide, particularly above 50° C. The action is

$$(2) \quad 4K_2FeO_4+10H_2O=8KOH+4Fe(OH)_3+3O_2$$

Grube and Gmelin[1] found that in 40 per cent. caustic soda solutions, in absence of air, active iron formed Na_2FeO_2 when anodically polarised, and that increased alkali concentration and higher temperatures both favoured this action. At 80° C. as much as 1·5 gms. iron per litre was obtained in solution. Continued anodic oxidation then led to the production of sodium ferrate, Na_2FeO_4, which decomposed above 50° C. in accordance with equation (2). The yield of ferrate in potassium hydroxide was found by Haber and Pick[2] to be less than in sodium hydroxide solution, probably on account of the smaller solubility of the potassium salt. The effect of temperature is also well brought out by the results of these workers, for, in 40-50 per cent. potassium hydroxide, no soluble iron compounds were formed at 0° C., while at 70° C. the current yield was nearly quantitative.

---

[1] *Z. Electrochem.*, **26**, 153, 459, 1920.

[2] *Ibid.*, **7**, 215, 1900.

Although these results refer to alkaline solutions which are considerably more concentrated than those used in alkaline accumulators, they are indicative of the actions which will tend to occur in cells operating at high temperatures. Some solution of iron as K_2FeO_2 and K_2FeO_4 is to be anticipated, and the decomposition of the latter will precipitate ferric hydroxide, which is thus lost to the plate. Some re-solution of the ferric hydroxide in the potassium hydroxide solution may occur, forming $K_2Fe_2O_4$. Iron is accordingly found present in the electrolyte of cells operating at high temperatures. This solution of the iron leads to a loss of active material from the plate and a corresponding loss of capacity. In cells with an excess capacity in the negative plate it is, however, the permanent loss of capacity of the positive plate, produced by the combination of the dissolved iron with the nickel oxides of the positive plate (see p. 106), that is the more serious permanent effect of high operating temperatures.

At 50° C. slight, but perceptible, gas evolution occurs from cells on open circuit, and the rate rapidly increases with temperature. From an Edison cell of 30 amp. hours capacity Turnock found about 1,300 c.c. of gas per hour were evolved on open circuit at 80° C., the gas consisting of about 90 per cent. hydrogen and 10 per cent. oxygen. This rate of hydrogen evolution represents a self-discharge of the negative plate at the rate of about 2·8 amps., almost the 10-hour discharge rate. The hydrogen is produced by the direct attack of the electrolyte on the iron, as already discussed, and the oxygen is formed by decomposition of the nickel peroxide and sesquioxide.

2. The Positive Plate.—Some very interesting observations of the effect of temperature on the nickel oxide plate were made by Turnock.[1] The discharge capacity reaches a maximum at about 50° C., but it is also influenced by the temperature at which the cell is charged. For a given discharge temperature the capacity becomes less as the charge temperature is raised above 50° C. The following table, consisting of data obtained by Turnock on Edison type cells with excess negative plate capacity, shows clearly the decrease of capacity above 50° C.

---

[1] *Trans. Amer. Electrochem. Soc.*, 30, 273, 1916.

TABLE 9

Temperature (° C.)	20°	30°	40°	50°	60°	70°	80°	90°
Input (A.H.) . .	60	60	60	60	60	60	60	60
Output (A.H.) .	29·9	34·4	42·7	46·8	37·6	32·7	30·1	28·1

The discharge rate was 15 amps., and both charge and discharge were carried out at the same temperature.

In Table 10 the effect of varying the charge temperature is shown, and it will be observed that, on raising the discharge temperature, little alteration of capacity occurred when both charges were carried out at a low temperature. On the other hand, raising the charge temperature from 60° to 80° C. considerably decreased the output at a constant low temperature. These results refer to discharges carried out soon after the previous charge, the cell not being kept standing on open circuit at the high temperatures before discharge.

