STORAGE BATTERIES

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A General Treatise on the Physics and Chemistry of Secondary Batteries and Their Engineering Applications

BY

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PREFACE TO THIRD EDITION

PREVIOUS editions of this book were published in 1924 and 1930. A French translation of the second edition by Monsieur Georges Génin, with supplementary notes, was published in Paris by Dunod in 1936.

The present book recounts advances made by the battery industry during recent years. New materials and new types of batteries are now available; performance and methods of operation are improved; and batteries are finding new uses which emphasize their dependability as sources of electric power. On the theoretical side, our present knowledge of the physical, chemical, and thermodynamic properties of sulphuric acid solutions provides basic data for a better understanding of fundamental reactions. A considerable part of the present book, therefore, deals with these recent engineering and theoretical developments.

By deleting obsolete and less important subject matter of the earlier edition, space has been provided for new material without increasing unduly the size of the book. Changes have been made in all chapters, with one exception. Chapter X on applications has been completely rewritten and extended to include many of the newer uses for storage batteries. About half of the illustrations have been changed.

The author wishes to thank many friends who have contributed generously of their time and knowledge toward the revision of this book. He thanks also the manufacturing companies and other organizations, mentioned below, which have supplied technical information and illustrations. Especial acknowledgment should be made to the following: Dr. D. N. Craig, Mr. C. L. Snyder, and Dr. Chester Snow of the National Bureau of Standards; Mr. A. E. Petrie, Mr. R. L. Young, Mr. R. P. Martin, Jr., and Mr. F. T. Foster of the Bell Telephone Laboratories; Dr. J. L. Woodbridge, Mr. E. W. Smith, Mr. F. G. Beetem, Mr. E. C. Kline, Mr. K. W. Green, Mr. L. E. Lighton, Mr. W. C. Leingang, Mr. R. W. Ritter, and Mr. J. A. Klingensmith of the Electric Storage Battery Co.; Mr. G. E. Stringfellow, Mr. E. W. Allen, Mr. W. M. Schleicher, Mr. W. H. Patterson, Mr. Don Moulton, and Mr. J. B. Goodell of the Edison Storage Battery Division, and Mr. F. Stallknecht of the Primary Battery Division of Thomas A. Edison, Inc.; Mr. H. N. Stover and Mr. F. W. Altrup of the Philco Corporation; Mr. C. C. Rose of the Willard Storage Battery Co.; Mr. J. L. Rupp of the Gould Storage Battery Co.; Mr. Grant Wheat of the Koehler Manufacturing Co.; Mr. E. F. Stevens of the Raytheon Co.; Mr. B. H. Schubert of the National Lead Co.; Mr. H. R. Harner of the Eagle-Picher Lead Co.; Dr. L. O. Grondahl of the Union Switch and Signal Co.; Dr. Anna P. Hauel; Mr. C. C. Shangraw of the Eclipse Aviation Corporation; Mr. G. B. Glaenzer of the American Hard Rubber Co.; Mr. W. H. S. Hamilton of the New York Central Railroad; Dr. O. B. J. Fraser of the International Nickel Co.; and Dr. A. J. Phillips of the American Smelting and Refining Co.; the Automatic Transportation Co. Permission was received to use certain illustrations which appeared in the following technical journals: *Transactions of the American Institute of Electrical Engineers; Transactions of the Electrochemical Society;* and *Diesel Power and Transportation.*

GEORGE WOOD VINAL

WASHINGTON, D. C
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PREFACE TO FIRST EDITION

Within the past ten years, storage batteries have entered into the daily life of millions of people. The name of "storage battery" no longer suggests only the massive stationary cells, familiar enough to the engineer, but almost unknown to others. Small batteries for a great variety of purposes have been developed. Railway trains, electrically lighted by storage batteries, have become universal in express service; electric trucks and industrial tractors, with long records of efficient service, have proved their worth; automobiles by the million now carry storage batteries; farm lighting plants have introduced the storage battery into rural life; and, last of all, the radio receiving apparatus, requiring one or more batteries for its operation, has been instrumental in making storage batteries a familiar factor in every-day life.

The published literature on storage batteries is more extensive than is generally supposed, but the valuable papers are scattered and many are in foreign languages. The author believes, therefore, that the present is an opportune time to present a book of moderate size which summarizes the physical and chemical facts and theories about storage batteries and describes their various applications.

In preparing this volume, emphasis has been laid on the scientific principles involved, without, however, permitting the text to become so technical as to restrict its usefulness. Descriptions of particular makes and types of batteries have been subordinated. The physical and chemical properties of the materials used in constructing storage batteries are discussed in so far as they relate to battery performance, and a general description of the methods of manufacture is given. Especial attention is devoted to the electrolyte and the rôle that it plays. The discussion of the theory is necessarily technical, and perhaps open to criticism by those who still hesitate to accept the "double sulphate" theory. This theory is presented because there is a preponderating amount of evidence in its favor. Brief mention is made of other theories. In discussing the factors which affect the capacity of storage batteries and the characteristics of the operation, the author has drawn liberally on test reports, and papers published by himself and his collaborators at the Bureau of Standards. The chapter on applications describes only the principal uses of storage batteries. A description of the various kinds of service and the type of battery for each is followed by a statement of the work that the battery has to do and a few records of performance, so far as they are available.

The author was encouraged to undertake the preparation of this book by Dr. S. W. Stratton, formerly Director of the Bureau of Standards, and by Dr. E. B. Rosa, late Chief Physicist of the same institution. He wishes to thank also Dr. G. K. Burgess, Director, and Mr. E. C. Crittenden, Chief of the Electrical Division of the Bureau of Standards, for placing unusual facilities at his disposal. Those of his colleagues who have assisted with valuable suggestions include Dr. H. D. Holler, Dr. J. F. Meyer, Dr. H. L. Curtis, and Dr. F. B. Silsbee.

The manuscript has been reviewed by engineers of several battery-manufacturing and other companies. It is a pleasure to acknowledge the helpful criticisms that have been received. While it is not possible to mention all of those who have thus aided, especial mention should be made of the following: Mr. R. L. Young, American Telephone and Telegraph Co.; Mr. R. C. Mitchell, Edison Storage Battery Co.; Mr. A. V. Morris, Dr. J. L. Woodbridge, Mr. Hugh Leslie, Mr. G. M. Howard, Mr. J. Tracy, and Mr. R. Whitehurst, Electric Storage Battery Co.; Mr. L. T. Beale, John T. Lewis and Bro. Co.; Mr. L. M. Ritchie, National Carbon Co.; Mr. W. E. Holland and Mr. W. H. Grimditch, Philadelphia Storage Battery Co.; Mr. D. S. Funk, Sangamo Electric Co.; Mr. O. W. A. Oetting and Mr. C. Reinhardt, Willard Storage Battery Co. Illustrations have been furnished by the battery companies named above and by the Baker R and L Co.; the Northeast Electric Co.; the Gould Storage Battery Co., and the Prestolite Co., Inc.

G. W. V.

WASHINGTON, D. C.
January 14, 1924

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STORAGE BATTERIES

CHAPTER I

INTRODUCTION

The storage battery is typically an electrochemical apparatus and as such must be discussed from three viewpoints. The first is chemical, involving the nature and properties of the materials used in its construction and the reactions which occur during charging and discharging. The second is physical, and this includes a study of the electrical input and output, the factors which affect the capacity, and the theory of the transformation of chemical energy into electrical energy or vice versa. The third viewpoint is the practical one dealing with the engineering applications of storage batteries. There is no sharp line of demarcation between the chemical, physical, and engineering aspects, but a full discussion of all is necessary to an adequate understanding of the nature and performance of storage batteries.

The scientific principles underlying the operation of storage batteries have now been so thoroughly investigated, both in this country and abroad, that they may be presented with some degree of confidence. They serve as the groundwork for an intelligent study of batteries as they exist today and as a guide for the future development of the art. The presentation of these principles is necessarily technical, but the author has endeavored to make plain the meaning and explain the applications as simply as possible. The more technical and mathematical parts are contained in Chapters IV, VII, and VIII. These constitute a relatively small part and may, of course, be omitted by those whose interest lies in other directions. A detailed description of the essential processes of manufacture of batteries and the properties of the electrolyte is contained in Chapters II and III. The factors which affect the capacity of batteries are described in Chapter V. Operation, which includes charging and discharging, the use of rectifiers, battery regulation,. costs of operation, and the sources of trouble to which batteries are subject, is contained in Chapter VI. Chapter IX deals with the principles to be observed in the testing of storage batteries and Chapter X describes in detail the various applications of the batteries and the nature of the service that they perform.

1. THE STORAGE-BATTERY INDUSTRY

The storage-battery industry began with the pioneer experiments of Planté in 1859. The development since that time naturally divides itself into epochs of about twenty years each. During the first of these, the storage battery was little more than a piece of laboratory apparatus, because of the labor and expense involved in preparing and charging the plates. In 1881 a great step forward was taken when the process of forming the active material from the oxides of lead was discovered. This simplified and cheapened the process of manufacture. About this time also, dynamo-electric machines became available for charging the batteries, which had formerly been charged by primary batteries. Invention and investigation were greatly stimulated, but this period was marred by bitter controversies over the relative merits of the different types of batteries, over questions of priority of invention, and over theories to explain the chemical reactions that take place when the batteries are charged and discharged. The batteries of this period were mostly of the stationary variety.

The storage battery was tried in a number of different services early in its history. The first installations often were not successful but they led to valuable results later on. Blizard[1] gives the dates and places of the first installations made in this country, including the following: central-station battery at Philipsburg, Pa., in 1885; trolley service at Dover, N.H., in 1893; train-lighting battery on the Pennsylvania Railroad in 1882; isolated lighting plant at Baltimore, Md., in 1883; central-station telephone service at Chicago, Ill., in 1889. The first successful use of batteries for the propulsion of electric vehicles was stated to have been in 1894, but there were many attempts prior to this date.

The third epoch, beginning with 1900, has been characterized by the development of compact, portable types of batteries and a great increase in the number of batteries used. Portable batteries have been produced for railway train lighting, propulsion of submarines and electric vehicles, starting and lighting of automobiles, signaling on the railroads and in military operations. Stationary batteries have also been developed during this period for stand-by and regulating service, telephone exchanges, and isolated lighting plants. The Edison alkaline storage battery was developed during this epoch.

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[1] *Electrical Review*, 38, p. 75, 1901.

In the twenty-year period now ending, storage batteries have found new applications in emergency lighting, air-conditioning of railway cars, starting of Diesel engines, and a variety of services on ships, buses, trucks, and aircraft. This period is significant for the intensive study of materials and construction of batteries for a highly competitive market.

The net result of the development has been to increase enormously the production of storage batteries and to place large numbers of the small sizes in the hands of non-technical people who are quick to appreciate reliable service, but who have little knowledge of the theory or construction of the cells. The growth of the industry since 1909 is shown by the following statistics compiled by the Census Bureau:

TABLE I

STATISTICS OF STORAGE-BATTERY MANUFACTURE

	1909	1914	1919	1925	1937
Weight of plates, pounds.......	23,119,331	41,079,047	148,951,766	388,264,038	....
Value...........	$4,243,984	$10,651,150	$56.648,347	$88,870,186	$78,250,221

Motor vehicles in the United States have increased from seven and one-half millions in 1919 to over thirty millions in 1939. Nearly all of these are electrically equipped, requiring a yearly production, for this one purpose, of about fifteen millions of batteries per year, if it is assumed that the average life of these batteries is from eighteen months to two years.

2. PRIMARY AND SECONDARY CELLS

An electric battery consists of two or more connected cells which convert chemical energy into electrical energy. The cell is the unit part of the battery, but the word "battery" is sometimes used to mean one cell. The essential parts of a cell are two dissimilar electrodes, immersed in an electrolyte in a suitable jar or container. Familiar examples of electrodes are the copper and zinc plates of a simple primary cell, or the lead and lead peroxide plates of a storage cell. The electrolyte is a water solution of certain acids, alkalies, or salts which have been found to be adapted to the purpose.

A number of different kinds of cells are in common use. These may be classified conveniently into two general groups as primary and secondary cells. The most familiar of the primary cells is the "dry cell." Secondary cells are generally spoken of as "storage cells" or "accumulators." The distinction between primary and secondary cells is based on the character of the chemical reactions which occur in them when they are in use. Primary cells convert chemical energy into electrical energy and in so doing they become exhausted. Dry cells, when no longer serviceable, are discarded, but some of the so-called "wet" cells may be renewed with new electrodes and electrolyte. The dry cells cannot be recharged by an electric current because some of the chemical reactions occurring in them are irreversible. Storage cells, on the other hand, convert chemical energy into electrical energy by reactions that are essentially reversible, that is, they may be charged by an electrical current passing through them in the opposite direction to that of their discharge. During this process, electrical energy is transformed into chemical energy, which may be used again at a later time as electrical energy. Electricity is not stored as electricity by these cells. They store chemical energy and so potentially electricity.

There are other cells, some of which are intermediate between primary and secondary cells. These are generally classed with the primary cells for practical reasons, although they may possess some of the essential characteristics of the secondary cells.

This book will be confined to the types of storage cells which are of practical importance. These are the lead-acid cells and the nickel-iron or alkaline cells. In the former, the plates are of lead and lead oxide, immersed in an electrolyte of sulphuric acid. The nickel-iron cells consist of nickel-plated steel grids containing tubes or pockets to hold the active materials of nickel and iron oxides. The electrolyte for the nickel-iron cells is a solution of potassium hydroxide, more familiarly called caustic potash. Another alkaline cell of the nickel-cadmium type is discussed briefly.

3. THE GROUPING OF CELLS

For most purposes storage cells are used in groups or batteries, the number of cells and their size depending on the service required. Several different arrangements are possible, and it is therefore desirable to arrange the cells in such a way as to secure the most economical service. Two factors are involved in arranging the cells; one is the voltage requirement and the other the capacity. When the cells are connected in series—that is, when the positive pole of one cell is connected to the negative pole of the next, and so on to the end of the row, as in Fig. 1, the voltage of the cells is additive. Two cells in series will give twice the voltage of one cell, and five cells will give five times the voltage of one, assuming that the cells, taken individually, are of the same voltage. The capacity of a row of series-connected cells, however, is no more than the capacity of a single cell.

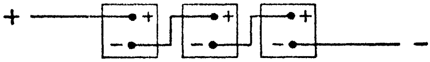

Fig. 1. Cells connected in series.

Cells may also be connected in parallel, by connecting like poles together, as shown in Fig. 2. The voltage of such a group is no more than the voltage of a single cell, but the capacity of the group is equal to the sum of the capacities of the individual cells. Such an arrangement of storage cells is not commonly made, because it is better to use a single cell of the required capacity rather than a group of small ones connected in parallel.

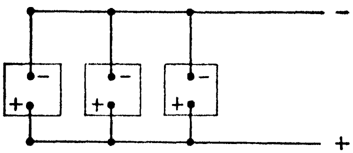

Fig. 2. Cells connected in parallel.

When more than three cells are involved in a series and parallel connection, there is a choice of arrangement, as shown in Figs. 3 and 4. The cells may be arranged in several rows connected in series, and these rows may then be connected in parallel (Fig. 3), or they may be arranged in parallel groups which are then put in series (Fig. 4). The voltage and capacity of either of these groups is the same, but the former is preferred for storage batteries although the latter is the best arrangement for dry cells. The paralleling of series-connected groups of storage batteries is found in cases where exceptional capacity is required, or for charging when the voltage of the charging source would not be sufficient to charge the cells if they were all connected in series.

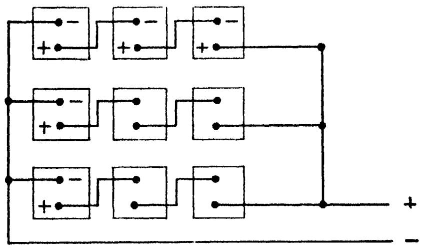

Fig. 3. Parallel of series-connected cells.

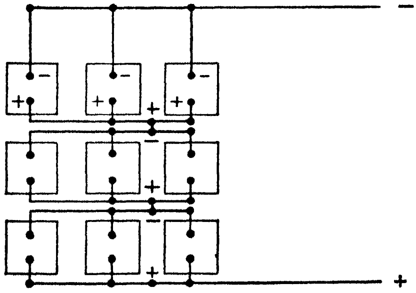

Fig. 4. Series of parallel-connected cells.

4. ELECTRICAL UNITS

Any measurement, whether electrical or not, must be expressed in terms of two factors. One of these defines a certain definite amount of the physical quantity measured, called the unit, and the other is a mere number, indicating the number of times the unit is taken. Thus we may say ten volts or a hundred amperes.

Relationships exist between various units, so that some of them can be derived from others, which we may regard as fundamental. Thus, Ohm's law, $I = \frac{E}{R}$, expresses a relationship between the current, I, measured in amperes, the electromotive force, E, measured in volts, and the resistance, R, measured in ohms. It is necessary to establish only two fundamental units, as the third may be derived from the equation. For the two fundamental units, the ohm and the ampere have been selected, because these are more easily and directly measured in mechanical units upon which they are based, but of the three quantities, resistance and electromotive force are the only ones for which convenient and portable standards are possible. This refers to the primary standards and not to electric meters of various kinds which must be calibrated in terms of the standards. Ordinary measurements of electric current are based, therefore, on standards of electromotive force and resistance.

From the standpoint of the electrochemist, the unit quantity of electricity is of particular interest. One ampere flowing for one mean solar second is one coulomb, or, if the current flows for t seconds, the product, It, is the number of coulombs. The amount of metal deposited or gas liberated is determined by the number of coulombs passing, unless secondary reactions intervene. Since the coulomb is a small quantity, it is convenient to use a larger unit. Thus, 3600 coulombs or one ampere flowing for one hour is one ampere-hour. The faraday is a still larger unit, equal to 96,500 coulombs or 26.80 ampere-hours. It is the quantity of electricity associated with one equivalent of chemical change.

Power and energy are common to all branches of physical science. Energy and work have the same dimensional formula, and power is the rate of doing work. The erg or dyne-centimeter is so small a unit of energy that 10^7 ergs are used as a larger unit called the joule which is more familiarly known in electrical measurements as the watt-second or volt-coulomb. In still larger units we have the kilowatt-hour and the kilowatt-year. Power is usually measured in watts. In electrical measurements the watt is the product of the volt and ampere and is equal to a joule per second. As a larger unit we have the kilowatt.

There are, therefore, four basic equations which will be used in various forms. They all apply to direct current measurements.

$$\text{Current (amperes)} = \frac{E}{R}$$

$$\text{Quantity (coulombs)} = It = \frac{Et}{R}$$

$$\text{Power (watts)} = EI = I^2R = \frac{E^2}{R}$$

$$\text{Energy (volt-coulombs)} = EIt = I^2Rt = \frac{E^2t}{R}$$

The same fundamental units serve for the measurement of alternating currents, but the equations must be modified to take account of the phase relations of current and electromotive force. The effective values of a-c voltage and current are the root-mean-square values, but rectified currents which are pulsating, require the average value as a measure of electrochemical processes.

CHAPTER II

MATERIALS AND METHODS OF MANUFACTURE

1. HISTORICAL DEVELOPMENT OF THE LEAD-ACID BATTERY

The storage battery of today grew out of the investigations of many early experimenters in the field of electrochemistry. Volta's discovery of the galvanic battery in 1800 initiated this line of research. Two years later, Gautherot discovered the polarization of platinum wires, produced by the passage of an electric current through a cell which he used for studying the decomposition of water. He found that a feeble current was returned when he connected the wires after having disconnected the source of current. Ritter repeated Gautherot's experiment in 1803 and went a step farther. He constructed small piles from plates of several metals, including gold and silver. Between the sheets of metal he placed moistened layers of cloth. He charged these piles with an electric current and obtained a discharge current from them after disconnecting the charging source. He thought that the piles stored electricity much as a condenser does, because, like a condenser, the pile had layers of metal of good conductivity alternating with layers of the poorly conducting cloth. Volta showed that this explanation was not correct and attributed the effect to the decomposition of water. Other experimenters entered the field, but it remained for Planté to develop a valuable form of cell as a result of his study of the properties of metals for the accumulation of oxygen.

In 1859 Planté began his study of electrolytic polarization. As a result of his experiments, he devised a battery for the storage of electrical energy, consisting of two sheets of lead separated by strips of rubber and rolled into the form of a spiral. The element thus formed was immersed in a dilute solution, about 10 per cent of sulphuric acid. He studied the charge and discharge of this simple cell and described it as storing the chemical work of the voltaic pile. He found it possible to increase materially the capacity of the cell by a process which is now known as formation. Following periods of charge, he discharged the cell or allowed it to rest for a time, during which local action transformed the covering of peroxide on the positive plate into lead sulphate. From time to time he reversed the polarity, and repeated the process of charge and discharge to build up the capacity of the cell.

One of the most interesting advantages which this storage cell possessed for the early experimenters was its ability to deliver much larger currents than could be obtained from the primary cells. There were serious disadvantages, however, chief of which was the time required for formation. The early literature records the expenditure of two years' time by the manufacturers for the formation of some cells, although others, said to be inferior in performance, received only three months of formation. Primary batteries were the only means available for charging these storage cells, which made the process costly

Planté's name has been perpetuated in connection with the storage battery by the so-called Planté plate. This type of plate, as distinguished from the others, consists of a sheet of lead on which the active material is formed electrochemically from the lead of the plate itself.

In 1881 Faure[1] patented a process for pasting the surface of the plates with a compound of lead which could be formed more easily into the active materials of the finished battery. He applied a coating of red lead to the surface of smooth lead plates, rolling them together with a layer of flannel between for a separator. This type of cell possessed marked superiority in capacity and ease of formation over the cell of Planté, but the adherence of the active material to the plates was rather poor. It is stated that a battery of this type capable of exerting one horsepower weighed 75 pounds and gave an energy efficiency of 80 per cent.

About the same time, Brush, an American, also discovered the possibility of preparing the active materials from compounds mechanically applied to the plates. He obtained patents covering this principle.

In the latter part of 1881, Volckmar patented the use of lead plates with numerous holes which were filled with a paste made of pulverized lead mixed with sulphuric acid. Swan[2] also obtained a patent on a grid of cellular structure. These supports for the active material were an improvement over the flat plates which Faure used, but the active material still fell out readily. Sellon patented, in 1882, a modification of the grid to make it hold the material better. He designed his grid in such a way as to lock the active material in place. Sellon is said to have made use of the alloy of lead and antimony instead of pure lead for this grid. The Correns grid, devised and patented in 1888, consisted of a double lattice of which the bars were triangular in cross-section with the apexes pointing inward so that the active material was held securely in place.

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[1] *Electrician*, 6, p. 323; 7, pp. 122, and 249, 1881.

[2] *Electrician*, 8, p. 142, 1882; British Patent, No. 2272, 1881.

Since 1881 the development of the storage battery has been rapid because of the decreased time required for formation of the plates and also because of the development of machines for generating electric current. Many of the types of plates and grids which have been devised are of historical interest, but only a few of them are of commercial importance today. Detailed descriptions of many of them have appeared in several of the books[3] previously published on this subject, and it is therefore unnecessary to describe them further.

2. PASTED PLATES

a. The Grids

The grids (Fig. 5) serve as supports for the active material of the plates. The grid of the positive plate has an important part in conducting the electric current also, since the resistivity of the lead peroxide is more than 10,000 times the resistivity for pure lead. The grids also have an important function in maintaining a uniform current distribution throughout the mass of the active material. If the current distribution is uneven, the changes in volume of the plates, during their charge and discharge, will be uneven, resulting in a tendency of the active material of the plate to buckle or crumble. Light grids are, in general, used in batteries designed for heavy discharges of short duration, but in batteries designed for long life for which the discharge is intermittent or extended over a long period of time heavier grids are employed. The grids are cast, for the most part, of an alloy of lead and antimony, and frequently have designs by which the manufacturer can be identified. The grids most commonly used at the present time have cross bars which pass either straight or diagonally across the plate and are designed to lock the active material in place.

Grids for positive and negative plates are frequently of the same design, composition, and weight; but it is possible to make the negative grid lighter, because this grid is not required to take as important a part in conducting the current and is less subject to corrosion than the grid of the positive plate.

Materials. The material used in greatest amount is lead, which is an element having an atomic weight of 207.21. The battery industry is the largest consumer of lead in the United States, 192,000 tons being required[4] in 1937. Much of this is returnable, however, as secondary metal when the batteries are discarded. Lead is obtained chiefly from

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[3] *Secondary Batteries*, by E. J. Wade, p. 19; *Les accumulateurs électriques*, by L. Jumau, pp. 474, 540 and 997; *The Storage Battery*, by A. Treadwell, pp. 14 and 50.

[4] *Minerals Yearbook*, Bureau of Mines, p. 133, 1939.

the ore, galena, which is the native sulphide of lead, PbS. Because the storage battery is affected by the presence of small amounts of impurities, it is of interest to note the more common of the metals and sulphides which occur in the ore. These include iron, silver, copper, zinc, and

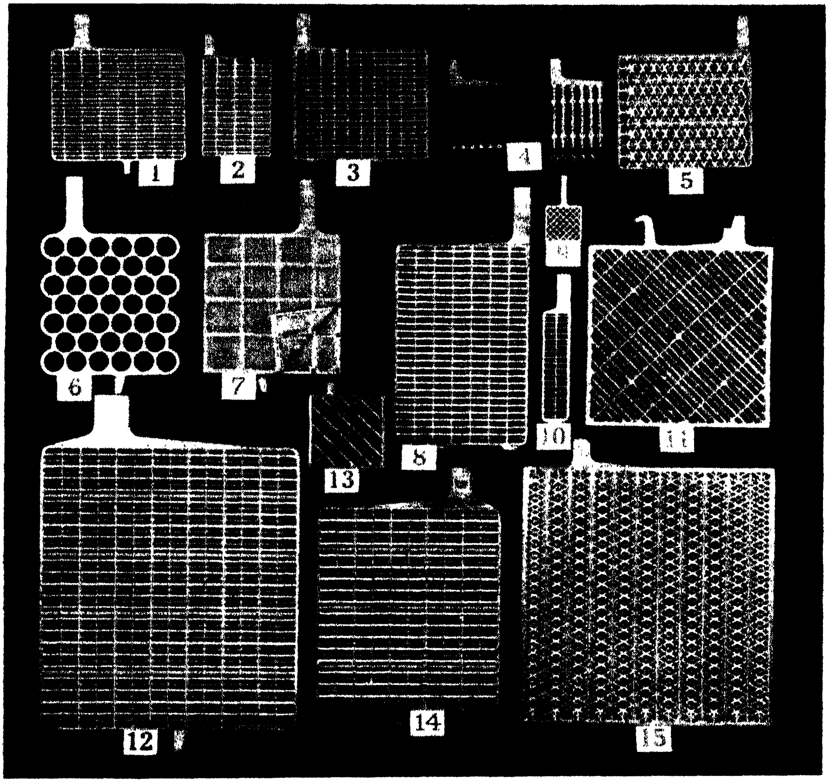

FIG. 5. Various types of grids. Numbers 1, 2, and 5 are grids for small glass-jar batteries; 3, grid for automotive battery; 4, smallest-sized grid of Ironclad construction, assembled and unassembled; 6, grid of the Manchester positive plate; 7, grid of the box-negative plate, corner opened to show construction; 8, grid of a motive-power battery; 9 and 10, grids for small experimental batteries; 11 and 13, Floté reinforced grids for stationary batteries; 12 and 14, Tytex reinforced grids for stationary batteries; 15, Diamond grid for stationary batteries.

arsenic. Galena is widely distributed, being found in nearly all countries. Other ores of lead of less importance are cerussite, $PbCO_3$, and anglesite, $PbSO_4$.