TABLE 10

Charge-Temp. (° C.) . .	80°	60°	25°	25°
Disch. Temp. (° C.) . .	25°	25°	60°	80°
Input (A.H.) . . .	60	60	60	60
Output (A.H.) . . .	20·2	28·9	39·3	40·3

This behaviour of the positive plate was attributed by Turnock to the instability of nickel peroxide. The nickel peroxide forms a solid solution with the nickelic oxide, and Turnock proposed the theory that the concentration of nickel peroxide which can exist in such solid solution is decreased as the temperature is raised, a theory which is supported by other data. The fall of capacity at higher temperatures is then due to the decreased proportion of nickel peroxide which can be formed in the charged electrode, but it is not until a temperature of 50° C. is reached that the inefficiency of the charging process becomes marked. If a plate is charged at a low temperature and then raised to a temperature of, for instance, 60°, and immediately discharged, *no capacity loss will be observed, since the previous charge* has been normal.

It appears questionable, however, whether this theory of decreased formation of nickel peroxide alone accounts for the large capacity losses found, as the amount of nickel peroxide normally present at 18° C. in a charged plate is comparatively small and does not account for more than some 10–12 per cent. of the discharge capacity. The decomposition of nickel sesquioxide, which sets in at about 50° C., and increases rapidly as the temperature is raised further, must also result in capacity loss and must be joined with the decreased formation of nickel peroxide as the cause of the breakdown of the positive plate at high temperatures. A continuous loss of capacity occurs in a plate which is kept on open circuit at a high temperature on account of this decomposition of the nickel oxides. The nickel oxides are quite insoluble in strong alkali, and no actual loss of active material from the plate occurs.

The permanent effects of high temperatures are the loss of capacity of nickel oxides due to combination with dissolved iron, the loss of iron by solution from the negative plate, and the formation of excessive amounts of iron oxide in the solid active mass.

CHAPTER VIII

THE CADMIUM-IRON NEGATIVE PLATE

ALTHOUGH the original cadmium plate was patented in 1900 by Jungner,[1] the modified cadmium-iron plate [2] in 1909, and the cell produced commercially soon after, very little work bearing on either the nature of this composite active material or its reactions has been published.

The cadmium plate was first introduced as an attempt to overcome certain disadvantages of the iron plate, such as the poor conductivity of the oxides and the tendency of the iron to become inactive, which necessitated the addition of a conducting and activating agent such as mercury. The pure cadmium plate as first proposed by Jungner was not, however, the success he anticipated. Cadmium oxide is a fairly good conductor and no additional conducting agent was required, but metallic cadmium is soft and has a tendency to cake, and so to reduce the porosity and capacity of the electrode. It was found that if the cadmium were mixed with iron the tendency of the cadmium to cake was eliminated.

This characteristic caking of the cadmium is doubtless partially due to the growth and interlocking of the metal crystals on successive discharge and charge; the action of the iron is to reduce the possibility of intergrowth by the mechanical separation of the individual cadmium grains. Many examples of a similar behaviour are known. Some metals can be prepared in a very fine pyrophoric state by reduction under suitable conditions, but on heating beyond a certain temperature the pyrophoric properties are lost due to incipient crystallisation, or sintering. The presence of a small percentage of alumina in intimate admixture

---

[1] Brit. Pats. 7892, 1899; 7768, 1900.

[2] Brit. Pats. 7338, 1909; 9964, 1910; 5545, 1912.

with finely-divided iron enables that metal to withstand a temperature of 650° C. without loss of pyrophoric properties, whereas the pure metal loses them at about 530° C. The alumina inhibits the recrystallisation of the iron and maintains its finely-divided condition.

As stated in a previous chapter, iron on excessive discharge forms ferric oxide, which has a detrimental influence on the plate, and at higher temperatures there is some tendency for the iron to pass into solution in the electrolyte. These defects of iron are still observed in a cadmium-iron mixture, and Jungner therefore proposed to limit the percentage of iron to the minimum amount necessary to prevent the cadmium conglomerating. A mixture of 85 per cent. cadmium and 15 per cent. iron was suggested, but in practice manufacturers usually employ a rather lower percentage of cadmium, though it remains the predominant constituent. These commercial plates are, despite the higher iron content, comparatively little affected by overdischarge. In some Jungner type cells the negative plate is of lower capacity than the positive, which renders it liable to overdischarge in battery operation, but no injurious consequences ensue.

The cadmium-iron plate has the advantage that, while its discharge potential is practically the same as that of the iron plate, its charge potential is, for the greater part of the charge, much below that of the iron plate. The high polarisation necessary when charging the iron plate is not required for the charge of the cadmium-iron plate, which proceeds without hydrogen evolution, with a corresponding gain in both capacity and energy efficiencies. The composite plate can, on this account, be charged at much lower rates than the iron negative plate.

Typical charge and discharge curves for the nickel oxide —iron, and nickel oxide—cadmium-iron, cells are shown in Fig. 19, Chapter IV. The discharge curves refer to cells which have stood on open circuit at least 15 hours after the previous charge. Cells discharged immediately after a charge show an initial discharge potential about 0·15 volt higher owing to the increased potential of the nickel oxide electrode, The discharge voltages and curves are very similar, differing only in that the Jungner type plate shows a rather flatter curve than the Edison type, but drops more rapidly in the final stages. The charge curves follow markedly different courses, and, whereas the iron—nickel oxide cell requires a charge voltage of about 1·65, the charge of the cadmium-iron—nickel oxide cell proceeds for a long period at a voltage between 1·40 and 1·50. Towards the end of charge the voltage rises steadily until it finally reaches almost the same value as that of the iron cell. It appears probable that during the lower voltage stage, *i.e.* below 1·6, the charge current is utilised in reduction of the oxide of cadmium formed on the previous discharge, while in the later stage reduction of the iron oxide occurs. The point at which the rise to the iron charge potential occurs is delayed to a later stage of the charge as the iron percentage in the plate is decreased. This behaviour of the cadmium-iron plate on charge shows that the introduction of cadmium into the negative plate renders the cell much more nearly reversible.

The cadmium-iron plate is of much interest as it represents the first case of a plate composed of more than one active metal which has proved technically successful as an accumulator electrode. In theory there are certain definite objections to a plate composed of a metallic mixture, and it is important to inquire if these are valid in the cadmium iron plate. It is possible that the plate is an alloy, that is, that a cadmium-iron solid solution or intermediate compound is formed, and that the metals do not exist as independent discrete constituents. The evidence for and against these alternatives may be briefly examined.

If cadmium and iron were present as a metallic mixture, some break in the discharge curve of the plate would be anticipated, though, if the potentials of the two metals were close together, it might be smoothed over and not appear. There has long been a controversy on the relative positions of the iron and cadmium potentials in the electrochemical series. Usually (cf. p. 30, Chapter III) iron is placed above cadmium, but U. R. Evans [1] has recently suggested a reversal of this order, since in the cell

$$\mathrm{Fe} \mid \mathrm{FeSO_4} \mid \mathrm{CdSO_4} \mid \mathrm{Cd}$$

cadmium has been found to be the anode. Rawdon [2] has also found that cadmium behaves similarly to zinc in protecting iron from corrosion in half normal sodium chloride

---

[1] *Jour. Inst. Metals*, 30, 242, 1923.

[2] *Trans. Amer. Electrochem. Soc.*, 49, 339, 1926.

solution, and hence that in such a solution the cadmium is the less noble metal and acts as anode. As this writer points out, however, this result does not necessarily confirm the order suggested by Evans for the normal potentials, since, in the case of two metals whose potentials are close together, relatively small alterations in ionic concentrations will reverse the order. In alkaline solutions Marsh[1] has given the following potentials, referred to a silver oxide electrode as zero.

Cd | CdO —0·95 volt.
Fe | FeO —0·85 volt.

These values indicate that cadmium is the less noble. Wilsmore,[2] on the other hand, quoting on the hydrogen scale, obtained the value —0·714 volt for cadmium in 1N potassium hydroxide solution, while Foerster and Herold[3] give the value of iron in a 2·85 N solution as —0·87 to —0·88 : a further value by Faust[4] is in agreement. It appears that the value for iron given by Marsh is low, and this is the more probable since iron in alkaline solution readily becomes passive and shows a more noble potential than the active metal.

When made the anode, iron oxidises at about —0·75 to —0·80 volt (Foerster and Herold), while Cohen and Osaka[5] found that cadmium oxidises anodically at about —0·34 volt.[6] This is confirmed by a value of —0·32 given by Jirsa and Loris.[7] These values not only indicate that cadmium oxidises anodically at a less base potential than iron, but also show that the difference between the two is large. There is also a large difference between these cadmium oxidation potentials and the open circuit potential given by Wilsmore, which approaches more closely to the iron potential.