Lead is a metal, bluish-gray in color, with metallic luster. It oxidizes readily in moist air, becoming a dull gray. Lead in its pure state is soft and malleable, but its tensile strength is low. Because of its plasticity it may be extruded into ribbons and other forms by hydraulic presses. The density of cast lead is 11.34, but this may be slightly increased by rolling. The linear coefficient of expansion is 0.0000292 per degree Centigrade. This is greater than the values for copper, iron, tin, and some of the other common metals. The melting point for pure lead is 327.°4 C. (621° F.). The resistivity of lead is an important factor in the design of storage batteries. The values given in the literature differ somewhat, probably because lead is very sensitive in this respect to cold working, such as bending, hammering, or drawing. A recently determined value on a cast bar gave 0.0000212 ohm-centimeter at 20° C. (68° F.), or about 12 times the resistivity of copper.

The chemical properties of lead are of great importance in relation to storage-battery performance. Lead is readily attacked by nitric acid, but not by cold hydrochloric acid, or cold sulphuric acid below 1.700 sp. gr. Lead forms a number of important combinations with oxygen, which will be discussed in later paragraphs. Small amounts of many impurities exert a marked influence on the mechanical and electrolytic properties of lead. Traces of arsenic, copper, zinc, and antimony render it harder. Lead, to be satisfactorily rolled, must be pure. The so-called white metal, or alloy of lead and antimony, is less subject to electrolytic corrosion than pure lead. The metallurgy of lead is interesting and is of some importance to the battery manufacturer.[5]

The composition of refined pig lead varies with the source of the material and the methods employed in purifying it. Standards for three grades of lead, known as "Corroding," "Chemical," and "Common" lead, have been established by the American Society for Testing Materials (A.S.T.M.). The limits specified are given in Table II, but reference should be made to the complete specification.[6] The methods of analysis of pig lead are described also in the society's specifications.[7]

Very pure lead, prepared by electrolytic methods, is now available. Percentages of 99.99943 have been reported. Such lead is soft, low in tensile strength and consists of large crystals.

The production of secondary lead from discarded storage batteries has increased to large proportions.[8] Lead recovered in this way con-

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[5] See *Metallurgy of Lead*, by Hofman; *Lead*, by Collins; *Handbook of Metallurgy*, by Schnabel and Louis, Vol. I; *Lead*, by Smythe; *Useful Information about Lead*, published by Lead Industries Assoc., 1931.

[6] *Standard Specifications*, A.S.T.M., B29–35, p. 678, 1936.

[7] *A.S.T.M. Methods of Chemical Analysis of Metals*, B35–36 T, p. 174.

[8] *Minerals Yearbook*, Bureau of Mines, p. 502, 1939.

TABLE II

GRADES OF PIG LEAD, ACCORDING TO THE STANDARD OF THE AMERICAN SOCIETY FOR TESTING MATERIALS

	Grade I Corroding Lead, Per Cent	Grade II Chemical Lead, Per Cent	Grade III Common Lead, Per Cent
Silver, max. (I, III)	0.0015	0.020 max. 0.002 min.	0.002
Copper, max. (I, III)	0.0015	0.080 max. 0.040 min.	0.0025
Copper and silver together, max	0.0025	......	......
Arsenic, max	0.0015	......	......
Antimony and tin together, max	0.0095	......	......
Antimony, arsenic and tin together, max	......	0.002	0.015
Zinc, max	0.0015	0.001	0.002
Bismuth, max	0.05	0.005	0.15
Iron, max	0.002	0.0015	0.002
Lead (by difference), min.	99.94	99.90	99.85

NOTE: In Grade I, bismuth, copper, and tin must not all be present in maximum amounts in the same sample. Grade II is sometimes known as "undesilverized lead" from Southeast Missouri ores.

tains antimony. Battery scrap, consisting of complete groups, loose plates, and oxides, is smelted in reverberatory or blast furnaces. Fusion and reduction of the material occur in the smelting zone and the products separate into three layers: molten metal, matte, and slag. The antimony content of the recovered alloy is adjusted to the required percentage, but laboratory tests are needed to assure the required degree of purity, if the material is to be used for casting grids or other parts of batteries. Specifications of battery manufacturers differ considerably in the amount of impurities permitted.

Antimony, which is combined with lead in making the grids, is an element having an atomic weight of 121.76. It is obtained chiefly from the ore, stibnite, which is the native antimony sulphide, Sb_2S_3. This ore consists of prismatic crystals, bluish-gray in color with metallic luster. It is often associated with arsenic and bismuth. The color of antimony itself is silver-white with a high metallic luster. It is hard and brittle. The density is 6.684 and the expansion coefficient

0.0000114 per degree Centigrade. Antimony melts at a temperature of 631° C. (1168° F.). The resistivity of antimony is 39 micro-ohm-centimeters, or about twice that of lead, and the alloys of the two have a higher resistivity than pure lead. Antimony is not readily oxidized by the air, but it combines directly with chlorine, forming $SbCl_5$. Antimony is oxidized by nitric acid to the trivalent state. Arsenic is the principal impurity that is associated with antimony and deleterious to storage batteries.

The percentage of antimony in storage-battery grids ranges from 5 to 12 per cent. There are a number of reasons for using antimony: (1) The material flows better in the mold. To increase the fluidity some manufacturers specify a small amount of tin also, ranging from 0.05 to 0.35 per cent. (2) The alloy produces sharp castings. Ewen[9] has stated that the alloy of lead and antimony expands when solidification takes place, but Dean[10] denies this. (3) The alloy is less subject to electrochemical corrosion and can be used as a support for the active material without losing its strength by being "formed" as the battery is used. (4) Antimony increases the stiffness of lead, and also its ductility and tensile strength within limits that are shown in Table III. (5) The temperature of complete liquefaction of the alloys, within the range of compositions used for the grids, is below the melting point of pure lead. (6) The expansion coefficient of the alloy is less than that of pure lead.

Lead and antimony form an alloy of which the eutectic composition is 87 per cent lead and 13 per cent antimony, melting at 247° C. (477° F.). Lead and antimony are miscible in all proportions in the liquid state. Dean[10] has found evidence of the solubility of antimony in lead to the extent of 2.5 per cent at the melting point of the eutectic. This percentage decreases to about 0.5 per cent at ordinary temperatures. The structure of the alloy used in storage batteries, therefore, consists of the eutectic embedded in a solid solution of lead and antimony, as shown in Fig. 6. The equilibrium diagram is given in Fig. 7. Age-hardening of alloys containing more than 0.5 per cent of antimony has been observed by Dean.

A metallographic examination of the alloy is often valuable in determining the quality. The specimens to be examined are first cut to a smooth surface, polished, and then etched. Various etching reagents which have been recommended include: (1) a solution of one part acetic acid, three parts of hydrogen peroxide, and three parts water; (2) nitric acid, 10 per cent; (3) an electrolytic process in a solu-

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[9] *J. Inst. of Metals*, 4, p. 135, 1910.

[10] *Trans. Am. Inst. Mining and Metal. Eng.*, 73, p. 505. 1926.

tion of perchloric acid. When suitably prepared and examined under the microscope, the microstructure of the specimen is revealed as in

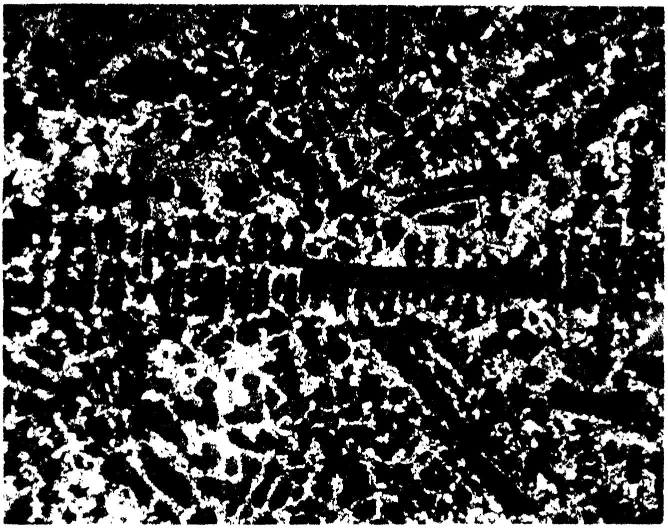

FIG. 6. Alloy of lead and antimony magnified 250 times. The dark portions are the solid solution and the light portions the eutectic. Antimony 8 per cent.

Fig. 6. Alloys that have been well mixed and cooled quickly after casting exhibit small crystals and are fine grained. Coarser structure

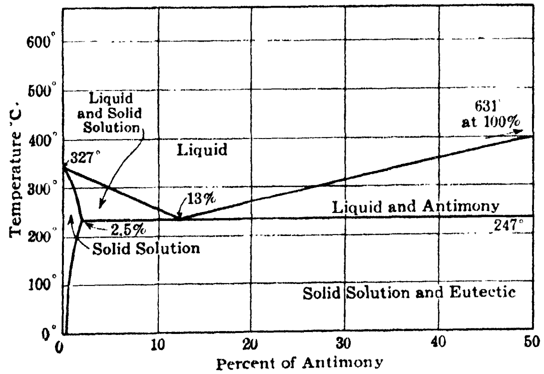

FIG. 7. Equilibrium diagram of lead and antimony.

indicates slower cooling. Segregated antimony, if present, appears as rectangular crystals. Irregular and unequal distribution of the eutectic is usually the result of poor mixing of the molten metals or uneven cooling. For a micrographic study of lead antimony alloys reference may be made to Villela and Beregehoff.[11]

The alloys of lead and antimony are of great commercial importance because of the wide variety of purposes for which they are used. Many investigations of their physical properties have been made, but very few of these have particular reference to storage batteries. Rosset[12] has determined values for the tensile strength, density, hardness, and resistivity of alloys for battery use, but not all of his results check with those more recently obtained. The metallurgical aspects of the alloy have been discussed by Dean,[13] who has also reviewed the work of many previous investigators, but without reference to the storage battery.

In Table III are found the results of several investigations made at the Bureau of Standards, on the alloys of lead and antimony. The results have been calculated for even percentages of antimony. Undoubtedly, the conditions of casting and the presence of small amounts of impurities may affect the physical properties considerably. The lead used for these investigations was of the grade known as "hardening lead," for which the manufacturer's analysis showed a purity of 99.9947 per cent. The antimony also was the purest that could be obtained.

Casting the Grids. The molds ordinarily consist of two parts. They are made of cast iron. Grooves are cut in the opposite faces of the mold, according to the design of the particular plates. Small grids are cast double and later cut apart. Large grids for stationary batteries or submarines are cast singly.

The molds should be evenly heated to 135° to 180° C. (275° to 356° F.) to make the metal run freely, and they must be provided with suitable vents to let out the air, which would otherwise be trapped in the mold when the molten metal is poured in. A slight head of the molten metal is required to make it run into all the recesses of the mold and the molten metal must be at a high enough temperature, when it is poured into the mold, to prevent premature solidification. The range of temperature is from about 425° C. (800° F.) to 525° C. (975° F.). Excessive temperatures, 975° F. and above, should be avoided since oxidation may change the composition of the alloy and affect the speed and quality of the casting.

Molds are prepared for the casting process by smoking, spraying, or dusting the faces after preliminary heating. This is necessary for

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[11] *J. Ind. and Eng. Chem.*, 19, p. 1049, 1927.

[12] *Centralblatt für Accumulatoren*, 6, pp. 138 and 259, 1905; and 7, p. 159, 1906.

[13] *J. Am. Chem. Soc.*, 45, p. 1683, 1923. *J. Ind. and Eng. Chem.*, 17, p. 1246, 1925.

TABLE III

PROPERTIES OF CAST LEAD-ANTIMONY ALLOYS

Per Cent of Antimony	Temp. of Complete Liquefaction		Density	Tensile Strength Lb. per Sq. In.	Elongation, Per Cent	Hardness, Brinell Number *	Expansivity Coefficient	Resistivity 20° C., Ohm-cm.
	°C.	°F.						
0	327	621	11.34	1780	....	3.0	0.0000292	0.0000212
1	320	608	11.26	....	....	4.2	0.0000288	0.0000220
2	313	596	11.18	....	...	4.8	0.0000284	0.0000227
3	306	583	11.10	4700	15	5.3	0.0000281	0.0000234
4	299	572	11.03	5660	22	5.7	0.0000278	0.0000240
5	292	558	10.95	6360	29	6.2	0.0000275	0.0000246
6	285	545	10.88	6840	24	6.5	0.0000272	0.0000253
7	278	532	10.81	7180	21	6.8	0.0000270	0.0000259
8	271	520	10.74	7420	19	7.0	0.0000267	0.0000265
9	265	509	10.66	7580	17	7.2	0.0000264	0.0000271
10	261	501	10.59	7670	15	7.3	0.0000261	0.0000277
11	256	492	10.52	7620	13	7.4	0.0000258	0.0000283
12	252	485	10.45	7480	12	7.4	0.0000256	0.0000289
13	247	477	10.38	7280	10	.....	0.0000253	0.0000293
14	...	...	10.30	7000	9	.....	0.0000251	0.0000293
15	...	...	10.23	6800	8	.....	0.0000248	0.0000292
16	...	...	.....	6620	6	.....	......	......

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* The hardness numbers given in this table are lower than others reported in the technical literature, probably because of the softness of the lead used in the investigation.

producing good castings which can be removed readily from the mold. The practice of dusting the mold frequently with pumice or other powder has been largely superseded by the application of a smoky acetylene flame or by spraying the mold with one of the several mold coatings which are now available. Spraying is done with an air gun: the nozzle is held 15 to 20 inches from the mold and the spray is directed from several directions. The mold must be hot enough to evaporate the water constituent instantly. A thin uniform coating is desired With occasional "touching up" this should suffice for several hours If the mold becomes too hot for the molten metal to solidify promptly, a little water may be used at the gate. The molds are sometimes filled from a ladle, by hand, but usually they are filled directly from the melting pot. Heavy grids, such as those for the Manchester plates, are cast under pressure, the molten metal being blown into the mold by compressed air.

The melting pot containing the molten alloy is usually fired by gas and contains several hundred pounds of the alloy. During the casting of the grids, the molten metal is stirred from time to time and the dross skimmed off. In the best practice the trimmings from the castings and scrap alloy, unless clean and free from sweepings, are not thrown back into the melting pot, since there is danger of contaminating it with impurities. Ventilation is necessary to carry off the fumes which may sometimes be seen over the melting pot. For this a forced suction through a hood is desirable, since the natural ventilation of the room does not provide satisfactory protection to the workers from poisonous fumes.

The most common flaws that are observed in grids are due to dross, to premature solidification of the metal in the mold, to webs which appear when the two faces of the mold do not fit well together, and to warping, which may be caused by mechanical injury in taking the newly cast grid from the mold. The grids are trimmed after casting, to remove rough edges and minor imperfections, but extensive trimming should be unnecessary. Grids for small batteries, such as those used on automobiles, are pasted while still double. After this they are cut apart, and the lugs, for connecting the grids to the connecting straps, are cut to the proper length and brightened by a scratch brush before the plates are burned to the straps. Large and costly grids containing minor defects are sometimes repaired by burning in new ribs. Before being pasted, the grids must be free from grease or dirt of any kind.

Cast grids are generally preferred to punched grids, but the latter have found some use. They are made by casting a continuous wide ribbon of the lead alloy which passes in turn through the punch press and pasting machine.

Other Alloys of Lead. Antimony, which is commonly alloyed with lead in making grids produces some detrimental effects in battery operation, chief of which are the spontaneous loss of charge and liberation of hydrogen at negative plates. Contamination of the active material results from small amounts of antimony liberated by corrosion of the grids of positive plates during the charge. Corrosion may proceed slowly, but small amounts of freshly deposited antimony are sufficient to cause considerable local action at the negative plates. This becomes increasingly severe in old batteries.

Various substitutes for lead-antimony alloys have been proposed. Many of these are patented. They include alloys of lead with copper, silver, cadmium, calcium, mercury, tin, bismuth, tellurium, and nickel and with some of the alkali and alkaline earth metals. Some of these are binary alloys, but others contain three or four constituents.

Bismuth, because of its position in the periodic table of the elements, appeared promising, but reports from several laboratories have shown that lead-bismuth grids are short lived and bismuth, like antimony, is itself a cause of local action.

Cadmium alloys with lead, described by Vinal, Craig, and Snyder,[14] gave a much better performance than the lead-bismuth grids, but they were not the equal of the customary lead-antimony alloys. Lead-cadmium alloys corrode more rapidly and they tend to produce "trees." The addition of one or two per cent of antimony to the lead-cadmium alloys improved their resistance to corrosion and reduced the tendency to treeing. Local action at the negative plates of batteries containing these alloys was reduced to a very small amount. Cadmium improves the mechanical properties of lead and is said to decrease the brittleness of alloys containing alkali or alkaline earth metals.

Silver, which has been found to reduce corrosion of lead anodes in certain electrolytic processes has been tried also in grid metal. Fractional percentages were used, but silver is not as effective in hardening lead as some other metals. An additional constituent seems to be necessary.

Tellurium in amounts of 0.05 to 0.10 per cent is said to produce fine-grained alloys of lead. The tellurium increases the tensile strength of lead and its resistance to corrosion. Lead-tellurium alloys have been used to a limited extent for both grids and Planté plates. It has been used also in combination with antimony.

Alloys of lead with calcium, described by Haring and Thomas,[15] have been the subject of many experiments. For grids, the percentage of calcium should not exceed 0.10 per cent. Lead-calcium alloys are available commercially, containing about 5 per cent calcium. These must be "diluted" for battery use. This can be done by heating lead under charcoal to 540° to 600° C. (1004° to 1112° F.) and adding a measured portion of the 5 per cent alloy which melts readily in lead at this temperature. As some of the calcium tends to burn out, it is preferable to make the dilution in two steps, 5 to 1 and 1 to 0.1 per cent. The alloy resulting from the first step can then be analyzed for calcium content before determining the amount required to make the final

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[14] *J. Research*, 10, p. 795, Bureau of Standards, 1933.

[15] *Trans. Electrochem. Soc.*, 68, p. 293, 1935.

alloy, which is prepared at a temperature not exceeding 540° C. (1004° F.). Excessive stirring of the molten metal should be avoided to reduce drossing. When casting thin grids ($\frac{3}{32}$ inch or less) the 0.10 per cent alloy is heated to 480° to 500° C. (896° to 932° F.), but for thicker grids the casting temperature may be 25° C. (45° F.) less. Several days after the grids are cast they should be given a heat treatment at 100° C. (212° F.) for 15 to 18 hours. The maximum tensile strength of the alloy is then about 8100 pounds per square inch. Calcium grids have been used more successfully in batteries limited to floating service than in those which are cycled. Excess charging, particularly at high rates is believed to be more destructive to lead-calcium grids than to the ordinary lead-antimony grids.

The search for an alloy to replace lead-antimony involves (1) metallurgical problems—availability of materials, structure and stability of the alloy, ease of casting; (2) mechanical problems—tensile strength, hardness, elongation, expansivity, and surface conditions which determine the adhesion of the active material to the grid structure; (3) electrochemical problems—potential relations of the alloying material to lead, the overvoltage for hydrogen discharge on negative plates and the resistance to corrosion of positives under conditions which are peculiar to the battery itself; (4) electrical problems—resistivity of the alloy, relation of charge to discharge voltage as it affects cost of operation or redesign of connected apparatus, high charging voltage which in some cases may amount to about 3 volts per cell in cycle service, gases liberated during charge (arsenic, for example, would not be permissible because of arsine), and finally the service life of the plates.

b. Pasting the Plates

The pasting of the plates is considered the most secret part of all the manufacturing process. Although a number of patents have been issued for formulas to be used in compounding the paste, comparatively few of the more valuable methods are available even in the patent literature. The formula for mixing the paste must be adapted to the physical and chemical properties of the lead oxides which are used and, since these vary widely, there is little value in a mere recital of formulas. The paste, having the consistency of mortar, is applied to the grids which have been described in the preceding paragraphs, and it is subsequently converted electrochemically into the active materials of the finished plates. Pastes have been made from the various oxides of lead, and also from finely divided lead and lead sulphate, but the oxides are the most used.

Oxides of Lead. Lead combines with oxygen to form a number of different oxides, the chief of which are: lead oxide, PbO, commonly called litharge, which is yellow; lead sesquioxide, Pb_2O_3, which is reddish-yellow; minium, Pb_3O_4, which is red; and lead peroxide, PbO_2, which is dark brown and sometimes almost black. The existence of a suboxide, Pb_2O, has been a matter of controversy. This material, whether a true oxide or not is gray or black. The paste could be prepared from any of these oxides, but litharge and red lead have been preferred. Litharge has the valuable property of forming a cement when moistened with any one of a wide variety of liquids which may be used in preparing the paste. Lead peroxide, although forming the active material of the finished positive plate, is not used in preparing the paste for this plate, because it is not ordinarily available and it is difficult to prepare chemically. An even more important reason is that the coherence of the lead peroxide is poor, so that any paste prepared with it rapidly disintegrates after drying. The cementing action of red lead is not as good as that of litharge in an acid paste, but battery red lead contains a liberal percentage of litharge and in some cases litharge is added to it in preparing the paste.

Battery manufacturers usually specify the grade of oxide that they believe to be best suited to produce the type of plate desired according to some particular manufacturing process. The oxide manufacturers have therefore been required to furnish a wide variety of grades of lead oxides. Several types of furnaces are used in producing the oxides and variations in the physical and chemical properties are produced by temperature conditions and methods of grinding as well as by the raw materials which are employed. Oxide manufacturers have marketed blended oxides under a variety of trade names. These are ready for use in accordance with directions for making pastes having properties adapted to particular service requirements. The oxides fall into four general classes, but in each of these there is considerable diversity of specific properties.

(*a*) *Reverberatory Furnace Oxides.* These are made in brick-lined furnaces fired by coal or oil. Air passes over the molten lead oxidizing it in about 24 hours to form massicot, which has the same chemical composition as litharge. This material is then ground in one of several types of mill. The product is usually called litharge, however, rather than massicot. Red lead is produced by a further oxidation of litharge which is reheated to just below dull redness in the air for a period of about 48 hours. It is customary to terminate the second oxidation when the required percentage of red lead has been obtained. These oxides have a comparatively high apparent density. They may not be as reactive with sulphuric acid as the pot oxides mentioned below, but they are commonly used and are well suited to produce batteries of satisfactory capacity and long life.

(*b*) *Pot Oxides.* These oxides are made by a continuous process of oxidation for which the heat is supplied by the reaction itself after being started. The fully oxidized litharge made by this process is called calcined pot litharge, but uncalcined pot litharge containing some unoxidized lead is also produced. Pot oxides are highly reactive with sulphuric acid. These oxides produce batteries of high capacity and a satisfactory life.

(*c*) *Cupel Oxides.* Furnaces for the preparation of these oxides are operated at a higher temperature than the reverberatory furnaces used to produce massicot. The lead oxide melts as it forms, but when cooled the mass breaks up into small flat plates or flakes. These are ground to the desired degree of fineness. They are useful in producing batteries of moderate capacity for long life.

(*d*) *Fume Oxides.* These are the lightest weight oxides. The plates made from these oxides have high capacity, but short life if excessive amounts are used.

Impurities. A high state of purity of the oxides used in the manufacture of storage batteries is required. The limiting percentages of impurities for both litharge and the red lead are about the same. A good grade of the oxides for storage-battery purposes would have about the following amounts of impurities:

	Per Cent
Silica	0.05
Calcium	0.05
Iron	0.02
Copper	0.01
Bismuth	0.05
Silver	0.001
Zinc	Trace
Chlorine	None
Nitrates	None
Arsenic	None

The methods for determining the impurities are described by Schaeffer, White, and Calbeck.[16] Moisture is determined by drying a sample of the material at 105° C. Red lead ranges from 65 to 94 per cent Pb_3O_4, the remaining percentage being chiefly litharge. For storage-battery purposes, the red lead is confined to the range between 65 and 80 per cent, but in any case it is desirable that the composition

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[16] *Chemical Analysis of Lead and Its Compounds*, 3rd ed., pp. 77 and 98.

of the material should be constant to within about 4 per cent, because the methods of preparing and applying the paste depend very largely on the physical and chemical properties of the oxides.

The physical properties are fully as important as the chemical properties in the preparation of the paste. The physical properties to be noted are:

(*a*) *Color.* Litharge may vary from a yellow or yellowish green to a color almost as red as that of the red lead itself. The color is dependent on the method of preparation and grinding. Litharge which is cooled rapidly after the lead is oxidized is yellow, and that which is cooled slowly is reddish. A greenish oxide contains some unoxidized lead.

(*b*) *Relation between Fine and Coarse Particles.* A proper balance of the oxide particles of various sizes is a matter of considerable importance in determining the life and capacity of the finished plates. Generally speaking the oxides used for batteries are coarser than those used for paints, but they are so fine, nevertheless, that the problem of classifying them according to size of particles is a difficult one. The Thompson classifier[17] is one of the well-known devices for determining the percentages of the fractions of varying degrees of fineness. The oxide to be analyzed is suspended in oil which flows through a succession of standardized cones, depositing particles within certain limits of size in each. Air classifiers have been used also. The obvious advantages of these are somewhat offset, however, by the difficulties with dust and electrostatic effects. Sedimentation methods are commonly used now. Fractions of fine and coarse particles obtained in the dry state from a sample of oxide have been found to differ in chemical and physical properties. The coarse particles of red lead contain less true red lead and are less reactive to sulphuric acid. They are much heavier in proportion to the bulk than the finer fractions.

(*c*) *The Apparent Density.* This is usually measured by the Scott volumeter, and the experiment consists in determining the weight in grams of one cubic inch of the oxide as it is sifted into a small box at the bottom of the apparatus. This anomalous unit of grams per cubic inch seems well established in the industry. The values range from 10 to 30 grams per cubic inch as the apparent density of the red lead, and from 12 to 45 grams per cubic inch for litharge. Storage-battery manufacturers endeavor to obtain material which does not differ by more than 5 grams from their standard. This measurement gives an indication of the uniformity of the product, but does not give

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[17] *Proc. A.S.T.M.*, 10, p. 601, 1910.

any indication of the true density or the relative percentage of fine and coarse particles. The limit of accuracy of this measurement is about one gram per cubic inch.

(*d*) *Acid Absorption.* This is an arbitrary test following in a general way the factory procedure for making the paste. Comparable results can be obtained, therefore, only by a strict adherence to some specified directions as to weight of sample, amount and concentration of acid, temperature and time of contact of the oxide and acid. The following method is recommended:

Weigh 50 grams of the sample into a 500-cc. glass-stoppered flask. Add 100 cc. (accurately measured) of sulphuric acid, specific gravity 1.100, and shake continuously for 10 minutes; then allow to stand 5 minutes and decant the clear liquid to a dry filter. Titrate 25 cc. of the filtrate with normal KOH. Having standardized the original sulphuric acid solution against the KOH, the difference in strength of the acid before and after shaking with the oxide indicates the degree of absorption. The acid absorption number is taken as the number of milligrams of H_2SO_4 absorbed by one gram of the oxide at a specified temperature such as 25° C.

In response to factory demands for a quicker test, the periods of shaking and settling are sometimes shortened to 4.5 and 0.5 minutes respectively, but these are hardly sufficient to give consistent results.

(*e*) *True Density.* The true density may be calculated from weighings of small portions of the oxides in kerosene in calibrated flasks of 50 cc. capacity. It is, of course, necessary that the portion of oxide be weighed before the kerosene is added.

Preparation of the Paste. The pastes commonly used at the present time are prepared by mixing litharge, PbO, or red lead, Pb_3O_4, or a combination of these oxides, with a dilute solution of sulphuric acid. Many variations in the conditions of preparing and applying the paste are possible. Experience is an important factor in perfecting the proper methods and technique. Variations in the physical and chemical characteristics of the oxides, the percentage of true red lead which is present, the temperature and strength of the acid solution, the time of mixing, the treatment of the plate during and after the pasting process, and even the humidity are among the conditions which affect the finished product. By attention to such details, control may be obtained of the bulk of the paste, the time of setting, the hardness of the plate, the time required for formation, the initial capacity when put in service, and, to a limited extent, the life of the plate.

(*a*) *Reactions.* When the sulphuric acid is added to red lead, a chemical reaction occurs which results in the formation of lead sulphate and lead peroxide and water. Although this reaction may not be complete so far as the utilization of all the materials is concerned, it probably follows the equation:

$$Pb_3O_4 + 2H_2SO_4 = 2PbSO_4 + PbO_2 + 2H_2O \qquad (1)$$

The formation of the lead sulphate is an important factor in determining the bulk of the paste as well as binding the material together. Lead sulphate is also formed when the sulphuric acid and litharge are made into a paste. The following equation suggests the reaction taking place:

$$PbO + H_2SO_4 = PbSO_4 + H_2O \qquad (2)$$

It is probable that hydration of the lead oxide occurs and that the cementing action is similar to that of plaster of paris.

Pastes are sometimes made by mixing the oxides with water only. Since the coherence of such a paste, when made from the red lead, is poor after the plate is dry, plates made in this way are commonly dipped in sulphuric acid to form a limited amount of lead sulphate on the surface.

Pastes are also made by mixing the oxides with solutions of magnesium or ammonium sulphate. Such solutions may have a specific gravity of approximately 1.2. It should be noted that these materials, before being made into solution, consist of clear and colorless crystals having a white appearance. The magnesium sulphate is $MgSO_4 \cdot 7H_2O$ and the ammonium sulphate $(NH_4)_2SO_4$. Commercial grades of these materials sometimes contain large amounts of impurities and may be gray. Such material is not suitable for use in a storage battery. Ammonium sulphate does not react with true red lead, but it does react with litharge according to the following equation:

$$PbO + (NH_4)_2SO_4 + H_2O = PbSO_4 + 2NH_4OH \qquad (3)$$

Battery red lead must contain about 25 per cent of litharge in order that this reaction may occur. A considerable amount of ammonia gas, NH_3, is liberated, and the odor can easily be recognized in the pasting room. No lead peroxide is formed during this reaction. The plates retain a pink color instead of turning brown after pasting. In addition to preparing the paste with solutions of these sulphates, the manufacturers sometimes mix them with the oxides in the dry form and then the paste is generally prepared with sulphuric acid.

(*b*) *Relative Amounts of Litharge and Red Lead.* Negative plates are made from litharge or a combination of litharge with a small amount of red lead. The red lead affects the capacity and time required for the formation of the plates. Contrary to theoretical expectations negative plates containing a small percentage of red lead can be formed more quickly than those made from pure litharge. This use of limited quantities of red lead in the negatives makes it possible to equalize the time of formation of the positive and negative plates, but too much red lead should not be used in the negative plates. The range is perhaps from 0 to about 25 per cent of red lead in the dry mixture.

Positive plates usually are made with more red lead than the negatives. Such plates can be formed very quickly. Battery red lead contains a liberal percentage of litharge and it has been common practice to make the positive plates from such material, containing 60 to 80 per cent of red lead. The solutions employed in preparing the paste are dilute sulphuric acid or ammonium sulphate. Low red lead mixtures for positive plates have come into use, containing 15 to 40 per cent of true red lead. Dilute sulphuric acid is used in preparing the pastes of low red lead content. Such pastes have good bulking qualities and produce batteries with a relatively high initial capacity.

(*c*) *Expanders.* These are added in small amounts to the paste for negative plates. They include lamp black, barium sulphate (commonly called *blanc fixe*), powdered charcoal, wood flour, and colloidal extracts of organic matter, usually wood extracts. The function of the expander is to prevent contraction and solidification of the spongy lead of the finished negative plate. If this occurs, the capacity of the plate is greatly reduced and the battery may become worthless. Microscopic observations by Scarpa[18] have shown that barium sulphate, which is insoluble in the electrolyte prevents the "soldering" together of the particles of which the sponge lead is composed. The effect of colloidal solutions in modifying the crystal structure of electrodeposited metals is well known. Photographic records of many experiments showing the effect of colloidal matter on silver deposited in crystalline form may be found in a paper by Rosa, Vinal, and McDaniel.[19] Expanders are used singly or in combination in the proportion of $\frac{1}{8}$ to $\frac{3}{8}$ per cent of the mix.

(*d*) *Mixing the Ingredients.* The dry materials, having been carefully weighed and placed in a mixing machine, are made into a paste with a solution which is usually dilute sulphuric acid. If this has a specific gravity of 1.100 or less, the solution can be added directly to

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[18] *Elettrotecnica*, 5, p. 371, 1918.

[19] *Bulletin*, Bureau of Standards, 9, p. 211, 1913; see also paper presented by Willihnganz of the National Lead Company at National Battery Manufacturers Assoc., May, 1940.

the dry mixture of the oxides and expanders, provided that these have been thoroughly blended. The more usual procedure, however, is to add a considerable portion of water to the oxides before adding a somewhat stronger solution of the acid (sp. gr. 1.200 to 1.400). This has the advantage of eliminating dust and prevents the formation of a gritty paste which would otherwise result from using a solution of such strength. The acid must be added slowly while mixing is continued. A final portion of water can then be added as required to bring the paste to the proper consistency.

The amount of H_2SO_4 in solution, regardless of its exact concentration, determines the amount of basic lead sulphate formed and consequently the expansion or bulking of the paste. If not carried too far, the capacity of the finished plates will increase as the expansion is increased. Too great expansion, however, is not desirable as the plates will fail prematurely by shedding their active material. Too little expansion, on the other hand, results in hard, dense plates of low capacity. These are likely to fail by buckling. For factory control, the expansion of the paste may be measured by determining the weight of a specified volume of the paste, as was done in determining the apparent density of the dry oxides.

When the acid solution is added to the oxides, the paste will become hot as a result of chemical reactions between these constituents. Mixing should continue until the maximum temperature has been passed in order to avoid premature solidification of the paste. Mixing must in any case be continued until the paste has become uniform and of the proper consistency to be applied to the grids.

Consistency of the paste is controlled largely by the amount of water. The finished paste should be reasonably stiff when it is applied to the grids. Too soft a paste produces soft plates and is liable to form slick surfaces which usually blister when the plates are formed.

The consistency of the paste can be measured either by a penetrometer, consisting of an inverted cone which is pressed into the paste by a specified pressure, or by the deformation of a cylindrical portion of the paste which is dropped from a specified height onto a glass plate. The change of axial length of the sample is measured. For soft pastes this will be more than for the harder pastes. To avoid uncertainty which may arise if the upper surface of the specimen of paste is dimpled or not horizontal after it has been dropped, a thin metal disk is placed on top of the specimen and this, falling with the paste, provides a definite surface to which measurement along the vertical axis can be made. Consistency is usually expressed by some arbitrary scale of numbers, which being properly interpreted, indicates whether the desired uniformity of the paste is being attained. Otherwise these numbers have little physical significance.

In order to obtain thorough mixing within five to fifteen minutes, mechanical mixers are commonly employed. These must not contaminate the paste with impurities which would be injurious to the battery. A mixer which can be cleaned easily is desirable.

(*e*) *Applying the Paste.* The paste is applied to the grids by hand labor in many of the smaller manufacturing plants and by machine pasting equipment in most of the larger plants. When the work is done by hand, the paste is spread upon the grids with a wooden spatula or a smoothing trowel. Before this is done, however, a group of grids is laid flat upon the table with a sheet of paper interposed between the table and each grid. Paper is used also to cover the plate after pasting. The paper keeps the paste from adhering to the table and also takes up some of the moisture. The papers are used only once and hence a cheap grade is used, but it is essential that the paper should have the proper absorbing quality. Sufficient pressure must be applied to force the paste into intimate contact with the cross bars of the grid. The grids must be free from grease and dirt before pasting is begun. Sometimes they are washed and dipped in a dilute solution of sulphuric acid before being pasted.

Machines of several types have been developed for pasting the plates. When operating the machines, the grids pass under a hopper from which approximately the right amount of paste is received. This is pressed into the grids as they pass along and the excess of paste is removed. Sometimes the plates are partially dried also before leaving the machine. The papers used in the hand-pasting process are not required in machine pasting.

The time that elapses between mixing the paste, particularly if the ammonium sulphate process is used, and the completion of the pasting process may have an effect on the finished plates.

(*f*) *Treatment after Pasting.* The manufacturer has the choice of completely drying the plates before formation or transferring them to pickling baths or forming tanks while they are still in the wet condition. Freshly pasted plates require rapid handling, because partial drying is likely to lead to difficulties when the plates are formed.

Plates which are to be dried are often dipped for a few seconds in a solution of sulphuric acid (1.100 to 1.125 sp. gr.). Before this is done, however, the papers, if used, should be stripped from them. After being dipped, the plates are drained, racked, and allowed to dry. Dipping increases slightly the amount of sulphation and lessens the tendency for the paste to crack or check. Drying at ordinary temperatures and humidities requires 2 to 4 days, but at 100° to 150° F. (38° to 65° C.) they may be dried in 12 to 15 hours. Ovens providing controlled humidity at elevated temperatures can be used to advantage. The humidity is initially high, usually at the saturation point, but this is reduced gradually and the temperature is raised as drying proceeds. Marshall[20] found that positive plates heated under pressure in saturated water vapor above 100° C. (212° F.) had longer service life than plates prepared by other methods. Thorough drying is necessary to avoid "popping" (loosening of the pellets) when the plates are formed. Abrupt changes in temperature and pressure during the drying process should be avoided. In no case should the plates be subjected to freezing temperatures.

Plates which are to be treated by the "wet" process must be protected by damp cloths or equivalent means after being pasted until they are transferred to the pickling or forming tanks. Pickling which differs from dipping, mainly in the longer time that the plates are immersed, is usually done in special tanks. The time required varies from a few hours to a day or more, depending on the strength of the solution. The specific gravity of the pickling solution falls rapidly at the beginning, but the rate decreases as time goes on. This decrease in specific gravity serves as an indication of the amount of lead sulphate formed in the plate. Knowing the initial strength and volume of the solution, reasonably accurate calculations can be made, if correction is made for dilution of the acid by moisture in the plates and for evaporation. The time is reduced if the acid is relatively strong, but more lead sulphate is formed when weaker solutions are used, provided that sufficient time is allowed for the acid to penetrate the plates. Table IV gives the results of experiments on small plates pickled in solutions of several strengths. A specific gravity of 1.250 is obviously too high and 1.050 too low. The time for pickling varies with the thickness of the plates. If the pickling process is omitted, the plates may go from the pasting room to the forming tanks.

(*g*) *Other Materials Used in Pasting Plates.* A lead compound consisting of 20 per cent lead oxide and 80 per cent lead sulphate chemically combined, known as "superite," has been produced for use with the ordinary lead oxides in preparing the paste with the object of increasing the bulk of the paste. From 5 to 10 per cent of this material may be mixed with the lead oxides and subsequently formed into the active material of the plates. Precipitated lead sulphate is also used similarly.

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[20] *Trans. Electrochem. Soc.*, 69, p. 233, 1936.

TABLE IV

WEIGHT OF ACID CONSUMED DURING PICKLING PROCESS

[Weight is given in grams for sp. gr. 1.250 to 1.050, 27° C. (80° F.)]

Time, in hours	1.250 sp. gr.	1.200 sp. gr.	1.150 sp. gr.	1.100 sp. gr.	1.050 sp. gr.
2	1 99	2.50	2 27	1.57	0 96
5	2.39	2.82	3.27	2.59	1 50
21	3.12	3.46	4.28	4.83	4 50
45	3 23	3.48	4.92	5 22	5 31

Uncalcined oxides, containing a considerable portion of lead, and pulverized lead, sometimes referred to as the black oxide, have found use in the manufacture of plates. These materials are highly reactive with sulphuric acid. When a drop of dilute acid is allowed to fall on a thin layer of the latter spread upon a glass plate, lead sulphate is formed, surrounded by a yellow ring which develops in a few minutes. This ring is evidently the result of the solution being deprived of the acid which combines with the lead, and as the remaining water spreads out in the material the latter is oxidized to litharge in the presence of the air. The width and diameter of the ring are dependent on the strength of the acid. Water alone produces a solid yellow spot. This material oxidizes in the air, if left exposed, and becomes yellow.

Hardeners and binders are occasionally added in the preparation of the paste, to increase the coherence and hardness of the plate. A great variety of substances has been used for this purpose. Glycerin and carbolic acid are probably the best known of these materials for making hard plates, but the present practice is to control the plate hardness by selecting the proper combinations of oxides and solutions rather than to resort to the use of hardeners. Glycerin and litharge when mixed together make a cement which is used for many purposes beside the preparation of storage-battery plates.

Another class of materials, called porosity agents, is sometimes employed in the preparation of the paste. These are substances which can be dissolved out of the paste when the setting process is complete. They increase the bulk of the paste. Magnesium sulphate is the best known of these, but other sulphates and even sugar have been used. A magnesium sulphate paste has a good cementing action because of the crystalline structure formed as the paste dries, but a reaction such as that given above for ammonium sulphate seems to be lacking.

The use of inert fillers, amounting in some cases to 10 or 20 per cent, as a substitute for the lead oxides appears to serve no useful purpose except to cheapen the plates. The capacity and life of the plates are likely to be considerably less when such materials are used.

(*h*) *Other Kinds of Paste.* In addition to the pastes which are commonly used as described above, there are a number of others which deserve brief notice. One of these is the so-called lead sulphate paste, which is made from lead sulphate mixed with ammonium hydroxide, NH_4OH. This paste is made into a thick dough and hardens when dried. The plate is formed in a bath of ammonium sulphate containing a small percentage of free ammonia. In this bath the sulphate can be reduced to the form of lead sponge, and positive plates are prepared by oxidation from the negatives. Glycerin paste consists of approximately 75 parts of litharge mixed with 25 parts of glycerin. This paste forms an unusually hard plate. Lead chloride paste is usually cast in the form required with 10 per cent of zinc chloride. Lead carbonate paste is made from basic or normal lead carbonate and lead oxide, and formed into a paste in an alkaline solution. Negative plates are prepared from this paste by reduction, and the positive plates are prepared by oxidizing the negative plates. Alkali pastes are prepared from litharge mixed with a solution of caustic potash having a specific gravity of about 1.10.

Character of the Plate as Affected by the Paste. Soft and porous plates are ordinarily made from soft paste, and hard plates result from a stiff paste. Heim[21] prepared four pastes from the same active materials, using in each case the same amount of red lead but varying the amount of acid, of which the specific gravity was 1.180. He also added a small amount of glycerin in each case. The consistency of the four pastes varied from a stiff paste, such as is ordinarily used, to a thin fluid. After the plates were dried and formed, storage cells were prepared and the capacity of the four cells, which were designated as A, B, C, and D, was determined. Since the volume of the active material was the same in each case, a comparison of the apparent density of the active material in the different positive plates of these cells could be made. It was found that the weight of the active mass of the positive plates of cell D was less than that for cell A, although the capacity was 21 per cent greater. The results indicate that the porosity of plates made from the thin paste was greater than for the others.

The measurement of plate hardness has been accomplished by modifying the familiar Brinell test. In preparing the plates for a hardness

[21] *Elektrotech. Zeit.*, 36, p. 281, 1915.

test they must be fully charged, since the presence of even a small amount of lead sulphate more than that ordinarily present in the charged plate will considerably increase the apparent hardness of the plate. The apparatus used for making the hardness test consists of a bed plate of steel on which the wet plate to be tested can be laid. A $\frac{3}{8}$-inch steel ball is pressed into the surface of the plate by a force of about 7 kilograms. The hardness numeral corresponding to the so-called Brinell test is obtained from the following formula:

$$\text{Hardness Numeral} = \frac{P}{\pi t D}$$

where P = force applied to the ball, D = the diameter of the ball, and t = the depth of the indentation. Since t cannot be measured directly, if we let d = the diameter of the indentation, t can be computed from the formula

$$t = \tfrac{1}{2}D - \tfrac{1}{2}\sqrt{D^2 - d^2}$$

The values for the hardness numerals obtained on positive plates found in familiar makes of starting and lighting storage batteries are from 0.45 to 6.5. The plates may be classified according to the following schedule:

Soft plates	0.4 to 0.6
Medium plates	0.6 to 1.25
Hard plates	1.25 to 3.50
Very hard plates	3.50 to 6.5

The faults which are most commonly observed as a result of imperfections in the pasting process are: (1) Imperfect contact between the grid and paste. This results in the sulphation of the active material at the surface of the grid, and since the sulphate is a non-conductor of the electric current, the active material becomes insulated and cannot be completely charged. (2) Cracking of the active material, which is generally due to the shrinkage that occurs while the plates are drying. (3) Loosening of the material from the grid. This defect is usually attributed to an unsatisfactory formula, or incorrect treatment subsequent to the pasting process. (4) Blisters and scaling of the active material, which are caused by the wet paste drying too rapidly on the surface. (5) Impurities contained in the oxides or other ingredients of the paste. These are frequently liberated in the electrolyte of the finished battery. An impurity such as copper may then be desposited upon the negative plate and result in local action. Iron, if present, passes into solution in the electrolyte and results in a slow discharge of the battery when standing on open circuit. (6) Inequalities in the amount of active material in the finished grids. This defect is due to flaws in the pasting process. The result of these inequalities is buckling of the plates because of the unequal expansion and contraction of the active material during the normal process of charging and discharging the battery. This, however, is only one of many causes of buckling of the plates.

c. Formation of Pasted Plates

The plates are electrolytically oxidized and reduced in ordinary dilute sulphuric acid or a sulphate solution. The plates which are to become the positives are made the anode in the forming tank and the plates for the negatives are made the cathode. The word "formation" applies primarily to Planté's process for increasing the capacity of the plates in his cell. This is a process quite different from that used for developing the pasted plate batteries, but the word "formation" is now in common parlance applied to the pasted plates as well. Formation, as applied to the Planté plates, means the creation of a layer of sponge lead on the surface of the negative plates and of lead peroxide on the positives to constitute the active materials of the cell. These active materials are formed from the lead of the plate itself by a series of charges and discharges. Formation of pasted plates, on the other hand, means the oxidation or reduction of the lead oxides or other materials which have been applied to the grids.

Positive plates, alternating with negatives, are mounted in tanks or other containers which provide for proper spacing of the plates and insulation between those of opposite polarity. The tanks may be of vitreous material, hard rubber, or wood with lead lining. Some manufacturers, however, prefer to assemble the plates in groups or complete elements before formation, which is then done in tanks or in the containers that are to serve for the finished battery. In any event it is presumed that the forming time for positives and negatives is about the same. This can be regulated by the composition of the paste and to some extent by the strength of the forming acid. Positive plates, more than negative plates are subject to harmful effects of overformation. It is preferable, therefore, that the negatives should finish first. Some variations in procedure of forming plates are indicated below, but experience in forming plates, prepared in a particular way, is the safest guide.

The strength and amount of acid used will depend upon the previous treatment of the plates. Usually it is in the range 1.050 to 1.150 sp. gr. Increasing the strength of the acid increases the time required for forming positive plates. Solutions having a specific gravity of 1.200

and above are regarded as too strong and should be avoided, except as some particular process may have been successfully developed to use such solutions. Dry plates and those which are still wet from the pasting process will sulphate when they are immersed in the solution and the specific gravity will decrease rapidly. The wet plates will cause further dilution of the solution, because they contain a considerable amount of water. Such plates are often allowed to pickle, partially at least in the forming solution. Plates which have been dried must be allowed to remain in the solution long enough for the acid to penetrate the pores of the plate before beginning the forming charge. The pores at this time are not as open as they will be later. When a large group of tanks is filled with plates, those plates in the tanks which are filled first are necessarily immersed longer than those in the tanks which are filled last. Some manufacturers, therefore, make a practice of allowing an hour or more to elapse after the last tank is filled as a "time of set" before starting the charging current.

Plates which have been pickled, on the other hand, have reacted with the sulphuric acid and they contain a relatively large amount of sulphate. They will, therefore, have less effect on the forming solution initially, but in the later stages of the forming process they will greatly increase the specific gravity, because of lead sulphate derived from the plates. For this reason the initial specific gravity of forming solutions used with these plates is usually low. The charging current can be started promptly after the plates are immersed.

Formation undoubtedly starts in the region where the poorly conducting paste is in contact with the better conducting grid bars. For this reason, formed material, particularly of pickled plates, is observed around the edges of the pellets while the center portion still has a hard white core. In such cases it may be necessary to interrupt the charge and to make a discharge before resuming formation. This helps to counteract the tendency to overformation and softening of the positive active material, but other corrective measures include decreasing the strength of the forming solution and decreasing the current density.

Completion of formation is indicated by (1) the color of the active materials, that is, the plates have "cleared" and are uniform in color; (2) plates gassing normally; (3) cadmium readings are constant and of normal values. The exact values of the cadmium readings will depend on various conditions, but they are usually in the range 2.30 to 2.45 volts for the positive plates and −0.05 to −0.20 volt for the negative plates. The cadmium readings on positives may reach constant values several hours prior to complete clearing, but this is usually not true of the negatives.

The proper charging current will depend on the thickness and type of plates, and on the temperature. For the more common sizes of automotive plates the current is usually specified as 0.75 to 1.50 amperes per positive plate. At one ampere the forming time is about 45 to 50 hours. Foaming and excessive gassing must be avoided. When either of these occurs the current should be reduced. The current is used more effectively at lower rates and these are desirable for thin plates. For plates in general a current density of 0.2 to 0.5 ampere per dm^2 (2 to 5 amperes per square foot) is reasonable. The area is reckoned as the apparent surface of both sides of the plate.

Some modifications must be made when the plates are formed in small tanks. These relate chiefly to the strength of the forming solution in relation to the available volume of solution. This is even more important when the plates are formed in containers which are to serve for the finished cells. In this case the elements are assembled with moist separators which carry enough water to dilute the forming solution appreciably. Assembled elements are usually allowed to stand in the forming solution over night before beginning the charge. After formation is completed, it is advisable to pour out the electrolyte and replace it with acid of a strength which will finish at a specific gravity of 1.280 to 1.300 when the battery is fully charged. The initial charge, distinguished from the forming charge, is usually done at a current rate of 0.75 to 1.00 ampere per positive plate of the automotive size.

Groups of plates which have been formed in tanks or slotted rubber cases may be drained at the end of the forming process. Individual plates are usually rinsed and dried. Negative plates will become hot during the drying, because of oxidation of the sponge lead in the air. They may be cooled somewhat by forced circulation of air. Such plates must be regarded as being in a discharged state, although they contain little lead sulphate. When they are assembled into batteries a prolonged initial charge is necessary.

In Europe the forming solutions are frequently made from neutral sulphates. The reasons for using such solutions will appear in later sections.

The following example indicates the general changes which take place in the composition of the material of the negative plate during the forming process.

Initial Composition		Final Composition
PbO	90 per cent	1 per cent or less
$PbSO_4$	10 per cent	1 per cent
Pb	....	98 per cent

Somewhat similar changes occur during the formation of the positive plate. A positive plate pasted with the red lead may be considered to contain a mixture of lead oxide and lead peroxide, since two parts of the lead oxide and one part of lead peroxide are equivalent to one part of the red lead. Red lead is converted, partially at least, during the pasting process and during its immersion in the sulphuric acid of the forming tank, into lead peroxide and lead sulphate. The following example indicates the changes in composition which occur in the case of a positive plate during the forming process.