---

[1] *Elec. World*, 39, 966, 1902.

[2] *Z. Physikal. Chem.*, 35, 328, 1900.

[3] *Z. Elektrochem.*, 16, 461, 1910.

[4] *Ibid.*, 34, 86, 1904.

[5] *Z. Anorg. Chem.*, 34, 86, 1904.

[6] These workers give the value +0·48 volt against a H_2 | 1N.KOH electrode which corresponds to —0·34 on the normal hydrogen scale taking the potential of the H_2 | N.HCl | N.KCl | N.KOH | H_2 cell as 0·77 volt (*Landolt. Börnstein Phys. Chem. Tab.*, 1923, 1025) and applying an approximate calculated correction for the diffusion potential.

[7] *Z. Physikal. Chem.*, 113, 235, 1924.

In Fig. 24 are shown single plate discharge curves for commercial negative plates of Edison and Jungner types. The potentials were measured against a zinc electrode immersed in the cell electrolyte. These curves refer to plates which have stood on open circuit some 16 hours after the completion of the previous charge. The open circuit potential of the cadmium-iron plate was 0·03 to 0·05 volt more noble than that of the iron plate, and during discharge a similar difference was observed throughout. The plate A had a somewhat greater capacity than the plate B, and the final drop took place after a correspondingly longer discharge period, as the discharge current was the same in both cases.

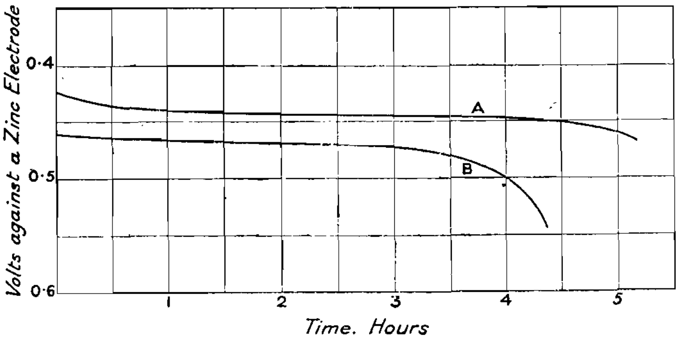

FIG. 24.—Discharge curves: A. Iron negative.
B. Cadmium-iron negative.

Similar potential differences were observed on plates discharged immediately following a charge, or after standing on open circuit for two weeks, though the magnitude of this difference varied somewhat. Taking Foerster and Herold's value of —0·88 for the iron potential, the potential of the cadmium-iron plate is about —0·85 to —0·82, the discharge of the iron plate takes place at —0·81 to —0·74, and that of the cadmium-iron plate at —0·77 to —0·70. If the discharge is carried further, the potential in either case commences to drop rapidly. These data show that in a 20 per cent. potassium hydroxide solution the cadmium-iron plate has a slightly more noble potential than the iron plate, but that the difference is small and far less than the difference suggested by the anodic oxidation potentials of cadmium given earlier. It is also seen that there is no indication of any break in the cadmium-iron discharge curve, which proceeds smoothly.

Although the above evidence does not appear to favour a metallic mixture theory, there is no known alloy of cadmium and iron. Isaacs and Tammann [1] found that cadmium was insoluble in fused iron and that when iron is brought into contact with fused cadmium it is either insoluble in it, or forms an insoluble compound. It therefore appears unlikely that any cadmium-iron alloy is formed in the Jungner plate, despite the discrepancies between the anodic solution potentials of cadmium and that of the cadmium-iron plate. The latter, it will be noted, is of a similar magnitude to the open circuit potential of cadmium found by Wilsmore.

The charge curve of the Jungner type plate (Fig. 19) offers the most definite evidence in favour of the metallic mixture theory, for it shows two definite and distinct stages. In the first stage the charge potential is about —0·90 volt and is only slightly more electronegative than the open circuit potential, while in the later stage it becomes similar to that of the iron plate, which is about —1·06. This behaviour shows that two distinct processes are occurring, and, while it might be inferred that during the first stage a cadmium-iron alloy is deposited, and iron alone in the second stage, it appears more probable, since cadmium is the predominating constituent in the plate, that the first and longer stage corresponds to cadmium deposition alone.

It is very significant that the rise to the iron charge potential occurs at a progressively later stage of the charge as the percentage of cadmium in the plate increases. This is clearly brought out by curves B and C, Fig. 19, p. 54. Curve B refers to a cell whose negative plate contained 65 per cent. cadmium and curve C to one containing 75 per cent. cadmium. The discharge curves show no such differences and are almost identical with one another.

The anodic solution potentials for cadmium are so far removed from the open circuit electrode potential as to suggest that the iron may play some rôle in maintaining the electrochemical activity of the cadmium and allowing it to discharge at a potential near to its true open circuit

[1] *Z. Anorg. Chem.*, 55, 58, 1907.

potential. The results of Jirsa and Loris indicate that cadmium tends to become passive at very low current densities, and that when it is anodically polarised oxygen evolution soon sets in in preference to metal solution. This is illustrated by the data obtained by Jirsa and Loris, who measured the potential of a cadmium plate when made anode at various current densities in a 1N NaOH solution. To complete the table, Wilsmore's value of the cadmium potential on open circuit has been added.

Current Density Milliamps. per cm^2.	zero.	0·00042	0·00243	0·005	0·20	0·8	8·8
Potential ϵ_h volts	−0·714	−0·383	−0·261	−0·096	+0·927	+1·239	+1·408

When the potential reached +0·96 oxygen evolution commenced. With such a plate in a cell the potential would fall rapidly when only small currents were taken from it. At the eight-hour discharge rate the current density at the negative plate of a Jungner type cell is about 3–4 milliamps. per cm.^{2} of plate surface. The available surface of active material is, of course, much greater than the plate area owing to the fine state of division of the metal, and the current density is correspondingly reduced. No estimate of the available surface area can be made, but the fall of potential with increasing current density shown in the above table is so rapid that it appears not unlikely that even a finely-divided cadmium electrode would exhibit some electrochemical inertness.

If the cadmium and iron formed a solid solution, the potential of the plate would vary with the composition, becoming baser as the percentage of the less noble metal (iron) increased. Some change of the plate potential during discharge would also be anticipated. The relation between the potential and composition of a solid solution is not always a smooth curve, but abrupt and rapid changes sometimes occur. The formation of an intermediate compound would also lead to abrupt changes in the potential-composition curve. For cadmium and iron existing as separate metallic constituents, the potential should be independent of the composition and be that of the less noble metal as long as any appreciable percentage of it is present. There is, unfortunately, no published information on the relation between the potential and composition of the cadmium-iron plate.

Jungner definitely states that the cadmium and iron are present as a metallic mixture, and, indeed, the iron was originally chosen merely as a diluent to the cadmium. The heat of formation of ferrous oxide is only slightly greater than that of cadmium oxide. This led Jungner to anticipate that the potentials of the two metals would be so close together that any self-discharge would be negligible.

In a plate consisting of the separate metals interaction between them and their oxides would occur according to the equation

$$Fe+CdO=FeO+Cd$$

This action would not result in any loss of capacity from the plate, but would cause a slight fall from the potential of iron to that of cadmium for that portion of the discharge which was thereby transferred from the iron to the cadmium. The plate would therefore tend to show the cadmium rather than the iron potential after standing on open circuit for some time. Energy losses due to this may correctly be regarded as of slight importance.

An action with the electrolyte might also be anticipated,

$$Fe+H_2O=FeO+H_2$$

the hydrogen being released at the cadmium surface. Since the potential of iron is about 0·07 volt more electronegative than that required to discharge hydrogen, a similar action would occur at a pure iron plate if it were not largely prevented by the overvoltage to hydrogen discharge at an iron surface. It is probable that a similar explanation holds good for the cadmium-iron plate, as in practice this plate shows no abnormal self-discharge. According to Glasstone,[1] the overvoltage to hydrogen discharge at a cadmium surface in normal sodium hydroxide solution is 0·81 volt at a current density of 10 milliamps per cm.^{2}, and 1·00 and 1·09 volts for current densities of 100 and 150 milliamps per cm.^{2} With such a high overvoltage no hydrogen evolution would occur, and hence no self-discharge of the composite plate.