	Initial Composition	Final Composition
PbO_2	20 per cent	90 per cent
PbO	55 per cent	7 per cent
$PbSO_4$	25 per cent	3 per cent or less

The lead sulphate which remains in the final composition of the plate is of great importance as a binder of the active material. This small percentage of sulphate remaining is not easily removed by excess charging.

Important changes in volume of the active material occur during the forming process. The lead sulphate is considerably less dense than the peroxide or sponge lead of the finished plates. The litharge used in pasting the negative plates is less dense than the lead of the formed material. During the forming process, therefore, the pores of the plate open. This permits the electrolyte to come in contact with the material in the inner recesses of the plate. The porosity which the plate acquires during the forming process is of importance not only in the formation but also in the subsequent operation of the finished cell. In the following table are given the densities for the various materials found in the paste and in the finished plates.

TABLE V

Densities of Materials

Material	Formula	Density
Lead	Pb	11.3
Litharge	PbO	9.5
Minium (red lead)	Pb_3O_4	9.1
Lead Peroxide	PbO_2	9.0
Lead Sulphate	$PbSO_4$	6.3
Lead Chloride	$PbCl_2$	5.8

It is of interest to consider the oxidation and reduction processes which take place during formation of the positive and negative plates, and to calculate the number of ampere-hours per kilogram of material which are required in accordance with Faraday's law. When litharge, PbO, is oxidized to lead peroxide, one atom of oxygen is added to the PbO molecule. The molecular weight of PbO is 223.2. The amount of oxygen to be added per kilogram of material is therefore

$$1000 \times \frac{16}{223.2} = 71.7 \text{ grams}$$

The equivalent of oxygen in ampere-hours per gram is 3.350. This value may be calculated from the following formula: 96,500 coulombs, representing the number of coulombs required for the liberation of 1 gram-equivalent of a substance, multiplied by 2, the valence, divided by 16, the atomic weight of oxygen, and divided by 3600, the number of seconds in one hour. The product of the equivalent of oxygen and the number of grams, 3.350×71.7, equals 240.2 ampere-hours per kilogram. Since the reduction of litharge to lead involves the taking away of one atom of oxygen from the molecule PbO, exactly the same number of ampere-hours per kilogram is required for the reduction of one kilogram of material. In the following table is shown the number of ampere-hours per kilogram of material required for the oxidation to the peroxide state or the reduction to sponge lead of the various materials which are used for pasting storage-battery plates. These are the minimum figures and are exclusive of the energy which is wasted by gassing during the forming process. In calculating the values for minium, it is assumed that Pb_3O_4 represents the composition of the material.

TABLE VI

AMPERE-HOURS PER KILOGRAM REQUIRED FOR THE OXIDATION AND REDUCTION OF OXIDES, CHLORIDES, AND SULPHATES OF LEAD

Material	Reduction to Lead, Ampere-hours	Oxidation to PbO_2, Ampere-hours
PbO	240	240
Pb_3O_4	313	156
$PbSO_4$	176	176
$PbCl_2$	193	193
Pb	...	514

Since the material of the plate at the beginning of the formation process consists of one or more of the oxides and a certain amount of lead sulphate, the following example is given to illustrate the use of the table in computing the theoretical number of ampere-hours which are required for the formation of a negative plate. In this example we shall assume that the plate, exclusive of the grid, weighs 300 grams and contains 20 per cent of lead sulphate and 80 per cent of lead oxide, PbO. From the table we compute at once that the number of ampere-hours required for the lead sulphate is $\frac{0.20 \times 300}{1000} \times 176 = 10.6$. Similarly, the number of ampere-hours required for the reduction of the lead oxide, PbO, is $\frac{0.8 \times 300}{1000} \times 240 = 57.6$. The total number of ampere-hours required, therefore, for both materials is 68.2. This example may be solved by another method if the electrochemical equivalent of lead is known. By this method the amount of lead in each of the constituents of the paste is calculated.

$$\begin{aligned} 0.20 \times 300 &= 60 \text{ grams of } PbSO_4 = 41 \text{ grams of Pb} \\ 0.80 \times 300 &= 240 \text{ grams of } PbO \;\;\;= \underline{223} \text{ grams of Pb} \\ &\qquad\qquad \text{Total weight} = 264 \text{ grams of lead} \end{aligned}$$

The electrochemical equivalent of lead is 3.865 grams per ampere-hour. The number of ampere-hours is therefore 264 divided by 3.865 = 68.2 ampere-hours, which is the same result as was obtained in working this example by the former method.

The efficiency of the formation process depends largely on the amount of gas which is evolved. Ordinarily the efficiency of the forming process will not exceed 50 per cent. It is necessary, therefore, to double the answer obtained in the example, in order to obtain the number of ampere-hours required in ordinary practice. If the formation process is continued beyond the ordinary stopping point, the efficiency will be considerably lower. The elimination of the last traces of sulphate in the plates is difficult and not desirable, since this small amount of sulphate is in effect a cement to hold the active material of the plates together.

The potential relations of the plates during the forming process are of importance, since the potential which must be applied to them multiplied by the number of ampere-hours determines the energy, and therefore the expense involved in the process. The potential of the negative plates during the forming process is measured against the positive plates or the dummies, which are essentially positive. The potential difference between the negative plates and the dummies increases toward the end of the forming process in accordance with changes in the ionic concentration. The lead sulphate of the plates dissolves to a slight extent in the electrolyte and in dissociating forms lead ions, Pb^{++}. These ions are deposited on the negative plates during the forming process. As they deposit, more lead sulphate dissolves, and when the lead sulphate is almost exhausted near the end of the process, the lead ions become scarce and the potential difference rises to the point where hydrogen ions, H^+, are liberated. The potential of the positive plates during formation is similarly measured against the negative plates or dummies in the forming bath. This potential difference is about 2.3 volts at the beginning. This voltage decreases to slightly less than 2 volts after the forming process begins, owing to the decrease in the resistance of the material of the plates. It rises again during the latter part of the formation period to 2.45 volts or higher.

Much gas is evolved during the formation process. Gassing begins normally before the time the theoretical number of ampere-hours for the reduction or oxidation of the material in the plates is completed. The conditions which determine gassing depend on the relative number of lead ions, Pb^{++}, and hydrogen ions, H^+, in the electrolyte when forming negative plates. Since a scarcity of the lead ions raises the potential of the negative plates, which, during this process, are the cathodes, to a point where hydrogen ions are liberated, it is possible to increase the efficiency of the formation process by maintaining a plentiful supply of the lead ions or keeping the hydrogen-ion concentration low. Some of the manufacturing companies in Europe have, therefore, made use of forming baths which are solutions of neutral sulphates of aluminum and magnesium, because the hydrogen-ion concentration in these baths is much less than in the sulphuric acid solutions. Heating the electrolyte is the only possible way of increasing the concentration of the lead ions, but this loosens the active material of the plates and is not a practicable method. Similar relations with respect to the oxygen evolution hold in the forming process for the positive plates. Neutral solutions have been used in Europe in forming these also.

The formation of plates pasted with materials other than the oxides which are ordinarily used is of much less importance, but it is interesting to note that plates have been successfully formed from lead sulphate and lead chloride pastes. The plates pasted with lead sulphate are formed very much as in the case of the oxide plates. Since lead sulphate is a non-conductor of electricity, the plates have a very high resistance initially, and the formation begins at the point of contact between the grid and the paste, spreading gradually as the formation progresses.

Plates pasted with lead chloride are formed in quite a different way. This paste is soluble and cannot be peroxidized directly, since the lead chloride would go into solution and the lead be precipitated on the cathode with the liberation of chlorine at the anode. The lead chloride paste is therefore reduced in a bath of zinc chloride with a plate of zinc which forms, with the lead chloride, the elements of a primary cell. During this process the lead chloride, $PbCl_2$, is reduced to lead, and the zinc becomes zinc chloride, $ZnCl_2$. Positives are formed electrochemically.

The positive plates, after formation, may be preserved in the dry state. Negative plates, however, if dried in air will become hot, owing to the formation of oxide, and will again require a prolonged charge before they can be made ready for use.

Several processes have been developed for drying and preserving newly formed plates in the charged state. Dry-charged batteries containing plates thus treated should be capable of delivering from 50 to 75 per cent of their rated capacity on the initial discharge at any time within six months after being manufactured, if properly sealed. There is little difficulty in preserving the positive plates, but the negatives are subject to oxidation by the air and must be dried with extreme rapidity or in an inert atmosphere, such as carbon dioxide, nitrogen, or hydrogen.

Batteries in the moist condition, to which electrolyte must be added when they are made ready for service, can be stored in a partially charged condition for six months or more. The freshly formed elements for such batteries are drained to remove excess acid before being placed in the jars. The batteries are then sealed to exclude the air, but at the same time provision must be made for the escape of any gas which may be formed within the cells.

3. PLANTE PLATES

a. Manufacture of Planté Plates

The essential difference between Planté plates and pasted plates consists in the fact that the active materials of the former are derived from the body of the plate itself, whereas for the latter they are formed from oxides or other pastes which are applied to the plate mechanically. The active materials of the Planté plate are obtained by oxidizing the surface of the lead plate or reducing this material to sponge lead. There is a plate intermediate between the pasted and Planté varieties. It consists of a soft-lead grid pasted with the oxides and formed. The active material gradually falls out, but the capacity is maintained by the corrosion of the grid. In this way the plate becomes essentially a Planté plate. Planté plates serve quite a different purpose from the pasted plates. They are ordinarily much larger and heavier than the pasted plates and have a relatively smaller capacity. They are used chiefly for stationary batteries in which considerations of space and weight are of less importance than durability. The essential parts of the Planté plates are the underlying portion of lead and the developed surface which consists of a number of leaves designed to increase the surface of the plate and thereby increase the capacity. The effective surface of the Planté plates is 6 to 10 times greater than the apparent surface. The blanks, as the sheets of lead are called before the surface is developed, are prepared by casting pure lead in the form of flat ingots, which are then rolled to the required thickness. Soft lead of a very high degree of purity is required for this purpose. From the rolled sheets the blanks are cut or stamped in accordance with the size and design of the particular type of plate to be made.

A number of different methods have been used for increasing or developing the surface of these plates. One of these is the so-called plowing process. The blank plate is placed in a machine similar to the shaper used in a machine shop. The tool of the shaper is designed to produce a leaf of the proper shape and width. One leaf is produced at each stroke. Ribs to make the plate more rigid are made by jumping the tool at certain points.

A second method of developing the surface of the Planté plates is commonly known as the swaging process. The master swaging block has the design for the plate cut in its surface, the ribs to produce recesses of the finished plate being in relief on the block. The swaging block is pressed against the surface of the soft-lead plate while it rocks back and forth and the lead is pressed into the desired form.

A third process for the development of the surface of these plates is called the spinning process. The soft-lead plate or blank is held in a frame which reciprocates between revolving mandrels having a large number of steel disks which are pressed gradually into the plate on either side. The lead of the plate flows in between these steel disks, forming leaves with grooves between. The depth to which the steel disk may penetrate the surface of the plate is so regulated as to leave a thin web of supporting material in the center of the plates. Horizontal ribs are obtained in these plates by spinning the plate in sections. Vertical ribs are obtained by spacing washers which are placed between the disks.

Other plates with highly developed surfaces have been obtained by casting (Tudor plates), but this method is used more in Europe than in this country.

An important type of Planté plate is made by the so-called building-up process. Heavy grids of lead and antimony are cast with a large number of round holes into which are pressed buttons of soft lead with corrugated surfaces. These buttons, or "rosettes," are prepared from lead ribbon which is extruded by a hydraulic press. The lead ribbon is passed through a crimping machine which crimps the surface, cuts the ribbon to the desired length, and then rolls the piece into the form of a rosette or button. The buttons are pressed into the holes of the lead-antimony grid by a hydraulic press. In order to lock the buttons in place, the holes are made with a slight bevel so that, as the lead button grows during the operation of the cell, it becomes more and more tightly locked in the supporting grid. This type of plate is familiarly known as the Manchester positive.

b. Formation of Planté Plates

The formation of the Planté plates is an electrochemical process which requires considerable time and the expenditure of a large amount of electrical energy. In the original process used by Planté and generally referred to at the present time as the Planté formation, the plates were alternately charged and discharged, with occasional reversals of the direction of the charging current, until the plates had acquired sufficient capacity. The demand for a more efficient process of formation led to the use of forming agents, which were added to the sulphuric acid solution to hasten the formation by chemically attacking the lead of the plates. This is the method most used at the present time. The formation of Planté plates has also been accomplished by dipping the plates in certain solutions which have a strongly corrosive action on the lead, resulting in a layer of finely divided material which may then be reduced to sponge lead or oxidized to lead peroxide.

When two plates of lead are dipped in a solution of sulphuric acid and an electric current is passed through the cell, a very thin layer of lead peroxide is formed on the plate which is the anode, and the oxide of lead covering the surfaces of the cathode is reduced to a very thin layer of sponge lead. The evolution of oxygen gas at the anode and hydrogen at the cathode begins almost immediately. If the charging current is cut off, the lead peroxide on the surface of the anode forms a very large number of little primary cells with the underlying lead, so that a vigorous local action begins. Lead sulphate is formed on the surface of the underlying lead, and in a few minutes the plate has lost its charge completely. The sponge lead on the surface of the plate which was the cathode has practically no potential difference from the underlying lead of the plate itself, and consequently no such vigorous local action takes place on this plate. If the charging current is again renewed, a larger amount of lead oxide is formed on the anode owing to the conversion of the lead sulphate previously formed as a result of the local action on this plate. Each time this process is repeated the amount of lead peroxide increases, but in order to obtain an increase in the amount of lead sponge on the surface of the negative plates it is necessary to reverse the current from time to time so that use may be made of the process which occurs at the positive plate. The strength of the sulphuric acid solution which is used has some influence on the amount of oxygen which is fixed on the surface of the anode. Experiments were made by Gladstone and Tribe[22] to determine the amount of oxygen fixed on the surface of electrodes which were 77 square centimeters in area by the action of one ampere flowing for twenty minutes. The solutions which they used consisted of various strengths ranging from 1 part of acid to 5 parts of water down to 1 part of acid to 1000 parts of water. In the following table is given the amount of oxygen, expressed in milligrams, fixed by the action of the current for the different strengths of acid.

TABLE VII

OXYGEN FIXATION

Acid Strength	Oxygen Fixed (mg.)
(Acid to water) 1/5	127
1/10	146
1/50	151
1/100	155
1/500	125
1/1000	Lower oxides and basic sulphates formed

The common method, at the present time, for the formation of Planté plates involves the use of forming agents which attack the lead of the plate. These agents are usually the salts of some acid, such as nitric, although a number of other substances have been used, including chlorates and perchlorates, chlorides and fluorides, bichromates, permanganates, formic acid, oxalic acid, alcohol, hydroxylamine, and sulphurous acid. The forming process with these addition agents is

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[22] *Lumière électrique*, 9, p. 25, 1883.

practically confined to the positive plates, which are the anodes in the forming bath Negatives are obtained by a reversal of the positive plates and the consequent reduction of the lead peroxide to the sponge-lead state.

In general, the action of the forming agents is to retard the early formation of lead peroxide on the anode which would otherwise make a protective covering on which oxygen would be liberated. The anions depositing on the lead surface give rise to relatively soluble lead salts and increase the concentration of lead ions from which lead sulphate may be formed. This is oxidized ultimately to lead peroxide.

The relative strength of the sulphuric acid and the nitric acid or other forming acid is a matter of importance both in determining the depth of the formation and the finishing of the plate. The current density and temperature also affect the depth of formation. Since the nitric acid is reduced at the negative plate, which is the cathode in the forming bath, any factor, such as increasing current density or increasing temperature, which tends to increase the rate of reduction of the nitric acid, decreases the effective amount of it in the forming bath. Increasing temperature hastens the reduction of the nitric acid by increasing the rapidity with which diffusion takes place. During the forming process the amount of the forming agent present in the bath steadily decreases. It is necessary that at the end of the formation it should decrease to zero, in order that the finished plates may not contain traces of the agents which would cause subsequent growth and buckling of the plates in service. At the end of the forming period the peroxidizing effect of the charging current must predominate over any chemical action of the addition agents, in order that the plates may be satisfactorily "sealed off." This "sealing off" process consists in completely covering the underlying lead with a peroxide film which serves both as the active material of the plate and as a protective coating. The forming bath is ordinarily a solution of sulphuric acid ranging from 1.050 to 1.150 in specific gravity, to which the forming agent may be added from time to time as the formation progresses. At the end of the forming process the current density is ordinarily increased and the plates, after being removed from the forming bath, are washed and given a further charge in a solution of pure sulphuric acid which is free from nitrogen compounds or other addition agents. Another method of finishing plates intended for positives is to reverse them in a pure solution of sulphuric acid and water followed by a second reversal to restore the peroxide condition. This process eliminates the forming agent.

The formation of these plates in solutions of sulphuric acid has been the common practice, but an extensive investigation of the use of neutral sulphates and alkaline baths has been made by Peters.[23]

In some cases plates have been dipped in strong solutions of nitric acid as a preliminary to the forming process. The corrosive action which takes place on the surface of the plates, particularly if the acid is concentrated, results in the formation of complex compounds of lead and nitrates and nitrites which are only slightly soluble. The lead plates, having a layer of this material on the surface, can then be formed into peroxide or sponge lead by ordinary forming processes. Another similar method has been to convert the surface of the lead plates into the carbonate.

4. SEPARATORS FOR LEAD-ACID CELLS

The development of thin, porous separators which are placed between the alternating positive and negative plates in storage cells has made possible the development of compact portable batteries. Prior to the use of these porous separators, rods of glass or hard rubber or perforated and corrugated hard rubber sheets were inserted between the plates of the cells to prevent possible short circuits through buckling of the plates. It was not possible, in the early types of batteries, to place the plates close together, because scaling of the active material or the formation of "trees" on the negative plates would make a metallic connection between plates of opposite polarity.

The primary object of the separators is to prevent metallic conduction between the plates of opposite polarity while freely permitting electrolytic conduction. The types of separators include those made of wood veneer, perforated and slotted separators of hard rubber, porous rubber, glass mats, and miscellaneous types made of celluloid, fibrous, or vitreous materials.

a. Wood Separators

Certain kinds of wood have been found suitable for the manufacture of separators. These include bass, poplar, some kinds of pine, Douglas fir, cedar, cypress, and redwood. The separators are made from a knife-cut or sawn veneer[24] in the form of a long, narrow sheet of the required width. Grooves are cut in one side (Fig. 8), leaving a series of narrow ribs, between which is a thin portion called the web.

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[23] *Centralblatt f. Accumulatoren*, series of papers beginning volume 2, p. 293 ,1901, and continuing through volume 5.

[24] For further details, see papers by Steidle, *Veneers*, 22, p. 18, 1928; Ulett, *Timberman*, 34, p. 45, Dec., 1932.

(*a*) *Rotary-Cut Separators.* The veneer is cut from the log as a wide thin sheet while the log is rotated in a lathe. Rotary-cut separators are commonly called "flat grained," because the cutting edge of the knife is applied nearly tangentially to the rings of the log. The grain, however, is usually irregular and not entirely "flat," which would not be a desirable condition.

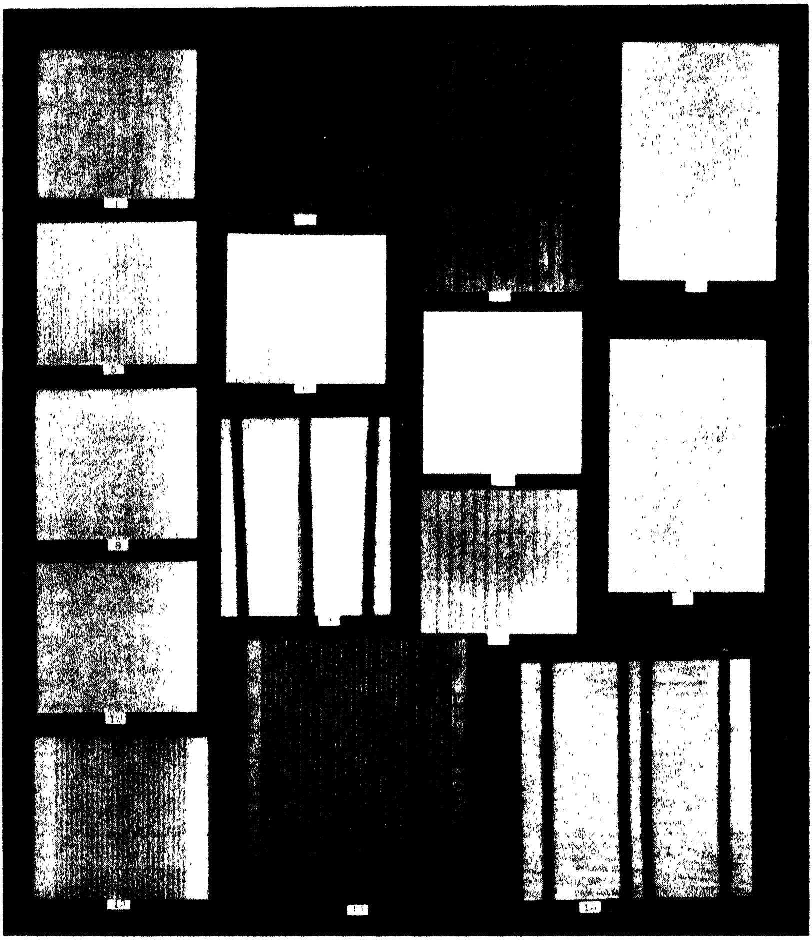

FIG. 8. Storage-battery separators. 1, redwood; 2 and 3, porous rubber, Darex; 4, glass mat; 5, Douglas fir; 6, spruce; 7, threaded rubber; 8, cypress; 9 and 15, flat-wood separators with rubber reinforcing; 10, porous rubber, Acesil; 11, porous rubber, Mipor; 12 and 13, Port Orford cedar; 14, redwood.

(*b*) *Sliced Separators.* This method of cutting separators came into extensive use about 1931. Blocks of wood, after being steamed, are placed in the slicing machine and the veneer is cut by a shearing motion of the knives. If the grain of the wood appears as parallel lines, it is called "vertical grain," but other positions of the block with reference to the knives result in "slash grain."

(*c*) *Sawn Separators.* These are cut by a saw, the direction of the grain depending on the position of the block. Quarter sawn separators show the grain as parallel lines extending through the separator, but the angle of the grain through the separator may vary as much as 45° and still present the appearance of parallel grain. As the angle approaches 90° the grain becomes nearly flat.

Classification of Material. Wood is divided into two classes, hard wood and soft wood. The hard woods are obtained from trees having broad leaves, while the soft woods are from the conifers, or trees with needles or scale-like leaves. The terms hard and soft often convey an erroneous impression, since some of the soft woods, such as cedar or cypress, are distinctly harder than many of the hard woods, as exemplified by basswood.

The structure of the hard woods differs essentially from that of the soft woods in having some cells which are of much greater diameter than others. Some of these cells are open, forming continuous tubes extending vertically in the tree. These tubes are known as vessels or pores. They are usually visible to the naked eye. The wood structure is composed of a vast number of cells, which are small hollow tubes generally closed at the ends and growing tightly together. The cells that are formed in the spring are of larger diameter than those formed in the summer when the growth of the tree is less rapid. The contrast between the size of pores defines the annual rings which are seen when the tree is cut horizontally to its axis. The rings are plainly marked in such woods as cypress, pine, and Douglas fir, while in poplar, white pine, and basswood they are not so pronounced. The woody fibers, which are small cells with thick walls, provide stiffness and strength.

The cells in the soft woods are so small that they cannot be seen without considerable magnification. They differ from the cells and pores of the hard woods, since they serve the double purpose of conducting the sap and providing the strength required by the tree. In some forms of conifers, such as pines and Douglas fir, there are, in addition, canals for the conduction of resin. These extend vertically, and in some cases radially also, among the other cells. Cypress, cedar, and redwood have none of these resin ducts, but they do contain appreciable amounts of resin.

The different kinds of wood used for storage-battery separators can be identified from their appearance and physical properties before they are immersed in sulphuric acid solutions. After they have been used in a storage battery it is difficult to identify them. The acid, if of greater specific gravity than 1.250, darkens the wood rapidly. Cherry, which was the first wood used for separators, has a characteristic red-brown color. Poplar is one of the softer of the hard woods and varies in color from white to a light greenish-yellow. The texture of this wood is uniform and the graining straight. Poplar is sometimes erroneously called basswood. Basswood is cream-white in color, soft, and without any definite figure. The pines are recognized by their characteristic color and the resin that they contain. Douglas fir is sometimes known as red spruce or Oregon fir. It is distinguished by a reddish color which, however, is not always distinct. Port Orford cedar is extensively used for storage-battery separators and is much like pine in appearance. It grows in the southern part of Oregon and takes its name from a seaport in the vicinity. It has a spicy, resinous odor. Redwood can usually be distinguished by its dark reddish-brown color. It is sometimes confused with red cedar, because of the similar color, but redwood is odorless and tasteless while red cedar has a characteristic odor and a bitter taste. Cypress varies in color and weight, depending on the locality in which it is grown. It presents a waxy or greasy surface. The mechanical properties of these woods are of interest in this connection and reference should be made to tables[25] which have been published.

The most common defects that are observed in woods used for separators are knots, checks, and shakes. Knots, unless very small, are detrimental in separators. Checks are splits in the log, extending in a radial direction from the center, and are caused by stresses occurring during the seasoning process. A shake is a separation between two annual rings. As a general rule, it occurs in only one part of the ring. Any one of these defects appearing in the finished separator is sufficient cause for its rejection. After wood separators have been grooved and cut to size, they should be examined individually before a strong light in much the same way as eggs are candled. In this way defective separators are easily detected. Because of the frequent occurrence of knots, checks, and shakes, the wastage in preparing separators is considerable.