It has been assumed in the foregoing discussion that the cadmium discharge reaction is $Cd \rightarrow CdO$. Edison [2] in one of his patents writes the action as $Cd \rightarrow Cd_2O$, but, since

---

[1] *Jour. Chem. Soc.*, 123, 1747, 1923.

[2] Brit. Pat. 20960, 1900.

the anodic solution of cadmium normally yields CdO, it is unlikely that the product of the cadmium-iron plate is other than this. The discharge reactions of the Jungner type plate may then be written

$$\mathrm{Cd} \rightarrow \mathrm{CdO}.x\mathrm{H_2O}$$
$$\mathrm{Fe} \rightarrow \mathrm{FeO}.y\mathrm{H_2O}$$

but it is doubtful to what extent the second reaction takes place, and, in any event, the iron is the minor constituent of the plate and supplies only a smaller part of the discharge capacity. The absence of any break in the discharge curve is to be attributed to the small difference between the potentials corresponding to these two actions.

CHAPTER IX

APPLICATIONS

BEFORE briefly reviewing the practical application of alkaline accumulators to various types of battery work, it is of interest to summarise the outstanding advantages and disadvantages of lead and alkaline cells.

DISADVANTAGES OF ALKALINE CELLS

(1) **Lower Efficiency.**—The energy, or watt-hour, efficiency of alkaline cells is about 50–55 per cent., as compared with 75 per cent. for lead cells. This factor is often of much less importance in practice than might at first sight be supposed. The actual cost of current for charging is only a small part of the total cost of operating a battery of any type, so that the difference in efficiency introduces a very small percentage addition to the expense.

In addition, the figure of 50–55 per cent. is only applicable when complete discharges are taken from the battery. Operating on partial discharges, as often occurs, much higher efficiencies are obtained; for example, discharging only half the capacity gives a watt-hour efficiency of 65–70 per cent.

(2) **Larger Fall in Voltage during Discharge.**—During the discharge at the 5-hour rate, the voltage of a lead battery falls by about 15 per cent. At the same rate the voltage of an alkaline battery falls by about 30 per cent.

This is a real disadvantage if the alkaline battery is used in an installation designed for a lead battery, but need cause no trouble if motors and other apparatus are suitably designed to accept this variation in pressure.

(3) **Large Difference between Discharge and Charge Voltage,** and inability to charge at low rates. The latter characteristic applies only to cells of the iron-nickel type; but the comparatively large difference between charge and

discharge voltage in all alkaline cells makes them unsuitable for operation by the method of " floating."

(4) **Larger volume for equal watt-hour capacity.**

(5) **Absence of indications of state of charge.**

(6) **Low capacity at low temperatures.**

(7) **High initial cost.**

ADVANTAGES OF ALKALINE CELLS

(1) **Longer Life.**

(2) **Simple and Cheap Maintenance.**—This feature should be borne in mind when comparing the initial cost of lead and alkaline cells. The skilled attention necessary for the satisfactory performance and life of a lead battery is dispensed with in the alkaline battery installation.

(3) **High capacity available at rapid rates of discharge.**

(4) **Alkaline electrolyte.** The absence of acid fumes and their corrosive effect on metalwork is a distinct advantage. An alkaline battery may be installed in the same room as machines and instruments which would be seriously damaged by the acid fumes from a lead battery.

ALKALINE CELLS IN PRACTICE[1]

(1) **Train-lighting.**—The essential qualities required in a train-lighting installation are mechanical robustness, and suitability for varied and intermittent use. Neither of these requirements is met by the lead accumulator, and, moreover, the conditions of working are often ruinous to the lead battery. Coaches normally in regular service may for some reason be standing out of use for prolonged periods. Over-discharge may result from accidents to the charging plant, or the lights may inadvertently be left alight. In any of these cases, the lead battery is liable to " sulphation," with the result that its useful life is impaired, and, as a rule, special treatment is necessary to put the battery in working condition.

The electrical conditions for a lighting supply necessitate that the variation of potential at the bus-bars shall be a

---

[1] An excellent discussion of the application to various purposes of alkaline cells, with special reference to the " Ionic " accumulators, has been published by Herold (" Etude théorique et pratique de l'accumulateur fer-nickel," *Bull. Soc. Belge Ing. et Indust.*, V., 1924, No. 2). Material has been freely used from this paper for the present chapter.

minimum. *A priori*, the alkaline cell seems in this respect to be at a serious disadvantage.

Excessive voltage across the lamps reduces their life, and must be avoided. A resistance is therefore automatically switched into the lamp circuit when the battery is on charge, so that the voltage never exceeds 27 volts on a 24-volt installation. It is sufficient to give this resistance a higher value for an alkaline battery than for a lead battery.

Actually nickel-iron cells have an advantage in the fact that the variation of voltage during the charge is less than in a lead battery. Hence, if the voltage across the lamp is regulated so as not to exceed the permissible maximum, it will remain more constant in different states of charge in the alkaline than in the lead cell.

Another system makes use of a constant potential generator, which is designed to give a voltage slightly above the open circuit voltage of the battery at all speeds, so that the battery is always kept charged, but the voltage is not allowed to become excessively high. This method is obviously better suited to the lead battery than to a nickel-iron battery, which is not capable of taking a charge at low rates, or a Jungner battery, which is stated to lose capacity progressively if the charging voltage is limited to a value below that normally reached at the end of charge.

Systems of voltage regulation specially designed for alkaline batteries have been produced and installed.

(2) Lighting and Starting Batteries for Cars.—The electrical equipment of a car includes a system similar to a train-lighting set, on a smaller scale, and a motor for starting the engine.

The starter constitutes a special problem. The maximum demand on the battery varies between 100 and 400 amperes. A lead battery of the usual capacity can yield such a current for 1–4 minutes, while the starting current is required at most for a few seconds. It may therefore be assumed that the capacity of the battery will be sufficient, provided that it can be recharged rapidly enough. In a lead battery, however, the rate of charge may not exceed a certain limit without damage to the cells. Hence the minimum capacity which must be provided in a lead battery depends not so much on the maximum demand of the starting motor, as on the rate of charge which it must be capable of accepting. The alkaline battery, on the contrary, may be charged at high rates without damage to the plates.

The alkaline battery has the disadvantage that the voltage falls to a much lower value than that of a lead battery when a heavy current is drawn from it. This drawback, due to the higher internal resistance of the alkaline cell, has been lessened to a certain extent by several makers who produce special "low-resistance" batteries, by using thinner plates or other modifications, but has not been entirely overcome. In order to obtain equal power in a high-rate instantaneous discharge, it is necessary to use an alkaline battery of greater capacity, or with a greater number of cells. Either method requires an increase in the weight and volume of the battery, and the latter necessitates the use of higher voltage lamps. If, however, such a concession is made and the higher initial cost is accepted, the result will in general be a greater satisfaction, owing to the longer life and freedom from troubles of the battery.

Probably the chief causes of the rapid destruction of lead batteries in car equipments are vibration and excessive charging—many sets being designed so that the battery is always charging when the speed of the car exceeds a certain limit. Continual gassing causes a rapid loss of positive paste in the lead accumulator. No harm is done to an alkaline battery by any amount of excess charging.

A further advantage which would result from the use of a permanently reliable battery would be the extended use of battery ignition instead of magneto, the only weak point in the system of battery ignition at present being the lead accumulators.

(3) **Electric Traction.**—This is a field in which alkaline cells have already proved their value. Lead traction batteries are manufactured with a view to high capacity per unit weight and volume, and their life is correspondingly short.

Alkaline batteries of somewhat larger volume, but slightly less weight, are capable of giving an electrical performance identical with that of a lead battery, at the rates of discharge used for traction purposes (compare the figures given in Table 11 of the Appendix).

The low efficiency of the alkaline cell is often cited as an objection to its use in traction batteries, and the question merits closer discussion.

A battery is always charged from a direct current supply in series with regulating resistances, which absorb the difference in pressure between the supply and the battery. The number of cells which can be charged is determined so that at the end of charge the voltage of the battery is almost equal to that of the supply. Thus on a supply voltage of 110 volts the maximum number of lead cells is $\frac{110}{2\cdot7}=40$, and of alkaline cells $\frac{110}{1\cdot84}=60$. The mean discharge voltages will be 74 volts and 66 volts respectively. The ampere-hour efficiencies may be taken as 90 per cent. for the lead battery, and 70 per cent. for the alkaline battery. These data give overall energy efficiencies of 60·5 per cent. and 42·0 per cent. respectively.