The principal constituent of wood tissues is cellulose, but with the cellulose are the so-called incrusting layers of lignin and the sap which

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[25] *Timber*, p. 10, 1919; "Mechanical Properties of Woods Grown in the United States," *Bulletin* 556, Dept. of Agric., 1917; *International Critical Tables*, II, p. 1, 1927.

contains resinous material, tannins, coloring matter, and various mineral salts. There are a great many varieties of cellulose, but they have certain properties in common.

Celluloses, considered as a whole, are insoluble in the simple solvents and have a composition characteristic of carbohydrates. The empirical formula for them may be written $C_nH_{2m}O_m$. Celluloses resist in various degrees the processes of oxidation and hydrolysis. Generally speaking, however, they are much less subject to oxidation and hydrolysis than the other substances which are closely associated with them in the wood fiber. The woody tissues consisting of cellulose and the incrusting material are frequently called ligno-celluloses. The non-cellulose part of these compounds is generally termed lignin, or lignone. The lignone complex is easily decomposed by hydrolytic or oxidizing agents, yielding acetic acid, which is generally known to be deleterious to the life and performance of storage batteries. For example, wood immersed in dilute sulphuric acid at 60° to 100° C. readily yields a considerable amount of acetic acid, and the same result is obtained at lower temperatures if an oxidizing agent, such as nitric acid, is also present. The amount of acetic acid that may be formed from the wood varies with the degree of hydrolysis or oxidation of the material. The discussion of the chemistry of cellulose is beyond the scope of this book, but the reader is referred to the books by Cross and Bevan, *Cellulose, an Outline of the Chemistry of the Structural Elements of Plants*, and by Hawley and Wise, *Chemistry of Wood.*

While it is known that acetic acid in appreciable quantities is harmful to positive plates of a storage battery, it has been claimed that a small quantity of acetic acid is beneficial to the negative plate. For reasons that are not fully understood, the presence of wood in the battery is beneficial and in some cases necessary for the continued functioning of the negative plates. The wood may be present as separators or be included as organic expanders in the active material of the negative plates. Patents covering the use of pulverized wood have been issued to Chamberlain[26] and to Willard.[27]

Treatment. The wood separators, after being cut to size, are subjected to a chemical treatment which has for its object the removal of soluble and easily hydrolyzed matter, and the expansion of the pores. Many different methods have been used, most of which are covered by patents. Some of these methods have been based on the methods used for the preparation of wood for paper-making. In general, the treatment consists of the removal of the mineral salts and other soluble

[26] U. S. Patent 1,379,900, 1921.

[27] British, 155,944, 1919.

matter contained in the sap, as well as the easily hydrolyzed parts of the ligno-cellulose, by the use of steam, boiling water, or dilute solutions of various chemical reagents, including caustic soda, sodium bisulphite, sodium sulphite, and sulphuric acid.

The more usual procedure is to pack the separators loosely in tanks which are then filled with a solution of caustic soda, 1 to 2 per cent, heated to the boiling point or slightly below. The time of immersion is seldom less than 5 hours and may be considerably longer, depending on the strength and amount of the solution. The separators are washed in several changes of hot water and then cold water. If the separators are to be bleached, they are placed in a dilute solution of sulphuric acid and again washed in cold water. The proper regulation of the solutions, including the concentration, the temperature, the time of immersion, and the subsequent washing of the separators, requires skill and experience. Insufficient treatment means high electrical resistance in the battery and incomplete elimination of deleterious substances; excessive hydrolysis, on the other hand, means an unnecessary loss in the mechanical strength of the separators.

b. Rubber Separators

Perforated or slotted separators of hard rubber, sometimes called retainers or envelopes, are commonly found in various types of storage batteries. They assist in holding the active material of the positive plates in place and they protect other separators used with them from the strong oxidizing conditions of the lead peroxide. Perforated separators are generally used in combination with other types of separators such as wood, porous rubber, or glass mats. Perforated-rubber separators are placed in immediate contact with the positive plates, except when glass mats are used between the plates and the perforated rubber. The thickness of the rubber sheets is ordinarily about $\frac{1}{64}$ inch. Perforations may be round holes, elongated slots, or special shapes. The advantage claimed for the slots is that, because of their narrowness, particles of active material are more effectively retained on the surface of the positive plates, without loss of conductivity which is provided for by the length of the slot. Some of the special shapes of perforations are said to release bubbles of gas more readily than others. Whatever the shape of the perforation, the average percentage of area punched out is usually specified and called the "porosity." Thus, the round perforations, which may vary in size and number from 19 to 210 per square inch of surface, provide porosity from 13 to 46 per cent. The elongated slots, which vary from 0.012 to 0.020 inch in width and 0.18 to 0.25 inch in length number 75 to 125 per square inch. Porosities up to about 40 per cent are available. Various types of perforated and slotted separators are shown in Fig. 9. The percentage of material punched out in these slotted and perforated separators is a matter of considerable importance in determining the performance of the battery. If too much material is punched out, the rubber separator is weak and liable to breakage, but, if too little material is punched out, the resistance of the cell is materially increased.

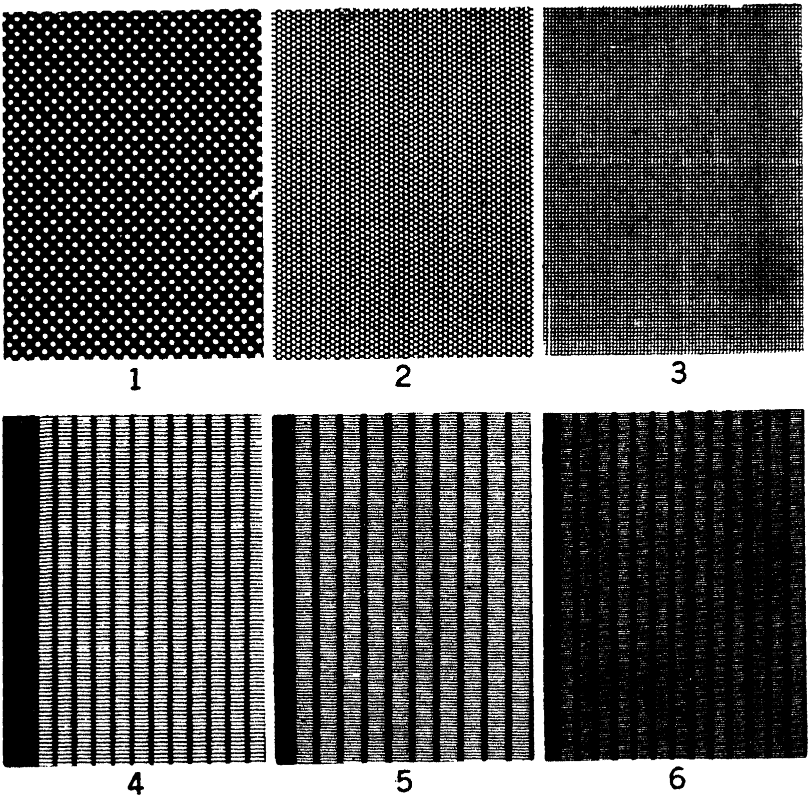

FIG. 9. Sections of perforated-rubber separators. 1 and 2, round perforations; 3, special shape of perforation; 4, 5, and 6, slotted perforations.

Porous-Rubber Separators. These may be divided into several classes according as they are made from latex or pulverized rubber, or by the smoked-sheet process.

Latex,[28] which is the secretion obtained principally from rubber

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[28] Latex is discussed in *Chimie et technologie du latex de caoutchouc* by Georges Génin, 1934; *Chemistry and Technology of Rubber Latex* by C. Falconer Flint, 1938.

trees, is a suspension of hydrocarbons in an aqueous serum containing also small quantities of proteins, resinous materials, mineral salts, and sugars. Fresh latex is slightly alkaline and contains 30 to 38 per cent of rubber hydrocarbon. The remainder is mostly water. On exposure to the air the latex becomes slightly acid and coagulates. To prevent this, ammonia is added before it is shipped. Because of the large amount of water which it contains latex is sometimes partially concentrated by centrifuging or by evaporation to decrease costs of transportation. Latex is sensitive to traces of copper, cobalt, manganese, and certain other metals, contact with which should be avoided.

In 1914 Schedrowitz and Goldsborough found that coagulated latex could be vulcanized in steam and the water in its pores thus prevented from escaping during the process. After vulcanization, evaporation of the water left a highly porous mass. More recently, Beckmann[29] has developed a process of making porous sheets of rubber for battery separators and other purposes. The trade names of these materials usually suggest the basic material or the microporous structure. Latex containing about 40 per cent rubber is mixed with the required amounts of sulphur and a dilute solution of magnesium sulphate. Other materials may be added also, such as (1) phenol or wood extracts to benefit the negative plates of the finished battery, (2) materials such as increase the porosity, and (3) still other materials such as casein to prevent too rapid setting of the gel. Vulcanization is accomplished with the water of the latex still in the pores. The porosity of the finished product, after drying, is governed by the water content of the coagulum before vulcanization. Porosities of 15 to 80 per cent have been obtained. For battery separators the porosity is about 50 per cent. The number of pores per square centimeter has been estimated at approximately 500,000,000.

Threaded-rubber separators, which were formerly made as thin sheets of vulcanized rubber through which several hundred thousand threads passed as tiny wicks, are now made as latex separators containing an open-weave fabric.

Porous-ebonite separators, such as the Wilderman[30] type, are prepared from pulverized, partially vulcanized rubber, or completely vulcanized rubber to which some unvulcanized rubber is added. The material is molded and compressed to the required shape and then agglomerated by further vulcanization. Soluble materials, wood flour, or absorbent colloids are sometimes added to the rubber. Following vulcanization, the soluble material is dissolved out. The finished separa-

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[29] *Elektrotech. Zeit.*, 51, p. 1605, 1930.

[30] British Patent 200,527, 1922.

tors are often impregnated with a thin film of silica gel which is said to increase the initial speed of penetration by liquids. The pores, although small, are considerably larger than in microporous separators. The porosity can be varied from 20 to 60 per cent.

Other porous rubber separators are formed under heat and pressure from comminuted rubber and silica gel.

c. Fibrous-Glass Separators

Increasing use has been made in recent years of fibrous-glass diaphragms as battery separators. These are placed next to the positive plates in order to retain the active materials in place and to provide a reservoir for the electrolyte. These porous-glass separators are always used in combination with other types of separators, such as perforated or porous-rubber or wood separators. The thickness of the individual glass fibers is said to be 0.0002 to 0.0003 inch. The material is supplied in sheets of matted fibers about $\frac{1}{16}$ inch in thickness, or thinner, as required. The glass fiber is available in several grades of soft and hard glass.

d. Flat Types of Separators

In certain types of glass-jar batteries where the spacing of the plates is greater than in the more compact portable types, flat separators of porous rubber or wood veneer are used. These are usually reinforced by split-wood dowels or by strips of rubber. Several of these are shown in Fig. 8.

The Exide-Ironclad batteries contain separators which are flat sheets of porous rubber without grooves. The construction of the positive plates provides the space required for the acid, and the rubber tubes serve the double purpose of a rubber separator and a retainer for the active material of the plate. The rubber tubes are slotted along the side to provide access for the electrolyte to the active material, but, as these slots are exceedingly narrow, the lead peroxide within cannot escape.

e. Relation of Design to Cell Performance

The grooved side of the separator is always placed next to the positive plate. This is done for several reasons. The actual contact of the separator with the highly oxidizing material of the positive plate is minimized and a greater volume of acid, for use by the positive plate during discharge, is provided. At high rates of discharge, the maximum capacity of the positive plate is attained only for moderately high concentrations of the acid. It is necessary, therefore, that the positive plate should have an ample supply of acid to maintain the concentration. The negative plate, on the other hand, reaches its maximum capacity at a relatively lower concentration. The flat side of the separator helps to retain the active material of the negative plate in place.

The proper thickness of the separators is determined by the use for which the battery is intended. Starting and lighting batteries for automobiles, which are required to deliver large currents, must necessarily have a low internal resistance. These require relatively thin separators, commonly $\frac{5}{64}$ inch in thickness. Signal batteries, on the other hand, for which the rates of discharge are small, are provided with thick plates and a relatively wide separation. Separators for these may be as much as $\frac{1}{4}$ to $\frac{3}{8}$ inch in thickness measured over the ribs, but the web of such separators is relatively thin.

f. Electrical Resistance

The resistance to the passage of the electric current through the separators is an important quantity, varying with the kind of material of which the separator is made, the treatment which it has received, and the direction of the grain, if the separator is of wood. In general, it is known that woods such as basswood and poplar have a lower resistance when saturated with electrolyte than cedar or cypress. Tests are commonly made at high rates of discharge to determine the voltage characteristic of the battery, since this in turn depends on the internal resistance of the battery and so in part upon the separator resistance. It is desirable to have more direct measurements of the separator resistance, however, and several methods have been devised for measuring the resistance of individual separators.

One method which has found use in the industry consists in measuring the electrolytic resistance of a specially constructed cell, with and without the separator interposed across the path of the current, under otherwise comparable conditions. The difference of the two measurements gives the effective resistance of the separator. The cell which is shown in Fig. 10 contains two negative plates at the ends of the cell which serve as current terminals, and two other plates set at an angle are used to measure the potential drop across the separator which divides the cell at the middle. The separator is inserted between the glass plates, which have a fixed circular opening. A 60-cycle alternating current is used to avoid polarization effects. The electrical circuits are shown in Fig. 11. A transformer with two secondary windings of 5-ampere capacity is used to reduce the 110-volt circuit to about 10 volts. The current from one secondary is passed through the cell and maintained at 5 amperes. The current from the other secondary is passed through a calibrated slide wire and a non-inductive resistance of about 100 ohms. This latter circuit serves as a potentiometer in phase with the current through the cell. An alternating current galvanometer can be used to determine the balance, care being taken to maintain the field of the galvanometer in phase with the potentiometer. The accuracy of the measurements is tested by measuring the value of a known resistance. The resistance of individual separators, from the same lot and similarly treated, may vary from 5 to 15 per cent, but the precision of the measurements is about 1 per cent. Several weeks' immersion in sulphuric acid solutions is required prior to the measurements, in order that the resistance of the separators may reach a constant value.

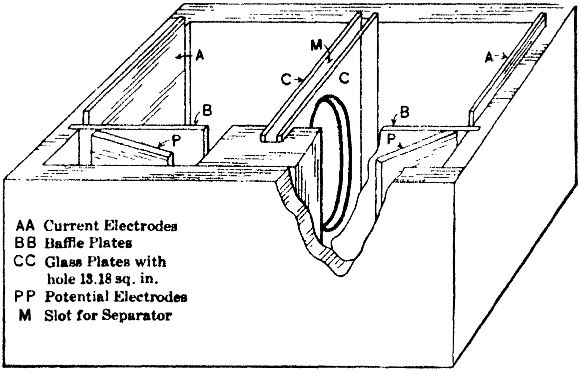

FIG. 10. Cell for measuring resistance of separators.

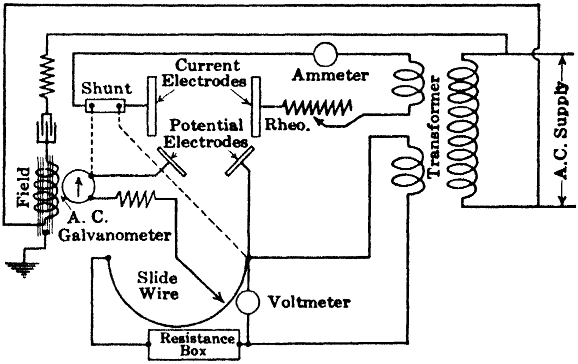

FIG. 11. Circuit for measuring resistance of separators.

A second method of measuring the resistance of separators consists of cutting disks about 3.5 cm. ($1\frac{3}{8}$ inches) in diameter from a considerable number of samples and measuring the change in resistance of a small electrolytic cell when the disks are placed between the electrodes. The disks are cut with a steel die of such size that they fit accurately in the glass tube of the cell. The electrodes are of lead with a formed surface of lead peroxide. The upper electrode may be removed to permit the disks to be inserted, but its position with respect to the lower electrode is fixed by the ground glass surfaces at the top and bottom of the glass tube. The cell is small and is placed in an outer vessel containing electrolyte of a specified concentration. (See Fig. 12.)

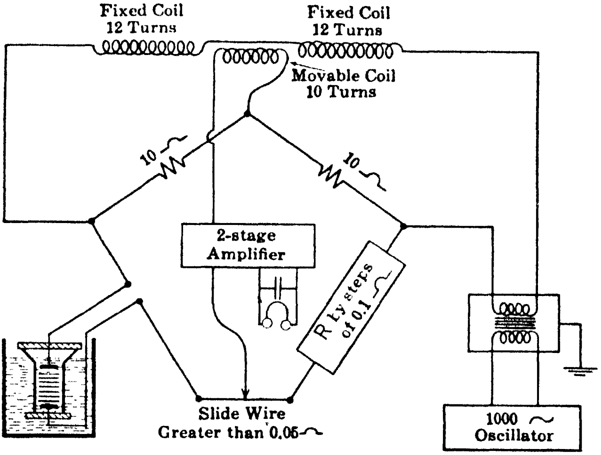

FIG. 12. Cell and bridge for measuring the resistance of storage-battery separators by the disk method.

This in turn can be placed in a temperature-controlled bath. The resistance is measured on a Wheatstone bridge having fixed ratio arms of 10 ohms each and a slide wire between the remaining arms for fine adjustment. The bridge is supplied with current from a 1000-cycle oscillator. Earphones connected through a two-stage amplifier are used in the detector circuit for balancing the bridge. Two adjustments are required. The first for an approximate balance, then the movable coil shown in Fig. 12 is adjusted for minimum sound in the earphones and the second and final balance is made. Accurate measurements depend (1) on the disks fitting well in the tube to avoid by-passing current; (2) on the use of a very small current through the bridge to avoid heating effects; (3) on the electrodes being well covered with lead peroxide to obtain minimum sound in the earphones; and (4) on satisfactory temperature control. The disks may be preserved in sulphuric acid solutions for subsequent measurements. By piling up eight or ten disks in the tube the actual resistance to be measured becomes considerably larger than in the case of the method previously described, but that method is convenient for factory-control measurements.

When the method of the small cell is used, successive measurements on the same samples show the progressive changes in resistance which occur particularly in the wood samples. These changes give some indication of the effectiveness of the treatment of the separators. After several weeks the resistance becomes relatively constant. When measurements are made at different temperatures, it is found that the percentage of increase in resistance of porous rubber separators is approximately the same as the percentage of increase in resistivity of the acid solution for the same decrease in temperature, but this is not true of wood separators which change in resistance more than proportionally to the change in acid resistivity. This effect is illustrated in Fig. 13.

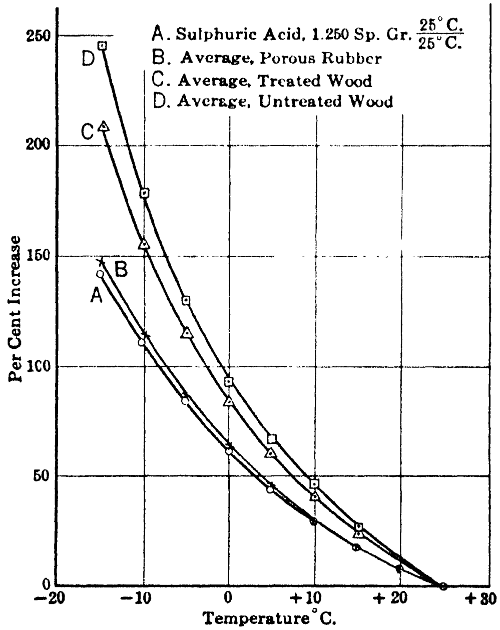

Fig. 13. Effect of temperature on resistance of separators compared with the resistivity of sulphuric acid solutions.

The resistance of the separators is expressed as the resistance per square inch of surface. To apply the figures of Table VIII to a particular case, it is necessary to estimate the area of the separators within the cell and to divide the figures which are given by this factor. For example, if there are 100 square inches of separator surface of a specified thickness, the resistance will be $\frac{1}{100}$ of the value given for the particular kind of wood.

TABLE VIII

MEASUREMENTS ON TREATED STORAGE-BATTERY SEPARATORS

Kind of Wood and Number of Samples		Breaking Strength (Wet) Cross Section 0.0386 sq. in		Electrical Resistance per sq. in. Average Thickness 0.0520 in.		Volatile Acid per Gram of Separator, Calculated as Acetic Acid (Grams)	Reducing Substances per Gram of Separator, Calculated for PbO_2 (Grams)
		Initial, in Water 24 Hours (Pounds)	After 7 Weeks in 1 250 sp gr. Sulphuric Acid (Pounds)	Initial, in 1 250 sp. gr Sulphuric Acid at 25° C (Ohms)	After 25 Days in Acid, 1.250 sp. gr at 25° C. (Ohms)		
Port Orford cedar. .	10	273	123	0.052	0.045	0.0039	1.35
Fir. .	6	200	90	0.043	0.037	0.0051	1.60
Cypress	3	236	87	0.063	0.052	0.0042	1.38
Redwood .	3	191	63	0.033	0.028	0.0044	1.23
Yellow cedar. . .	2	262	102	0.046	0.041	.	1.40
Spruce.	2	228	73	0.035	0.032		1.07

Notes on Table VIII:

1. Samples consisted of a considerable number of separators obtained from various sources These had been treated according to the manufacturer's customary methods.
2. Breaking strength was measured on four strips cut from each sample. Each strip included two or three ribs and the web portion between, but the results have been calculated to a uniform cross section of 0.0386 square inch. The tensile stength machine in which the test pieces were broken was calibrated to read to one pound.
3. Electrical resistance measurements were made on ten disks cut from each sample. Diameter of disks was 1.395 inches and diameter of tube was 1.41 inches. These were nominally $\frac{5}{64}$-inch separators, but the average thickness over ribs and web was 0.0520 inch and all results have been calculated to the same basis.
4. Volatile acids were determined by extracting the materials in H_2SO_4 solutions followed by distillation in accordance with Craig's method described in his paper, *BS J. Research*, 6, p. 169, 1931. The results are expressed as grams of volatile acid, calculated as acetic acid, per gram of separator. Untreated separators yielded much higher amounts.
5. Reducing substances were measured by a permanganate method. The results are expressed as the amount of PbO_2 reduced per gram of separator. After separators have been in a battery for about 18 months, the amount of reducing substances that can be extracted is about half that from new separators.

The porosity of the separators is an important factor in determining the physical performance of storage batteries, since it affects not only the internal resistance, but also the equalization of the acid concentrations during charge and discharge. The resistance of the separators depends on the length and cross section of the pores and indirectly on the direction of grain of the wood. As an approximation, it may be assumed that the porosity of the wood is inversely proportional to the resistance. No standard of porosity has been established for the determination of quality of the separators. The figures given in Table VIII are for separators of the type used in starting and lighting batteries.

g. Effect of Acid on the Wood

In judging the quality of wood separators, it is of importance to determine the effect of acid on the wood as well as to determine the electrical resistance. Sulphuric acid chars the wood, as may readily be observed. The extent to which this action takes place depends very largely on the concentration and the temperature of the acid. When the specific gravity of the acid is 1.250 or below, the charring action is relatively slight, even when the wood is immersed for a long period of time. At 1.300 the charring action is noticeably greater, and it becomes serious at concentrations higher than this. A series of experiments has been carried out at the Bureau of Standards to determine the decrease in strength of several kinds of wood as a result of being immersed in several concentrations of acid for a period of seven weeks. Samples in the form of strips were cut from separators of different kinds of wood. Each strip included two or three ribs and the web portion between, but all the results were calculated to the same cross section. The samples were kept in the solutions at a constant temperature of 20° C. (68° F.) for the duration of the experiment, and they were then taken out and subjected to tensile-strength tests while still wet. The results of this experiment are shown in Table VIII. Each value is the mean of four determinations. The effect of the acid in weakening the wood fiber is clearly shown.

5. CONTAINERS FOR LEAD-ACID CELLS

a. Rubber Jars and Containers

Rubber is commonly used for the containers of starting and lighting, radio, airplane, vehicle, marine, and submarine cells. The container for a single cell is called a jar, but others are divided into several compartments for two or more cells. The biscuits of crude rubber are ground, washed, dried, and mixed with fillers and sulphur, after which the material is calendered. When the mixture is heated, a combination of rubber and sulphur takes place, with the formation of a new substance of markedly different mechanical properties. This process is called vulcanization. The degree of vulcanization varies with the proportion of sulphur and with the temperature and duration of the heating. The quality of the final product, as for example the battery jars, depends on these factors and also on the percentage of rubber in the compound. It is, therefore, not surprising that the quality should differ widely. Containers have superseded the use of the individual jars for automobile batteries. A hard-rubber container for three cells is shown in Fig. 14.

The covers are molded. These differ greatly in shape and arrangement of the openings. Covers for the smaller cells, such as for starting and lighting batteries, vehicle batteries, etc., generally have three holes in the cover; two of these are for the protruding terminal posts and the third for the combined vent and filling aperture. (See Fig. 15.)

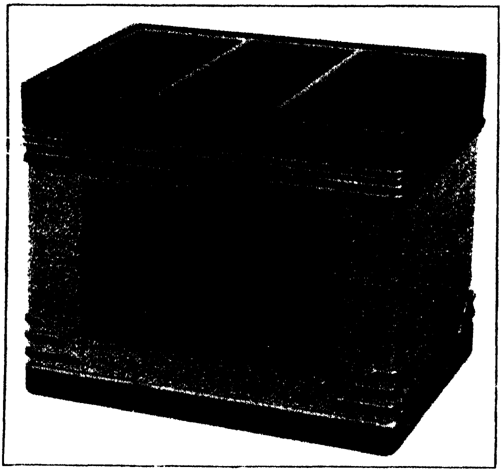

FIG. 14. Hard-rubber container for three cells of an automotive battery.

The sealing compound is a blown oil asphalt with a melting point of about 200° F. The softer compounds melt below this temperature and the harder ones above it. As the compounds contain volatile constituents which are driven off if melted for any considerable time, it is not desirable to use the compound a second time.

The method of sealing the terminal posts at the point where they pass through the cover is a matter of great importance. Unless the posts are satisfactorily sealed, they are likely to work loose in the cover and cause leakage of the electrolyte. Each manufacturer has his own design for locking the post and cover together, but not all of these have

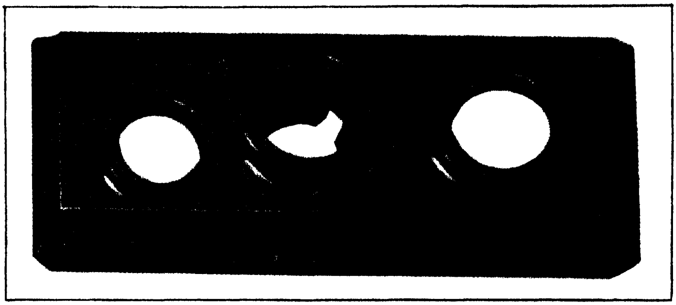

FIG. 15. Cover of a cell of the automotive type.

been found satisfactory. Five of the familiar arrangements are shown in Fig. 16. The sealing nut of rubber or lead alloy is screwed down on the post, thus pressing the cover against a soft-rubber gasket.

The vent plugs in common use are of three kinds: bayonet, screw, and soft rubber. The bayonet type is fastened in place by a partial turn; the screw type is threaded as its name implies; soft-rubber plugs are pushed into place. The vent plugs provide for the escape of gas during charging, and by removing the plug a larger opening is provided for filling the cell with electrolyte or water. Since the vent plugs provide free access of the air to the interior of the cell, electrolyte may be spilled through the vent if the battery is inverted, and some sloppage

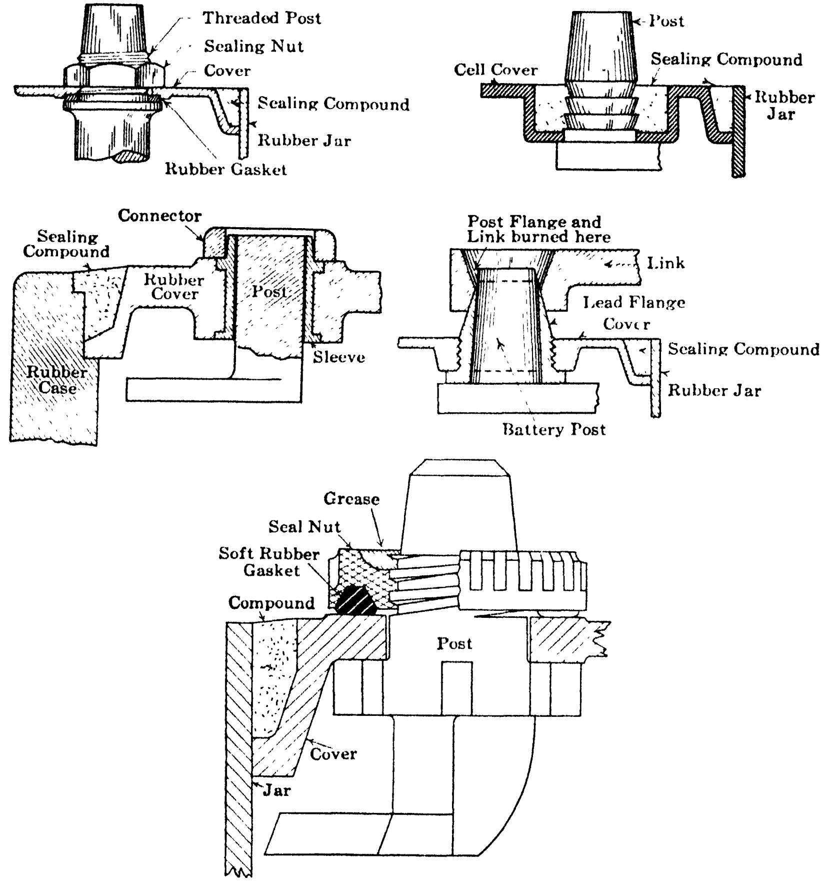

Fig. 16. Five methods of sealing the terminal posts.

may occur because of shock. The method of overcoming this difficulty most frequently used on batteries for automobiles is to insert in the vent plugs a baffle plate which effectively prevents sloppage or the escape of electrolyte during charging under the ordinary conditions of service. Batteries for certain kinds of signal service and for use on airplanes are required to be of the non-spill type. Various valves, to permit the free escape of gas without liquid when the battery is inverted, have been devised, but none have come into common use, except the "double chamber." Above the element is a compartment sufficiently large to hold all the liquid which will drain from the element when the cell is inverted. The vent plug is elongated and the hole at its lower tip is so placed as to be out of the liquid, whatever position the cell may be in. This is an effective device, but has the disadvantage of increasing the size and weight of the cell. The electrical resistance is also increased because of the extra length of the terminal posts. This type of construction is shown in Fig. 113 and also in Fig. 163.

b. Composition Containers

Composition containers are molded products of thermoplastic, bituminous materials, usually containing asphalts, asphaltites, inert fillers, fibrous materials, lampblack, and sometimes mineral waxes and comminuted rubber. Many specific compositions of these materials have been patented.

Asphalt is a term applying to a species of bitumen and certain pyrogenous substances of dark color and variable hardness, which are composed of hydrocarbons that are comparatively non-volatile and free from oxygenated bodies. These include native asphalts and pyrogenous asphalts which are residues from the distillation or the blowing of petroleums. Asphaltite is a species of bitumen of which Gilsonite is the variety generally used in making battery cases. This class of materials consists of comparatively hard, non-volatile solids of a dark color.

Inert fillers which are used include infusorial earth, pumice, and other forms of siliceous material. The fibrous materials are usually cotton or asbestos, but mention is made in the literature of animal fibers. Of the native mineral waxes, Montan wax is sometimes employed. Petroleum fluxes are sometimes added also.

The cases are cast under pressure while the material is hot. As it flows into the mold, it is important that the material coming from one direction should form a satisfactory bond with the material coming from another direction. Cases are removed from the mold when sufficiently cooled.

The finished product must resist attack by sulphuric acid solutions of a strength commonly used in batteries; it must not become porous or deformed; it must not contaminate the electrolyte with impurities of which iron and particularly manganese are the most important.

c. Celluloid Jars

Celluloid is a plastic material prepared from cellulose nitrate and possessing good mechanical properties. It is transparent, light in weight, may be machined or molded, and is not attacked by dilute acids. It has therefore found some use in the manufacture of storage-battery jars, but for this purpose it has two serious drawbacks: (1) It is highly inflammable, and (2) leakage of electrolyte may occur at the seams. The seams are cemented together by the use of glacial acetic acid or by a solution of celluloid in amylacetate. The use of celluloid jars has been more common in Europe than in America. Investigation of the causes of several fires occurring in batteries equipped with celluloid jars has shown in one case clear evidence that the celluloid was ignited by the heat generated at a broken terminal post. A less inflammable substitute for celluloid is made from cellulose acetate.

d. Glass Jars

Glass jars are very commonly employed for stationary batteries except for the largest sizes. Desirable qualities in the glass jars are transparency, freedom from attack by the acid, the absence of blow holes, and the ability to withstand temperature variations.

e. Lead-Lined Tanks

These are used for large stationary batteries and are generally applicable where considerations of space and weight are not of importance. The wood casing must be of good quality, since the lead lining has little mechanical strength and is liable to deformation. The best wood available is a resinous long-leaf yellow pine. The upper rim of the lead lining is usually reinforced and is called the crown.

6. ASSEMBLY OF LEAD-ACID CELLS

The remainder of the process for the manufacture of lead storage batteries deals with problems which are of comparatively little interest to a student. They will, therefore, be described very briefly. The plates, after formation, are assembled into positive and negative groups by burning the plate lugs to the connecting straps or bars (Fig. 17). These groups are interleaved, the positive and negative plates alternating. The separators are then placed between the plates of opposite polarity, with the grooved side of the separator facing the positive plate. If slotted or perforated rubber separators are used, they are inserted between the positive plates and the wood separators. The assembly of positive and negative groups with separators is called the element of the storage cell. After assembly of the element is complete, it is placed in the jar or container, and the cover of the cell (Fig. 15) is sealed on.

Connectors between the individual cells may be of several different kinds. Pure lead connectors are used when high conductivity is required without severe mechanical conditions. The most common type of connector is made from a casting of lead-antimony alloy. These connectors may be burned to the projecting terminals of the cell and are more durable than the soft-lead connectors. Copper connectors with heavy lead plating are sometimes used in batteries for vehicle or locomotive work, since they combine high conductivity with flexibility, the latter property enabling them to absorb the strains that might otherwise crack the jars of the battery. The copper strips usually have a loop in the middle to increase the flexibility and have alloy castings on the ends which may be burned to the terminals of the cell. Intercell connectors are commonly referred to as burned or bolted, these terms indicating whether the connectors are attached to the cell post by the lead-burning process or clamped by a threaded bolt. A combination of burned and bolted connectors is now used to some extent as a matter of convenience. The burned end of the connector is at the positive where corrosion is most likely to occur. The bolted connection is at the negative.

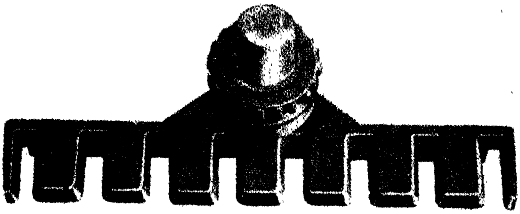

FIG. 17. Connecting strap, showing sealing nut.

The resistance of the intercell connectors is a matter of considerable importance, since the energy which is wasted in the form of heat in these connectors varies as the square of the current. If the intercell connectors are made very large for the current which the battery is designed to carry, unnecessary material is used and the weight of the battery unduly increased. In Chapter X a discussion of the resistance of the intercell connectors is given for the automobile, vehicle, and airplane types of batteries.

7. TYPES OF LEAD-ACID BATTERIES

In the previous discussion, pasted and Planté plates have been described. They find many uses in a wide variety of cells, of which only a limited number can be mentioned here. Reference should be made to published catalogs of manufacturers for details of construction and features which make their batteries adapted to specific kinds of service.

a. Batteries with Flat Pasted Plates

Pasted plates are employed in many types of batteries. Without doubt the most familiar is the automotive battery which is made in greater numbers than any other. Pasted plates are used also in sealed glass-jar batteries for stationary service. In size, pasted plates range from small plates used in potential batteries to the largest sizes used in tank batteries. Typical pasted plates for automotive batteries are shown in Fig. 18. Distinguishing features are the grids and active material which extends through the plates. Positives have dark active

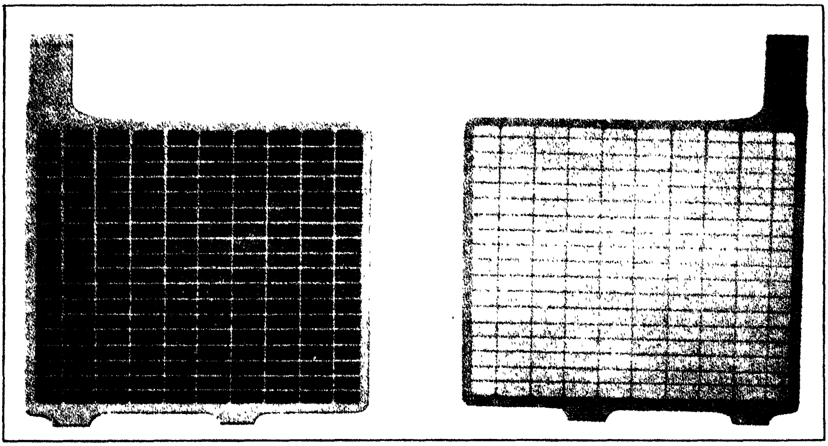

FIG. 18. Pasted plates of the type for starting and lighting batteries; positive left, negative right.

material, which is lead peroxide, and the negatives have gray sponge lead as the active material. Assembled in a completed cell, these plates with intervening separators are shown in Fig. 19. Although the ordinary flat pasted plate is easily adapted to many services, other types

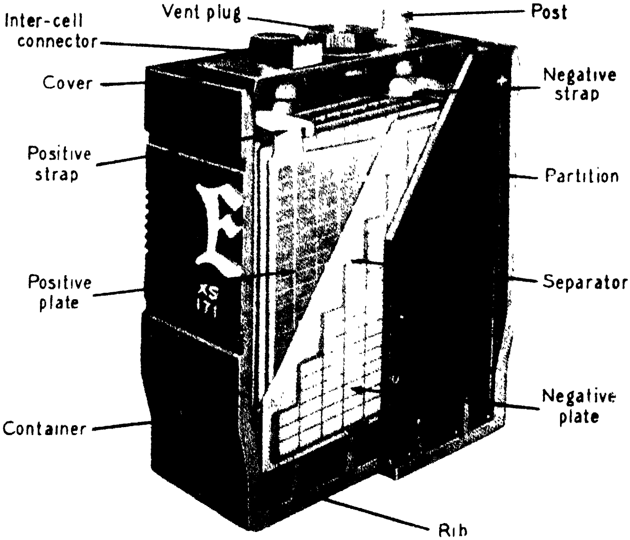

FIG. 19. Cutaway cell of the automotive type, showing details of construction.

of plates and methods of constructing batteries may have distinct advantages for particular services. The choice of a battery for any service depends on features which are inseparable from operating conditions.

b. Batteries with Reinforced Grids

The first of these was developed primarily to provide a battery of longer life in floating service. Mechanical strength is one feature, but an equally important characteristic is the greater cross-sectional area of some of the grid bars to withstand corrosion, particularly in floating service. Reinforced, that is, heavier grid bars are provided at intervals, but the mass of the metal is within the active material of the plate and only the narrow edges of the bars are exposed. Lighter grid bars of the usual type are interspersed between the heavier members. Several grids of this type are shown in Fig. 5. The essential points in design relate to the distribution of the metal in positive grids. The grid weight is about 50 per cent of the weight of the finished dry plate. The outer frame with lug is from 21 to 30 per cent of the grid weight. The reinforcing members are about 40 per cent or more of the grid weight while the surface members account for only about 15 per cent of the grid weight. Positive grids usually exceed 0.3 inch in thickness. Two cells of this type are shown in Figs. 20 and 21. These are the Philco-Floté and the Exide-Tytex, respectively. The outside negatives of the latter have reinforcing bars and clamps and differ in this respect from the inside negatives. The Floté element is provided with corner clamps or tie rods at the bottom. Each type of cell is provided with slotted-rubber separators and grooved-wood separators.

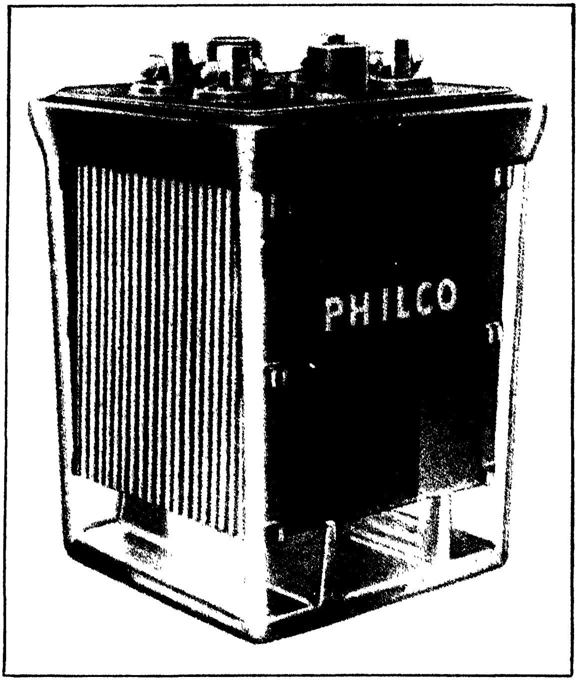

FIG. 20. Floté cell, containing reinforced grids.

c. Batteries with Manchester Positives and Box Negatives

These are cells of the Planté type familiarly known as the Exide-Chloride type. The grid of the Manchester plate is a casting of lead-antimony (Fig. 5) providing openings for the active elements which are buttons of soft-lead ribbon. These are corrugated and rolled into spirals which are forced into the grids by hydraulic pressure. The buttons are electrolytically formed by the Planté process, and the active material is therefore provided by the lead itself. However, initial formation penetrates only part of the lead ribbon, the remainder being available for gradual conversion into active material to replace other active material which may become dislodged and deposited as sediment in the bottom of the cell.

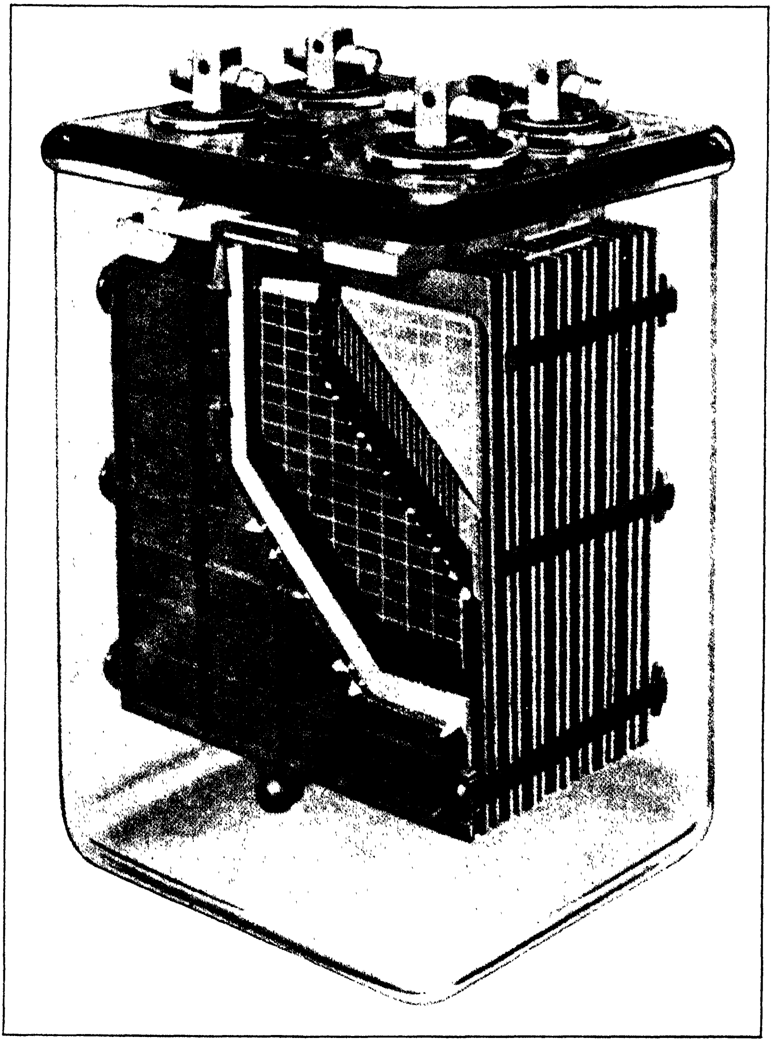

FIG. 21. Tytex cell, containing reinforced grids.

The negative plate consists of a lead-antimony grid of horizontal and vertical ribs providing pockets of rectangular shape which are closed on either side by sheets of perforated soft lead. The active material of sponge lead is confined within these pockets or boxes. A grid of this type is shown in Fig. 5 and a fully assembled cell is shown in Fig. 22. These cells are made in a variety of sizes.

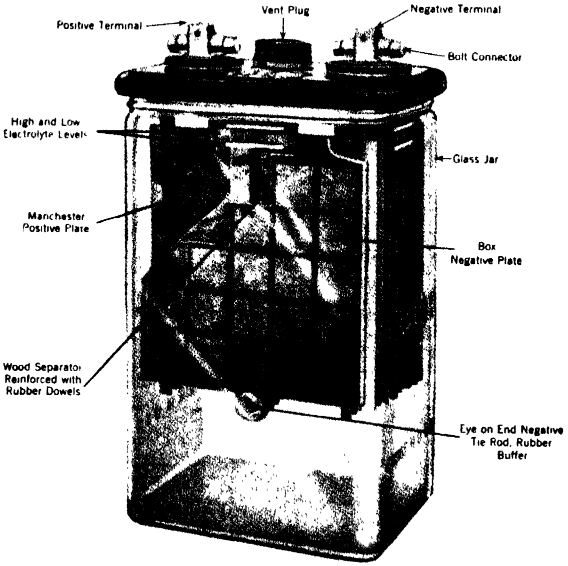

FIG. 22. Exide-Chloride cell with Manchester positives and box negatives.

d. Batteries Containing Exide-Ironclad plates

The distinguishing feature of this type of lead-acid battery is the positive plate which consists of vertical tubes of finely slotted rubber within which the active material is contained. The grid of this plate is composed of a number of parallel vertical rods of lead-antimony, which are burned to supporting frames at top and bottom. Each rod forms the core of a pencil consisting of the active material and the enclosing rubber tube. The slots provide access of electrolyte to the active material but prevent the active material from being washed out. The rubber tubes at the outside edges of the plates are reinforced by leaving the exposed edges solid. Each tube has two vertical ribs projecting on opposite sides at right angles to the plate. These ribs not only reinforce the tubes, but also serve as insulating spacers, taking the place of the ribs on wood separators. A small grid is shown in Fig. 5. The negative plate is a flat pasted plate differing from the ordinary type chiefly by having a vulcanized rubber sheathing along the top and bottom edges. The separators are flat sheets of microporous rubber, called "Mipor." One of these cells is shown in Fig. 23. These batteries find use in motive power, marine, and other services. They are made in five sizes of plates, for which operating data are given in the section on truck and tractor batteries in Chapter X.

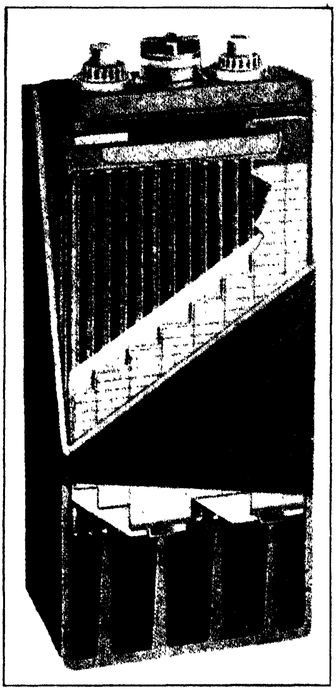

FIG. 23. Exide-Ironclad cell, cut away to show construction.

e. Kathanode Batteries

Glass mats, one of which is shown in Fig. 8, are placed on both sides of pasted positive plates which have been treated with a dispersion which the manufacturer (Gould) calls "ananide." The glass mats are made of filaments of spun glass, matted together and laminated to form a porous retainer of approximately 0.060 inch in thickness. Outside the glass mats there is a perforated-rubber envelope of about 44 per cent porosity which holds the glass mat in contact with the surfaces of the positive plate. Unperforated at the edges, these envelopes serve to prevent treeing. The Kathanode units, each consisting of one positive plate, two glass mats, and the envelope, are assembled with pasted negative plates to form the element. Wood separators between positive and negative plates are used in glass-jar cells for stationary service, and porous-rubber separators, called "Durapor," are used in rubber-jar cells for motive power or other purposes. A cell of this type is shown in Fig. 24. Other cells with glass mats have recently been developed.

f. Planté Cells and Modifications

In addition to the Planté plate, described above and widely known as the Manchester positive plate, there are other varieties of these plates. Of historical interest is the Tudor positive plate which is cast in cellular form. This plate is not now made in this country, insofar as the author is aware. Spun plates described on page 41, and sometimes known as C. P., or "chemically pure," plates, are now used in combination with pasted negative plates. The term "chemically pure" relates to formation of the plates in solutions which are without the usual forming agents. A cross section of a portion of such a plate is shown in Fig. 25. The layer of crystalline lead peroxide is rather thin initially, thus leaving space for expansion of the active material during discharge when an increase in volume occurs. Combinations of Planté plates with pasted negatives (Fig. 26) are sometimes known as Planté-paste cells. The use of true Planté negatives, similar to the positives, has declined in recent years. The cells are usually provided with wood separators. Planté cells find their chief applications in stationary service. They are in glass jars for capacities up to 1140 ampere-hours and in lead-lined tanks for larger capacities.

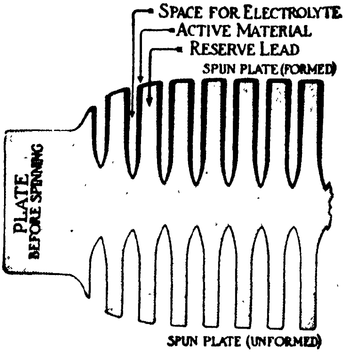

FIG. 25. Cross section of a spun plate.

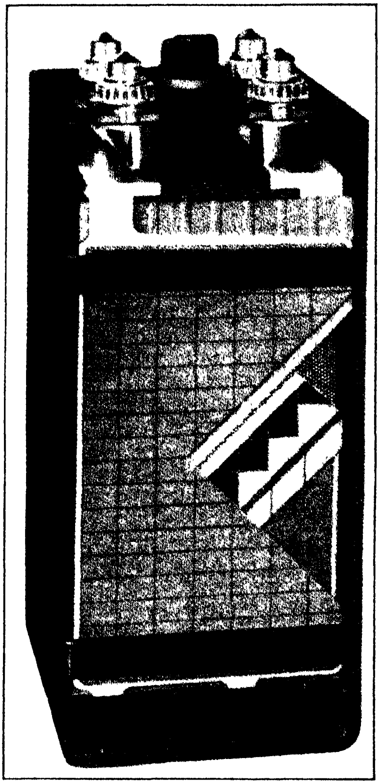

FIG. 24. Gould Kathanode cell with glass mats and perforated rubber envelope.

g. Batteries for Low Rates

Low discharge rates imply discharge over long periods of time. A storage battery to be suitable for such a purpose must have very little local action or self discharge, otherwise a considerable portion of its capacity will be spent without doing useful work. The development of Willard's low discharge battery [31] makes possible the use of lead-acid storage cells in circuits where the interval between charging may be a year or more, provided the current drain is not enough to exhaust the battery in a shorter time. The self discharge occurring in these cells has been reduced to less than 15 per cent per year by the use of pure lead grids without antimony. The cells are made in three sizes. Plates in the largest size are $\frac{15}{16}$ inch thick, 6 inches wide, and $8\frac{3}{4}$ inches high. Although designed for cycles of service of not less than three months,

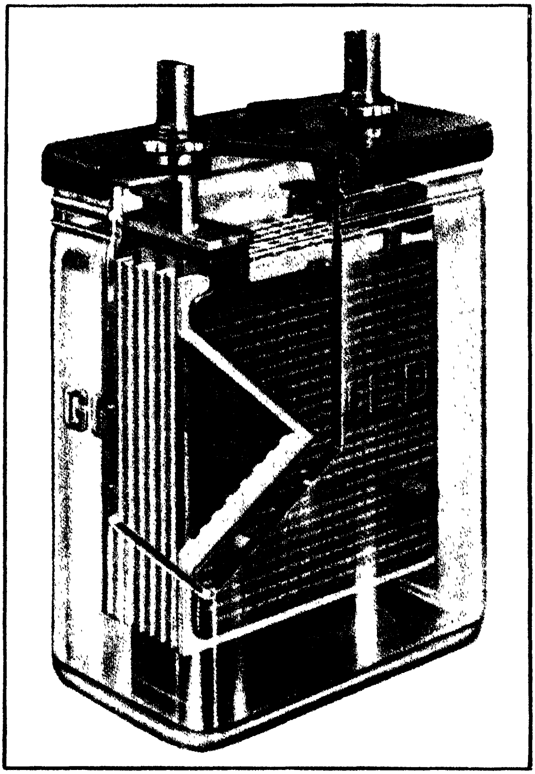

Fig. 26. Planté cell with spun positives and pasted negatives.