It has been found that the consumption of energy in lead batteries used for electric traction accounts for about 7 per cent. of the total operating costs. On the basis of the data given above, the energy consumption of the alkaline battery would be about 10 per cent. of the total costs. It seems evident that the economies realised by the smaller outlay on maintenance will very largely suffice to balance the small additional cost of energy.

(4) Stationary Batteries.—For this use, lead batteries of the Planté type are to be preferred to any other class of battery, when regular daily service is called for. They have a high efficiency, steady voltage characteristic, and a long life, and their suitability for this application cannot be doubted.

In stationary batteries which are required only at intervals, such as lighting installations in country houses occupied only for part of the year, and in all cases where the battery must be capable of giving a high discharge at long intervals, alkaline accumulators are to be preferred, because they require no maintenance during idle periods, there being no danger of sulphation.

(5) Telegraph, Telephone and Radio Batteries.—Alkaline cells are admirably suited to all those applications which call for intermittent or slow discharges, with charges at long intervals. They are capable of holding their charge for long periods, and there is no danger in leaving them for considerable intervals in a discharged or nearly discharged condition.

APPENDIX

TABLE II

Electrical Data for Different Types of Alkaline Cells, and for Typical Lead Cells.

Type of Cell.	Rate of Discharge.	Capacity Amp.-hrs.	Mean Voltage.	Capacity. Watt-hours.	Weight of Cell (kg.).	Volume of 6-cell Crate (cub. decim.).	Watt-hours per kilogram.	Watt-hours per cubic decimetre.	Remarks.
Edison A.6 . .	45 amps.	245	1·20	294	9·4	40·0	30·2	44·0	Taken from maker's published data.
	220 amps.	240	0·836	200	9·4	40·0	21·4	30·0	
Ionic	$\frac{1}{10}$ Capacity						24·5	33·0	From curves given by Herold (*Bull. Soc. Belge Ing. et Indust.*, V, 1924, No. 2).
	$\frac{2}{3}$ Capacity						15·5	20·8	
Nife J.24 . .	30 amps.	240	1·20	288	12·0	63·5	24·0	27·2	Taken from maker's published data.
	240 amps.	240	0·93	223	12·0	63·5	18·6	21·0	
Alklum A.25 .	31·2 amps.	250	1·22	305	12·2	53·2	25·0	33·4	Taken from maker's published data.
	212 amps.	212	1·15	244	12·2	53·2	20·0	27·6	(Mean voltage for high-rate discharge is probably less than the figure quoted.)
Lead Cell . .	50 amps.	250	1·96	490	22·2	59·0	22·0	50·0	Mean values from three types of vehicle battery.
	146 amps.	146	1·84	269	22·2	59·0	12·1	27·4	

TABLE 12

Details of Different Types of Alkaline Cells.

(This table includes only a few typical cells of each make. For complete lists of types, etc., the makers' pamphlets should be consulted.)

Make and Type of Cell.	Capacity. (A.H.)	Number of Positive Plates.	Number of Negative Plates.	Weight per Cell (lbs.).	Electrolyte Volume (pints).	Dimensions of Cell (inches).			Remarks.
						Width.	Length.	Height.	
Edison A.4	150	4	5	14·9	2·0	5·0	2¼	13	Dimensions approximate.
,, B.6H	112·5	6	7	13·8	2·7	5·0	3⅝	10¼	,, ,,
Nife J.O.4	4	3	2	0·8	0·115	3·15	1·15	4·14	From makers' published data.
,, J.1	10	3	2	1·41	0·18	3·15	1·15	5·9	,, ,,
,, J.2	22	3	2	2·75	0·31	4·14	1·15	8·55	,, ,,
,, J.24	240	13	12	26·5	4·9	6·15	3·86	14·85	,, ,,
Alklum W.3.	3	—	—	0·62	0·10	3·2	0·7	5·0	From makers' published data.
,, A.1	10	—	—	1·88	0·25	3·2	1·25	6·12	,, ,,
,, A.10	100	—	—	12·0	1·8	5·12	2·5	14·0	,, ,,
,, A.50	500	—	—	50·0	8·0	7·12	1·0	16·12	,, ,,

INDEX

PRINTED IN ENGLAND BY WILLIAM CLOWES AND SONS, LTD., BECCLES.