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[31] Rose and Zachlin, *Trans. Electrochem. Soc.*, 68, p. 273, 1935.

they can deliver very appreciable currents for short periods of time in intermittent service. The initial voltage is 2.12 volts per cell. With a high cutoff voltage of 1.95 volts per cell the average voltage is 2.05 volts. These batteries find use in signal devices, alarms, light beacons, program systems, and laboratory installations. A cell of 600 ampere-hour capacity is shown in Fig. 27.

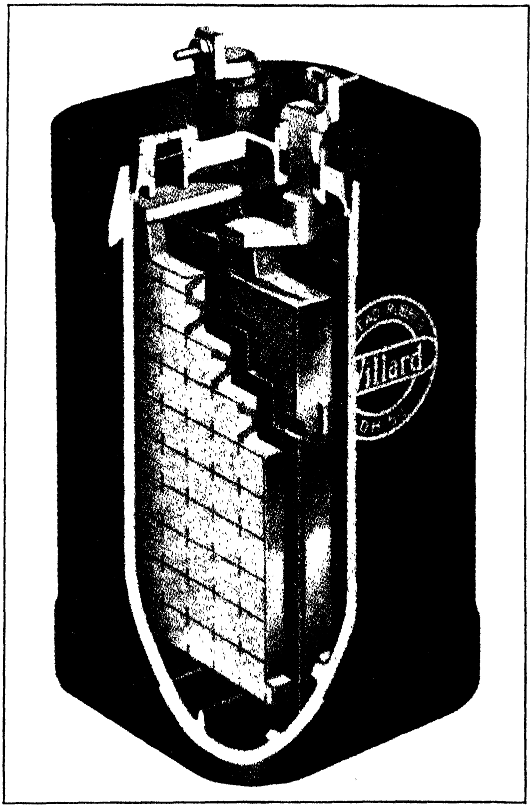

FIG. 27. Willard cell for low discharge rates. Local action in this cell has been reduced to a minimum.

h. Closed-Tank Cells

One of the newest developments in storage batteries is the closed-tank cell, of which there are several makes differing somewhat in details of construction. One of these is shown in Fig. 28. There has been a strong tendency to supplant open-cell battery installations with closed cells. Rubber-jar batteries for portable service have necessarily been closed. Stationary cells in glass jars are now almost universally closed also, but tank batteries are the last to be provided with closed cells. Their size, ranging from 4000 to 7000 ampere-hours, and the possible accumulation of considerable amounts of explosive gases, unless forced ventilation is provided, have undoubtedly been factors retarding their development. These difficulties appear now to have been solved. Closed cells have obvious advantages from an operating standpoint and they can be installed in rooms with other equipment.

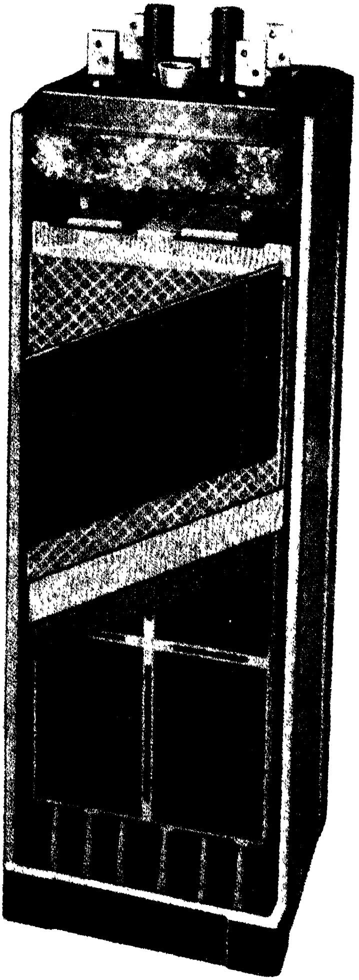

Fig. 28. Closed-tank cell with explosion-proof feature.

i. Approximate Sizes and Capacity of Plates

Although a great many different sizes and kinds of plates for lead batteries have been made from time to time, certain sizes have come into common use, and it is therefore worth while to give a table indicating the most common sizes for different types of service and the nominal capacity per positive plate of cells containing them. In the case of plates for stationary batteries, it will be noticed that there is a simple relation between the capacity of the various sizes, which is hardly suggested by the irregularity of the dimensions. In making use of Table IX it should be remembered that the list of sizes is by no means complete and that the capacity will vary somewhat with the quality and thickness of the plates. The figures which are given here serve as a general guide to the size and performance of these plates.

TABLE IX

Plate Sizes, Lead Batteries

The sizes listed are those most commonly used, but there are variations in dimensions and capacity. The capacities are calculated from the rated capacities of ordinary types.

	Width, Inches	Height, Inches	Nominal Capacity per Positive Plate, Ampere-hours	Rate of Discharge, Hours
Starting and lighting	$5\frac{5}{8}$	5	16	20
Isolated plant	$5\frac{13}{16}$	$5\frac{7}{8}$	22	8
Isolated plant	$7\frac{3}{4}$	$7\frac{3}{4}$	44	8
Car-lighting plates	$7\frac{3}{4}$	$10\frac{1}{8}$	50	8
Vehicle plates	$5\frac{3}{4}$	$8\frac{5}{8}$	28	6
Stationary plates	3	3	5	8
Stationary plates	$4\frac{3}{8}$	4	10	8
Stationary plates	6	6	20	8
Stationary plates	$7\frac{3}{4}$	$7\frac{3}{4}$	40	8
Stationary plates	11	$10\frac{1}{2}$	80	8
Stationary plates	$15\frac{5}{16}$	$15\frac{5}{16}$	160	8
Stationary plates	$15\frac{5}{16}$	$30\frac{3}{4}$	320	8
Stationary plates	$18\frac{5}{8}$	$18\frac{5}{8}$	184	8

8. HAZARDS IN THE PROCESS OF MANUFACTURE

The poisonous nature of lead and its compounds[32] gives rise to certain hazards which deserve attention in the processes of manufacture. Governmental regulations with respect to the conditions of work, however, have greatly lessened the number of cases of lead poisoning occurring among the employees. The sources of poisoning are primarily the dust of lead and its oxides, and the fumes from the melting pots and lead burning. The compounds of lead are poisonous practically in proportion to their solubility.

Bluish fumes may often be observed over the melting pot when the alloy is ladled out or the dross skimmed off. The quantity of these fumes probably depends on the temperature of the molten metal, but they are generally present, and a hood with a forced-air suction is

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[32] *Bulletin* 165, Bureau of Labor Statistics, "Lead Poisoning in the Manufacture of Storage Batteries," by Alice Hamilton, M.D.; see also Hamilton, *J. Indus. Hyg.*, 9, p. 346, 1927; Greenburg *et al.*, U. S. Public Health Reports, 44, p. 1666, 1929; Hackett, *Am. J. Pub. Health*, 24, p. 917, 1934; Russell *et al.*, *Bulletin* U. S. Public Health 205, 1933.

necessary. The dross should not be thrown on the floor. The process of burning the plates to the straps and the connectors to the posts gives rise to lead fumes and requires that good ventilation be provided. Some dust arises from trimming the grids and cleaning the lugs, but the greater quantity of dust is due to the oxides of lead used for pasting the plates. The material for the paste must be weighed and mixed dry. This is a dusty process that requires especial attention. It should be carried on in a separate room provided with forced ventilation, and the operatives should wear respirators. There is less danger in the pasting process when the paste is wet, but scraps of paste falling on the table or floor produce dust. The dust from litharge is not as readily observed as the more brilliant red oxide, but is sometimes said to be more dangerous. Pasting rooms should always be provided with adequate cleaning facilities and ventilation.

The forming rooms are often filled with fumes that are irritating to the throat of a person not accustomed to them. These fumes are caused by the acid being sprayed into the air by bursting bubbles of gas as they rise to the top of the forming tanks. Although the discomfort is greater in such a room as this, the hazard is less. Medical evidence is conflicting as to the possible bad effects of the fumes. It is, of course, necessary that the ventilation be sufficient to carry off the hydrogen generated, in order to avoid explosions, and the sulphuric acid content of the air must be kept low to preserve the insulation as well as to avoid discomfort to the workers.

The larger and more progressive companies making storage batteries have provided the necessary ventilation of various rooms and have also provided washrooms, locker rooms, and in some cases lunch rooms and medical inspection. Sometimes the workmen fail to make intelligent use of the facilities provided and thereby expose themselves to unnecessary risks.

9. THE EDISON CELL (ALKALINE TYPE)

The alkaline type of storage battery is familiarly known in this country as the Edison storage cell. Other forms of alkaline storage batteries are made in Europe, including several forms of the Jungner battery. The names of some of the alkaline batteries are: NIFE, Britannia, Alklum, and Alconum, made in England; S. A. F. T., made in France; DEAC and KAW, made in Germany; NIFE, made in Sweden; and the Drumm battery made in Ireland. The general character of the reactions occurring in these is the same, but they differ in materials and methods of construction.

The positive plates of alkaline batteries are filled with nickelous hydroxide which is converted to a higher oxide of nickel by the process of formation. Since this material is a non-conductor, additions of flake nickel or graphite are made to provide the necessary conductivity. An early form of Edison cell employed graphite for this purpose, but with the change in construction of Edison cells in 1908 the use of graphite was discontinued, flake nickel being used in its place. Some alkaline batteries, however, use graphite.

The negative plates of the Edison type are filled initially with a finely divided mixture of metallic iron, ferrous oxide, and mercuric oxide. Negative plates of the Jungner cells contain a mixture of iron and cadmium. At one time cadmium alone was tried in these cells. The combination, however, proved to be better suited to the purpose.

The electrolyte for all these alkaline cells is a solution of potassium hydroxide in water. To this a small amount of lithium hydroxide is always added for the Edison cells.

Since the Edison cell is the one of chief importance among the alkaline cells in this country, the following discussion relates primarily to this type.

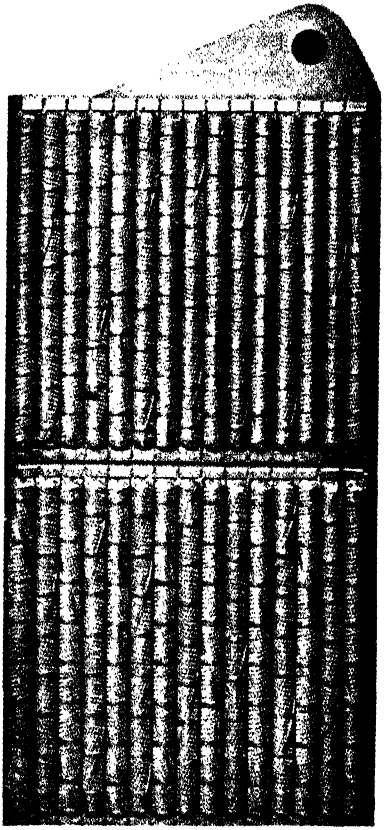

FIG. 29. Positive plate of the Edison cell, type A.

a. Positive Plates

A positive plate is shown in Fig. 29.

Preparation of Nickelous Hydroxide. Metallic nickel in finely divided form is dissolved in sulphuric acid. The hydrogen which is evolved during this process is collected and saved for use in connection with other processes in the manufacture of the cell. Certain impurities, such as copper, zinc, antimony, and iron, are usually present in the solution and must be removed. The solution of nickel sulphate is then sprayed into tanks containing a solution of hot sodium hydroxide. Nickelous hydroxide is precipitated as a result of the reaction which takes place. The precipitate is collected and dried, but it contains considerable amounts of sodium hydroxide, carbonates, and sulphates. These may be removed by leaching the mass with hot water. The nickelous hydroxide is then dried again and tested to determine its quality. If it is found to be satisfactory it is ground and sifted, the material used ranging between 30 and 190 mesh.

Preparation of the Flake Nickel. The flake nickel which is added to the nickelous hydroxide in making the plates is required to give the active material sufficient electrical conductivity. The flake nickel consists of small squares $\frac{1}{16}$ inch on the edge and 0.00004 inch in thickness. It is prepared by an interesting nickel-plating process. Ten revolving copper cylinders are carried by a crane and dipped alternately in copper- and nickel-plating baths for sufficient time to deposit the thin layers of metal which are required. The cylinders are washed by sprays of water between each immersion in the plating tank. This process of alternately plating copper and nickel is repeated 125 times so that the sheet of deposited metal on the cylinders consists of 125 layers each of copper and nickel. The copper-nickel sheet is then stripped from the cylinders and cut into squares $\frac{1}{16}$ inch on the edge. The copper is dissolved chemically, leaving the nickel as thin flakes, each little square yielding 125 of these flakes. The flake nickel is washed and centrifuged and dried over steam coils. In its final state a bushel of the material weighs only $4\frac{1}{2}$ pounds.

FIG. 30. Positive tube of Edison cell.

Tubes to Contain the Active Material. Since 1908, the active material for the positive plates of the Edison batteries has been contained in steel tubes (Fig. 30). Prior to this time the material was contained in pockets somewhat similar to those which are used for the negative plates. This earlier construction was abandoned because of the strains created by the swelling of the active material. The tubes are prepared from cold-rolled carbon-steel ribbon which is perforated by passing through special rolls which punch 560 holes to the square inch. The burrs are removed by emery wheels and the ribbon is cleaned by revolving wire brushes, to insure that the perforations are open so that the electrolyte may have free access to the active material of the plate. The steel ribbon is then nickel-plated. This is done as it passes continuously through a series of tanks containing the necessary solutions for cleaning, plating, and washing. The first of these tanks contains a solution of sodium carbonate to remove the grease from the steel ribbon. This is followed by a tank of hot water to wash off the alkali. The next tank contains a solution of nickel sulphate, in which the nickel plating is done. This is followed by two washing tanks containing hot and cold water, and finally the steel ribbon is passed through a tank containing a dilute solution of ammonium hydroxide. The time required for a given point on this ribbon to pass through the series of plating and other baths is about eight minutes. After the nickel-plating process is finished, the ribbon is dried and annealed in an atmosphere of hydrogen. The purpose of this annealing is to fuse together the nickel plate and the underlying steel in order to prevent possible scaling off of the nickel plating. This is done in an atmosphere of hydrogen to prevent oxidation or discoloration that might otherwise take place.

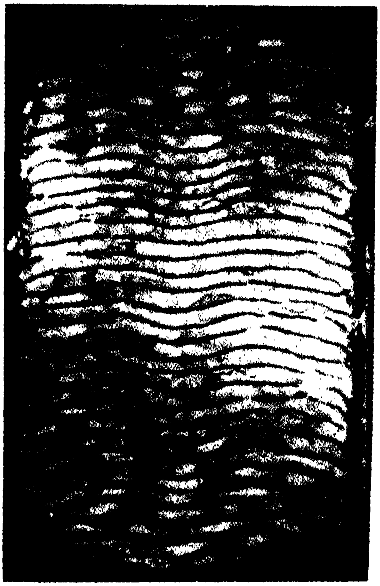

FIG. 31. Magnified section vertically through a positive tube, showing the alternate layers of nickelous hydroxide and flake nickel.

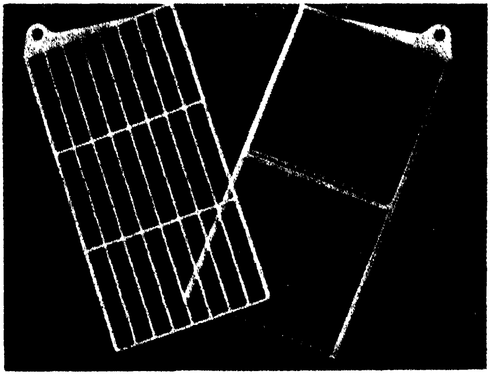

FIG. 32. Grids of the Edison cell; negative left, positive right.

The tubes which contain the active material of the positive plates are made from the nickel-plated steel ribbon, by winding it spirally. The seams are lapped and swaged flat. These tubes are made in rights and lefts, which are alternated in the assembly of the plate, thereby equalizing the strains which would tend to cause buckling. The tubes are made ¼ or $\frac{3}{16}$ inch in diameter with a standard length of 4½ inches.

Filling the Tubes. A cap is placed at the bottom of each tube, and a group of tubes is then put into a filling machine which tamps the active material into them. Eight tubes are mounted in molds below a row of weighted ramrods that fall by gravity, striking a blow of 2000 pounds per square inch. The filling machine is provided with two hoppers, one of which dumps a specified charge of nickelous hydroxide into each tube, and the other a certain quantity of the flake nickel. This is followed by a blow of the ramrod. The process is repeated 315 times, so that there are 630 layers of alternate nickelous hydroxide and flake nickel (Fig. 31). The layer of the nickel is somewhat thinner than the layer of the hydrate, the nickel constituting about 14 per cent of the contents of the tube. After the tubes are completely filled, the ends are pinched shut to form terminals which are suitable for clamping into steel grids. Before being placed in the grids, however, the tubes are reinforced by eight seamless nickel-plated steel rings. These are put on each tube to prevent possible bursting of the tube because of the swelling of the active, material which takes place during the forming process. The active material of the positive plate is said to contract somewhat on discharge.

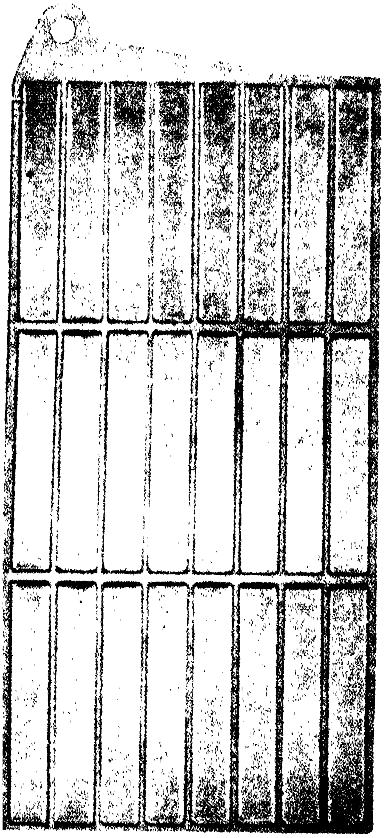

FIG. 33. Negative plate of the Edison cell, type A.

Positive Grids. These are steel punchings (Fig. 32) which are nickel-plated and annealed as has been described above. The pinched ends of the tubes are caught underneath ears projecting from the sides of the plate. The tubes are clamped in place by a hydraulic press.

b. Negative Plates

A negative plate is shown in Fig. 33.

Active Material. Pure iron is dissolved in sulphuric acid. Hydrogen gas is evolved during this process, and this is saved for other uses in the manufacture of the batteries. The iron, in the form of ferrous sulphate, is recrystallized and then centrifuged to free it from mother liquor. It is dried at a temperature of 500° C., and roasted in an oxidizing atmosphere to the ferric state (Fe_2O_3). Traces of sulphate in this material are removed by leaching and it is dried and reduced in an atmosphere of hydrogen in a muffle furnace. The material is allowed to cool in an atmosphere of hydrogen. It is then partially oxidized to ferrous oxide and subsequently dried, ground and mixed with a small per cent of yellow oxide of mercury. The latter is reduced to mercury when the plate is first charged. The mercury serves to increase the conductivity of the mixture and keeps the iron active, overcoming any traces of the ferric oxide.

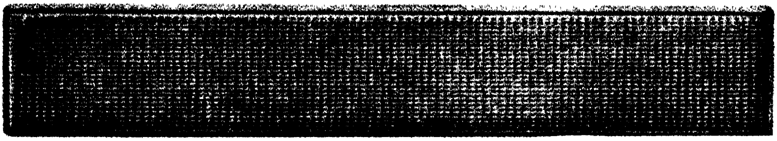

FIG. 34. Negative pocket of Edison cell.

Negative Pockets. The active material for the negative plates is contained in steel pockets (Fig. 34) with perforated sides. These are prepared from nickel-plated ribbon similar to that used for making positive tubes but more finely perforated. The ribbon is cut to the proper length and pressed into a form similar to a box, one end being left open for filling with active material. The pockets are fastened in the negative grid (Fig. 32), which is a nickel-plated steel punching having a series of parallel openings of the proper size to take the pockets of active material. The pockets are put in place and a hydraulic press seals the boxes and crimps the sides. The dimensions of the pockets are given in Table X.

c. Assembly

The necessary number of plates of each kind for any particular size of cell are mounted on steel rods which pass through the eyes of the grids at the top of the plates. The plates are separated from one another by means of washers fitting on this rod and are locked in place by a lock washer and nut on the end of the rod. Groups of positive and negative plates, corresponding to the positive and negative groups of the lead storage batteries, are assembled in this way. The rod which supports the positive or negative plates and connects them

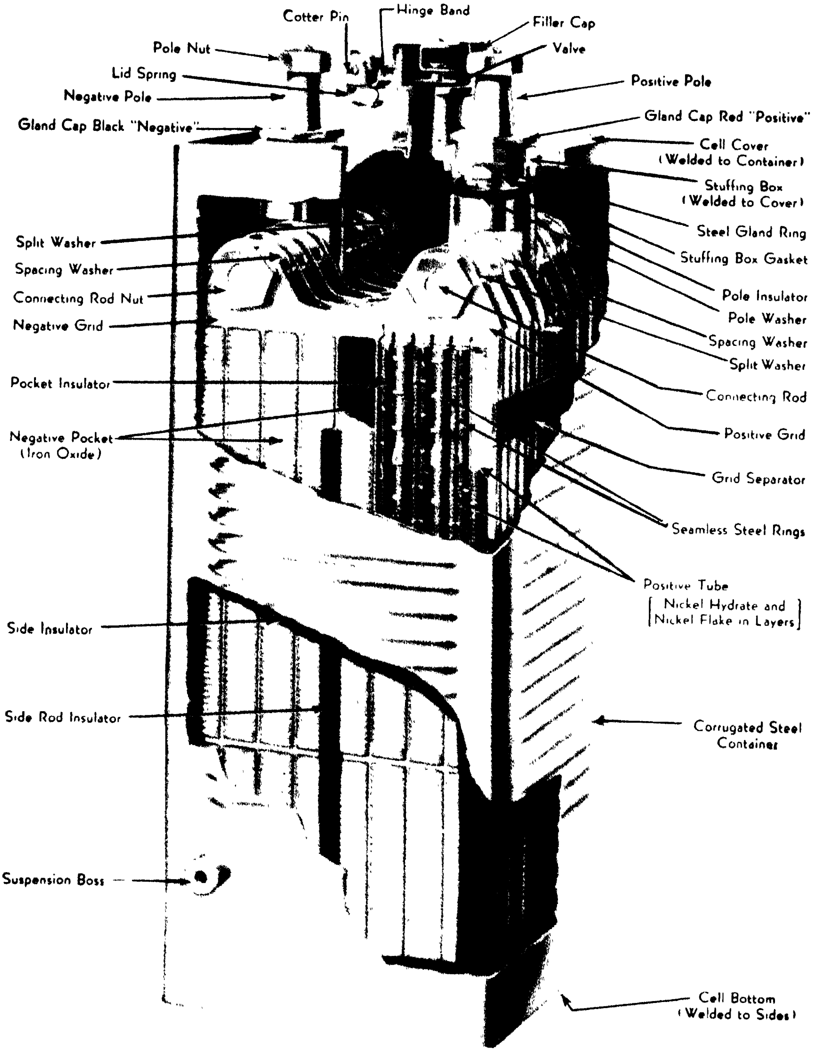

FIG. 35. The Edison cell, nickel-iron or alkaline type of storage cell.

electrically is called the "connecting rod." The groups of positive and negative plates are intermeshed to form the element and the plates of opposite polarity are separated by hard rubber pins. Side separators, consisting of flat sheets of hard rubber, are used around the outside of the element to insulate it from the walls of the container. The element, when completely assembled, is slipped into the containing jar or can and rests upon a bridgework of hard rubber at the bottom. A complete cell is shown in Fig. 35. The can is made from sheet steel, nickel-plated, with sides corrugated to provide additional strength. Some types of the newer cells are without corrugations, however, as thicker metal provides the necessary strength. The metal is bent into shape around a form and the side seams are welded by an oxyacetylene flame. The bottom of the cell is welded to the sides of the can, and after the element is in place the top seams are welded also. The container parts, such as cover, sides, and bottom, are nickel-plated before welding and after welding also. The terminal posts for the plate groups pass through openings in the top of the cell and are sealed into place by a combination of hard and soft-rubber gaskets and bushings. The bushing around the positive pole is red, while that around the negative pole is black. In this way a clear indication of the polarity of the cell is given. In the center of the cover is a combination valve and filler (Fig. 36). This consists of a hemispherical valve equipped with a spring which permits the valve to be opened for filling the cell with electrolyte or water, but normally presses the valve against the seat. As the pressure of gas in the cell rises when it is on charge, the valve is displaced, allowing the gas to escape. This gives rise to the familiar popping sound which is often heard when batteries of this type are being charged. The satisfactory operation of the cell depends in considerable measure upon the gas valve, since the electrolyte, potassium hydroxide, has a strong tendency to absorb the carbon dioxide from the air. The valves may be easily opened, however, for filling the cells with water.

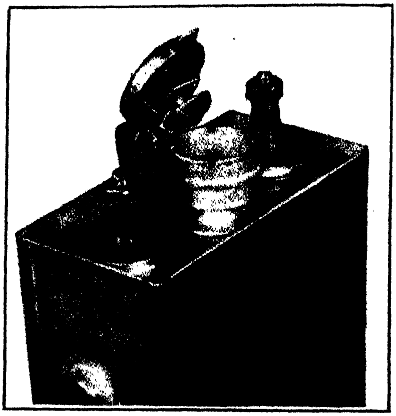

FIG. 36. Gas valve and vent on the Edison cell.

The terminal posts for the cells are of steel, tapered and ground to fit the lugs of the intercell or intertray connectors. The top of the post is threaded to take a lock nut. The lugs of the intercell connectors are drop forgings of steel, bored, reamed, and ground to fit the taper of the terminal posts. Both the terminal posts and the lugs are finished by nickel-plating and annealing in an atmosphere of hydrogen. This prevents the corrosion of the steel and provides a satisfactory contact surface in spite of the thin oxide film that exists on the nickel surfaces. The connecting links are copper swaged into the lugs and the whole nickel-plated. The lugs may easily be removed from the terminal posts by the use of a wrench and jack; these tools are necessary because the lug generally becomes "frozen" to the posts.

d. Electrolyte

The electrolyte for the alkaline cells is a solution of potassium hydroxide in water. For the Edison cells a small amount of lithium hydroxide is added because of its beneficial effect on the capacity of the cells. As a substitute for the potassium hydroxide, an electrolyte of sodium hydroxide has been tried, but the physical properties of this solution are not as good for the purpose as those of the potassium solution. The preparation of the electrolyte and the physical properties of it are described in Chapter III.

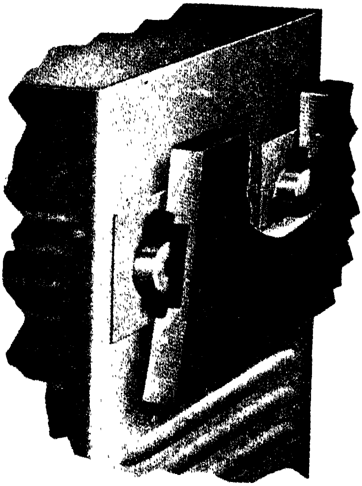

FIG. 37. Method of supporting Edison cells in the tray.

e. Trays

The cells are usually mounted in trays which have open sides and in most cases are bottomless. Some of the larger locomotive batteries are now available in steel cradles or steel boxes. The cells are supported in these trays by bosses (Fig. 37) on the sides of the cans of the individual cells. The bosses fit into rubber buttons in the sides of the tray. These supports serve also to separate and insulate the cells, which is quite necessary because the containers for these cells are metallic conductors. The outside surface of the cells is coated with an insulating paint and a film of rosin or liquid "Esbaline" is used to protect the top.

f. Types and Sizes of Edison Plates

The sizes of the Edison batteries are described in Chapter X in connection with the discussion of applications which are made of them. In this place, however, will be given a table analogous to that which has been given for the lead batteries, showing the different types of plates for Edison storage batteries, the number of tubes and pockets that they contain, with dimensions, and the nominal capacity of these plates at the normal rate of discharge. The nomenclature for the Edison cells is simple. The type of cell is designated by a letter followed by a number. The letter indicates the type of plate which the cell contains, and the number indicates the number of positive plates. An exception to the above rule in the case of the Edison batteries is made for the smaller sizes; for these the number indicates the number of positive tubes instead of the number of positive plates.

TABLE X

TYPES OF EDISON STORAGE-BATTERY PLATES

The types of plates are designated by letters; the types of cell by letters and numbers, the former indicating the type of plate and the latter the number of positive plates in the cell, except in case of the smaller sizes, Types M and Ratings are based on 5-hour discharge for types A, B, C, D, M, N, F and on $3\frac{1}{3}$ hour discharge for types G, J, and L.

Type of Plate	Number of Tubes per Positive Plate	Dimensions of Tubes		Number of Pockets per Negative Plate	Dimensions of Pockets			Nominal Capacity per Positive Plate, Ampere-hours
		Diameter, Inch	Length, Inches		Length, Inches	Width, Inch	Thickness, Inch	
A	30	$\frac{1}{4}$	$4\frac{1}{2}$	24	3	$\frac{1}{2}$	$\frac{1}{8}$	37.5
B	15	$\frac{1}{4}$	$4\frac{1}{2}$	16	$2\frac{5}{32}$	$\frac{1}{2}$	$\frac{1}{8}$	18.75
C	45	$\frac{1}{4}$	$4\frac{1}{2}$	40	†	$\frac{1}{2}$	$\frac{1}{8}$	56.25
D	60	$\frac{1}{4}$	$4\frac{1}{2}$	48	3	$\frac{1}{2}$	$\frac{1}{8}$	75.0
G	40	$\frac{3}{16}$	$4\frac{1}{2}$	24	3	$\frac{1}{2}$	$\frac{3}{32}$	25.0
J ‡	20	$\frac{3}{16}$	$4\frac{1}{2}$	16	$2\frac{5}{32}$	$\frac{1}{2}$	$\frac{1}{8}$	12.5
M	7	$\frac{1}{4}$	$3\frac{1}{8}$	3	3	$\frac{1}{2}$	$\frac{1}{8}$	5.62
L	10*	$\frac{3}{16}$	$4\frac{1}{2}$	8	$2\frac{5}{32}$	$\frac{1}{2}$	$\frac{3}{32}$	6.25
N	7	$\frac{1}{4}$	$3\frac{1}{8}$	3	3	$\frac{1}{2}$	$\frac{1}{8}$	5.62
F	4	$\frac{1}{4}$	$4\frac{1}{2}$	4	$2\frac{5}{32}$	$\frac{1}{2}$	$\frac{1}{8}$	5.0

* The numbers for types M and L indicate the number of positive tubes in the battery instead of the number of positive plates.

† Twenty-four pockets are 3 inches and 16 pockets are $2\frac{5}{32}$ inches.

‡ No longer made.

The standard plate for the Edison battery is called the A plate. This is designed for general purposes, electric vehicles, trucks, locomotives, isolated farm lighting plants, and railway train lighting. The next most common plate is known as the B plate. It is used for lighting service, ignition, fire- and burglar-alarm systems, and clocks. B plates have half the capacity of A plates. C plates are equal to an A plate plus a B plate. D plates have double the capacity of A plates. The G plate contains positive tubes of $\frac{3}{16}$-inch diameter instead of the more usual $\frac{1}{4}$-inch tubes and is designed especially for service on electric locomotives which require a battery of small internal resistance because of the heavy demands made upon the battery for current. The G-type plate was designed to act similarly to the thin plates used in lead batteries and it has some of the same disadvantages, such as shorter life than the standard A plate. The L-type is used in cells for hand lanterns. The M and N types contain positive tubes $3\frac{1}{8}$ inches long and seven tubes to the plate. These are small plates designed for use with mine lamps, clock circuits, and time recorders. In addition to the types named above, there is also the F plate, used in mine-lamp batteries. The J type is not made at the present time.

Some types of cells are designated by additional letters H or HW. These signify variations in the container, thus A6H is an A6 cell in a container that has extra height and A6HW has extra height and width. The additional space allows more electrolyte to be used so that flushing is required less often.

10. NICKEL-CADMIUM CELLS (ALKALINE TYPE)

Although nickel-cadmium cells are little known in this country, their production in Europe has increased greatly since 1930. They are used for train lighting, mine lamps, tractors and trucks, military purposes, and, since 1935, for starting and lighting service on buses and trucks. Cadmium is said to be less subject to self discharge than iron and is relatively free from passivity at low temperatures. The average voltage of a cell on discharge is about 1.2 volts.

Nickel-cadmium cells have many points of similarity with nickel-iron cells. The active materials of the positive plates, the electrolyte, and some features of construction are essentially the same. The chief difference lies in the negative plates which contain cadmium or a mixture of cadmium and iron as the active materials. Jungner[33] patented a cell having cadmium in the negative plate about the same time Edison patented his nickel-iron cell.

The fundamental chemical reactions in a nickel-cadmium cell are somewhat uncertain, especially in regard to the hydrated state of the active materials and the part which iron takes in the reactions at the

[33] British patent 7768, 1900; German patents 110,210, 113,726, and 114,905, 1899.

negative plates. The net result of the reaction, however, is the transfer of oxygen from the active material of one plate to that of the other, without measurable change in the electrolyte as a whole. The reactions are usually written as follows:

$$Cd + Ni_2O_3 \rightleftarrows CdO + 2NiO \quad \text{(main reaction)}$$

$$Cd + NiO_2 \rightleftarrows CdO + NiO \quad \text{(secondary reaction)}$$

The principal part of the current is supplied by the main reaction, but the secondary reaction may supply part, if discharge is made within a few hours after completing the previous charge.

The positive and negative plates are usually similar in construction, consisting of perforated pockets which contain the active materials. However, the positive plates in some types of nickel-cadmium cells are of tubular construction and resemble closely those found in Edison cells. The pockets for both positive and negative plates are made from perforated steel ribbon which has been nickel-plated and annealed in hydrogen. Provision must be made for expansion of the positive active materials within the pockets. This expansion which occurs during the first few cycles of charge and discharge may increase the thickness of the pockets by as much as 35 per cent. The pockets are joined together in the grid as shown in Fig. 38.

FIG. 38. One form of connection of negative pockets in plates of nickel-cadmium batteries.

The active material for the positive plate is nickelous hydroxide. This is precipitated from solutions of nickel sulphate, $NiSO_4$, by solutions of sodium hydroxide, NaOH, under conditions that must be carefully controlled in order to obtain material of the required structure. The precipitate comes down as a fine dispersion with strong adsorptive properties. This precipitate is then treated with caustic solutions and dried. The nickel content of the final product is usually less than 63.2 per cent, corresponding to the formula. When used in plates of tubular construction, nickel flakes are added to increase the conductivity, as in the Edison cell, but in plates of the pocket construction a highly purified (ash less than 1 per cent), flaky, natural graphite is employed. Precautions must be taken to avoid impurities such as iron which can decrease the activity of the nickel oxides.

Pockets of the negative plates are filled initially with cadmium oxide, CdO, or cadmium hydroxide, $Cd(OH)_2$, either of which is reduced to metallic cadmium in a spongy form on the first charge. Most manufacturers of these cells add iron (5 to 30 per cent) to the cadmium in order to obtain the required degree of fineness of the cadmium. The beneficial effect of the iron seems to be a more or less empirically determined fact, and the real function of the iron is not entirely clear. Some have thought that it forms an alloy with the cadmium, others have regarded it as an expander, while others think that the sole function of the iron is to bring about a finely divided state of the electrolytically precipitated cadmium. Iron in the metallic state undoubtedly increases the conductivity of the active material, but cadmium oxide itself is a reasonably good conductor. Whether iron oxidizes during discharge is also subject to differences of opinion. Crennell and Lea[34] indicate that it may do so and contribute a small part of the discharge capacity, but Hauel[35] is of the opinion that the iron takes no part in the current-producing process.

The electrolyte is a solution of potassium hydroxide, KOH, having a specific gravity of 1.19 to 1.25. To this, some, but not all, manufacturers of nickel-cadmium cells add a small amount of lithium hydroxide, $LiOH$. The lithium is without action on the negative plates but affects the positive plates as in the case of Edison cells. Absorption of carbon dioxide from the air, or its presence in water used to flush the cells, eventually necessitates renewal of the solution. Opinions differ as to how much carbonate is permissible in the electrolyte, but this may depend in part on the conditions of service. Some place the limit at 30 grams per liter of solution while others may permit as high as 90 grams per liter in batteries operated at currents not above the normal rate. Hauel has found, as a result of single-electrode measurements, that the detrimental effects of carbonates are at the negative plates while the positives are unaffected. She concludes, therefore, that poorly conducting layers of $CdCO_3$ form over the active materials of the negative plates and produce the sluggishness characteristic of cells containing excess carbonates. Renewal of the electrolyte is usually sufficient to restore the cells to full capacity. The freezing point is $-28°$ C. regardless of the state of charge. The electrolytes have a resistivity that is slightly higher than the sulphuric acid electrolyte used in lead batteries. This is a handicap for alkaline batteries that must deliver large currents, but it has been met in part by increasing the plate area and decreasing the separation of the plates, with the result that nickel-

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[34] *Alkaline Accumulators*, p. 120, 1928.

[35] *Trans. Electrochem. Soc.*, 76, p. 435, 1939.

cadmium batteries are finding use for starting service on buses and trucks in Europe. Within the past five years such batteries have been made with plates 1 to 2 millimeters thick and spaced less than 1 millimeter apart by hard-rubber strips serving as separators. This alone would not make automotive starting possible if it were not for the added fact that the cadmium plate does not become passive at high-current rates and low temperatures. Characteristic curves are shown in Chapter VI.

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CHAPTER III

THE ELECTROLYTE

The electrolyte for lead storage batteries is a solution of sulphuric acid. This has been used since the beginning of the industry. In this chapter a brief description of the preparation of sulphuric acid and the physical and chemical properties of its solutions, which are of importance in studying the general subject of storage batteries, will be given.

Sulphuric acid is one of the most important of chemical compounds because of the great variety of its uses. Its manufacture antedates the beginnings of modern chemistry. It is marketed under a variety of names, depending on the strength and purity of the acid. *Chamber acid* is a dilute acid containing from 62 to 70 per cent sulphuric acid; *tower acid* contains 75 to 82 per cent acid; *oil of vitriol* contains 93 to 97 per cent acid; *monohydrate* contains 100 per cent acid; *fuming acid*, or *oleum*, contains sulphur trioxide dissolved in concentrated sulphuric acid. The strongest acid that can be prepared by evaporation is about 98.5 per cent. The significance of these names will appear in later sections. For the storage battery, the chemically pure oil of vitriol, diluted to the proper concentration, is of greatest importance. Since the term "oil of vitriol" is often used to designate the more impure or technical grade of acid, including the brown oil of vitriol, it is better to adhere to the term "sulphuric acid," meaning thereby the chemically pure acid. The amount of this concentrated acid used per year in this country for storage-battery purposes is probably in excess of 50,000,000 pounds.

1. THE PRODUCTION OF SULPHURIC ACID

Sulphuric acid in the free state occurs in small quantities in volcanic regions, and natural sulphates are abundant; but these sources are not utilized for producing the acid in large quantities. The commercial processes are based on the oxidation of sulphur dioxide to the trioxide state, which in combination with water yields sulphuric acid.

The combustion of sulphur in the air results in the formation of sulphur dioxide, SO_2, which is a colorless gas having a suffocating odor. This dioxide is not combustible, but may be further oxidized to sulphur trioxide, SO_3, through the agency of nitrogen oxides or in the presence of certain catalysts. The trioxide of sulphur is also called sulphuric anhydride. It is a transparent crystalline solid that unites with water, with explosive violence, and with the evolution of a large amount of heat, forming sulphuric acid. The general reaction may be represented by the following equation:

$$SO_2 + O + H_2O = H_2SO_4$$

This reaction, however, is not as simple as the equation would indicate. The oxidation of the dioxide to the trioxide state is a slow reaction that is difficult to perform, and the sulphuric anhydride forms, with the water, a series of compounds that are called hydrates. These may be represented by the formula $m \cdot SO_3 \cdot n \cdot H_2O$ in which m and n are whole numbers indicating the number of gram-molecules of the anhydride and water, respectively. If m is less than n or equal to it, the acid is of the ordinary non-fuming variety. When m exceeds n, the formula represents fuming sulphuric acid. This fact enables us to distinguish the fuming from the non-fuming acid by the percentage content of the sulphuric anhydride. One gram-molecule of the anhydride weighs 80.06 grams, and a gram-molecule of water weighs 18.016 grams. The limiting percentage of the anhydride in the non-fuming acid is, therefore, the ratio of 80.06 to 98.076 which equals 81.63 per cent.

Since 98.076 is the molecular weight of sulphuric acid, according to the formula H_2SO_4 it is possible to compute from the limiting percentage of the anhydride the amount of it present in any solution when the percentage of sulphuric acid is known. For example: The acid of specific gravity 1.300, commonly used in certain types of batteries, contains 39.1 per cent of sulphuric acid and $39.1 \times 0.8163 = 31.9$ per cent of the sulphuric anhydride.

Two processes are used at the present time for the manufacture of sulphuric acid. These are commonly called the "chamber" and the "contact" processes. The difference between them consists in the method employed to oxidize the sulphur dioxide to the trioxide state. The contact process is supplanting the chamber process for the preparation of concentrated acid, but about half of the sulphuric acid produced in the United States is made by the chamber process.

As a preliminary to either of these processes, the production of sulphur dioxide is necessary. The purest sulphur dioxide is produced by the direct combustion of sulphur, but a common method is by the roasting of iron pyrites, which contain ordinarily from 40 to 50 per cent of sulphur. Other raw materials include zinc blende, galena, and the spent oxides of gas works. The oxide obtained by burning pure sulphur is free from arsenic, iron, copper, and zinc, which usually appear in the gas obtained by roasting the pyrites.

In the chamber process, the oxidation of the sulphur dioxide is effected by the aid of oxides of nitrogen in a series of lead-lined chambers, from which the process takes its name. The hot gases from the sulphur burners or the roasting ovens pass into a tower, called the Glover tower, filled with broken firebrick over which flows a stream of dilute sulphuric acid (part of the acid from the chambers), which cools the gases and effects a partial concentration of acid. Concentrated sulphuric acid, containing oxides of nitrogen, also flows in this tower. The oxides of nitrogen are liberated near the top of the tower by the dilution of the strong acid by the weak acid. The oxides of nitrogen and sulphur mix, starting the formation of the sulphur trioxide, which process is continued in the chambers to which the mixed gases next pass. Water and nitric acid are sprayed into these chambers. The former absorbs the trioxide as it forms. The oxides of nitrogen pass on to the Gay-Lussac tower, where they are reabsorbed by concentrated sulphuric acid and are used again. The principal product of the plant is the chamber acid drawn from the chambers. As this is relatively dilute it is concentrated by evaporation. Platinum, iron, silica, and glass serve as materials for the concentrating apparatus. These materials are not entirely inert. About one gram of platinum is lost per ton of acid that is concentrated in platinum stills or dishes. This represents about one part of platinum in one million parts of the acid, which would be sufficient to cause trouble in a storage battery. Platinum has become so expensive that it is rarely used now for this purpose.

The contact process is simpler. Sulphur dioxide may be oxidized to the trioxide state in the presence of sponge platinum and certain other catalysts, at a temperature of about 400° to 450° C. The process will proceed with evolution of much heat after being started. Other catalysts that are sometimes employed for this purpose are iron oxide and vanadium. The combination of pure water and pure sulphur trioxide results in the formation of pure sulphuric acid, which may be made of any desired degree of concentration. The contact process also requires two stages for the formation of sulphuric acid. These may be represented by the following formulas:

$$SO_2 + O = SO_3$$

and

$$SO_3 + H_2O = H_2SO_4$$

Impurities, such as arsenic from the pyrite, must be removed, as they interfere with the action of the catalysts.

Storage batteries require the highest purity of sulphuric acid. For this reason acid made from pure sulphur is preferable to acid made from pyrites. The source of the acid cannot always be ascertained, and it is important, therefore, to have specifications to insure an adequate degree of purity.

The conditions for storing and shipping sulphuric acid vary with the concentration. Acid up to about 75 per cent has little effect on lead; above this strength the acid attacks lead if hot. Concentrated acid readily dissolves lead at about 250° C. Monohydrate and fuming acid attack lead at ordinary temperatures. Strong acid, particularly the concentrated acid, has very little effect on iron. Cast iron is somewhat more resistant than wrought iron, except that the former is not suitable for use with fuming acid. Alloys of iron and silicon are very resistant to the non-fuming acid and are extensively used for concentrating the acid up to 98 per cent. Dilute acid cannot be stored in iron containers, and glass carboys or lead-lined tanks are generally used for this purpose.

2. PROPERTIES OF SULPHURIC ACID SOLUTIONS

Concentrated sulphuric acid is a clear, colorless, and odorless liquid having the consistency of a light oil. Its specific gravity is 1.84 at 15° C. (59° F.) and it contains about 95 per cent acid. It is miscible in all proportions with water, forming a series of hydrates, several of which are of interest in battery investigations. When the acid is mixed with water a large amount of heat is evolved. Its affinity for water is so great that it can extract the elements oxygen and hydrogen to form water from some organic substances, such as the wood used for separators in storage batteries. Wood becomes charred if immersed in moderately strong acid. The acid extracts the oxygen and hydrogen from the wood, leaving the carbon which gives the wood a darkened appearance. The concentrated acid boils at 338° C. (640° F.). When boiled, it liberates a gas of the same composition, which appears as a dense white vapor because of the absorption of water vapor from the air.

a. Heat of Dilution

The amount of heat which is liberated when one gram-molecule of acid is diluted with *n* gram-molecules of water is shown in the following table. When the amount of water added is so great that the solution may be considered to be infinitely dilute, the total heat evolved is found to be 23.54 kilogram-calories. In Table XI, the difference between amounts of heat liberated at any two different concentrations represents the amount of heat that would be liberated in diluting the more concentrated to the less concentrated solution. For example: By diluting $H_2SO_4 \cdot 3H_2O$ to $H_2SO_4 \cdot 100H_2O$, the amount of heat evolved is $17.92 - 11.88 = 6.04$ kilogram-calories. The kilogram-calorie is the amount of heat required to raise the temperature of one kilogram (2.2 pounds) of water one degree Centigrade, the initial temperature being 15° C.

TABLE XI

Relative Heat Content, Heat of Dilution, and Specific Heat of Sulphuric Acid Solutions

(One mole of sulphuric acid is diluted with *n* moles of water.)

n Moles of H_2O	Per Cent of H_2SO_4	Specific Gravity at 25° C.	Relative Molal Heat Content at 25° C., in Kilogram-Calories	Heat * of Dilution at 25° C., in Kilogram-Calories	Specific Heat (Heat Capacity) at 25° C., in Calories per Gram
0	100	.....	23.54	0	0.337
....	93.19	...	20.35	3.19	0.370
1	84.48	1.774	16.72	6.82	0.442
2	73.13	1.648	13.58	9.96	0.466
3	64.47	1.548	11.66	11.88	0.501
5	52.13	1.416	9.45	14.09	0.582
10	35.25	1.262	7.30	16.24	0.722
20	21.40	1.150	6.23	17.31	0.831
50	9.82	1.066	5.78	17.76	0.918
100	5.16	1.034	5.62	17.92	0.955
200	2.65	1.017	5.41	18.13	0.976
400	1.34	1.009	5.02	18.52	0.987
1,600	0.34	1.002	4.04	19.50	0.997
6,400	0.08	.....	2.90	20.64	......
25,600	0.02	.....	1.54	22.00	......
∞	0.00	1.000	0.00	23.54	0.9989

* The heat liberated when the ordinary concentrated acid (93.19 per cent) is diluted can be calculated by subtracting the respective molal heat contents from 20.35 kilogram-calories.

The relative heat content of sulphuric acid solutions is of importance in the theory of storage batteries because of the relation that exists between the voltage and the concentration of the acid. In Chapter IV it will be shown that the voltage of a lead storage cell varies in a definite way with the concentration of the acid in the pores of the plates. It is possible to calculate, as Dolezalek[1] has done, the voltage corresponding to various concentrations of electrolyte, by an application of the laws of thermodynamics.

Although the amount of heat evolved when the acid is diluted with a given portion of water is accurately known, the temperature to which the mixture rises will depend on the specific heat of the liquid (which varies somewhat with temperature) and the radiation of heat from the solution. When a large amount of acid is prepared for use in storage batteries by dilution in a lead-lined tank, the radiation of heat is proportionately less than when smaller amounts are mixed in containers having less heat insulation. In any case, if it is assumed that the radiation of heat is negligible, it is possible to compute the maximum temperature to which the solution will rise from the heat evolved and the specific heat. For example: If 1 gram-molecule of acid (98 g.) is mixed with 10 gram-molecules of water (180 g.), the initial temperature being 15° C., the temperature rise (neglecting radiation) will be

$$(t^\circ - 15^\circ) = \frac{16{,}240 \text{ cals.}}{0.722 \times 278} = 81^\circ$$

whence $t^\circ = 81^\circ + 15^\circ = 96^\circ$. By experiment with a glass beaker wrapped in a towel, the maximum temperature attained was 85°.

Storage-battery electrolyte is sometimes prepared from the acid of 1.400 sp. gr. In such a case the heat of dilution is $16.00 - 14.35 = 1.65$ kilogram-calories, which is only 10 per cent of the heat evolved if electrolyte of 1.280 sp. gr. is prepared from the concentrated acid.

b. Contraction of the Solution

When one volume of sulphuric acid is diluted with one volume of water, the volume of the solution is not two volumes, but slightly less after the solution has cooled to the initial temperature. So it is, also, for any proportions of the acid and water; the sum of the original volumes exceeds the volume of the solution. The contraction is greatest for solutions having a specific gravity of 1.600. Table XII shows the contraction of solutions of various concentrations.

It is often convenient to dilute the sulphuric acid by measured volumes to obtain a required percentage strength or specific gravity. Allowance must be made for the contraction of the solution in estimating the required proportions of acid and water. To facilitate the preparation of such solutions, the percentage content of sulphuric acid solutions by both weight and volume is given in Table XIX.

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[1] *Theory of the Lead Accumulator*, p. 61.

TABLE XII

CONTRACTION OF SOLUTIONS OF SULPHURIC ACID

(The contraction is expressed as cubic centimeters per kilogram of the solution, 18°C.)

Specific Gravity	Contraction *	Specific Gravity	Contraction *
1.000	0	1.500	60
1.100	25	1.600	62
1.200	42	1.700	60
1.300	51	1.800	48
1.400	57		

* Calculated from Pickering's results, *J. Chem. Soc.*, 57, p. 148, 1890.

To illustrate the application of Tables XII and XIX to the preparation of electrolytes of various concentrations for storage batteries, the following example is given: Required the percentage of sulphuric acid by volume in a solution of 39.1 per cent by weight (1.300 sp. gr.). One liter of the concentrated acid weighs 1840 grams, whence $\frac{1840}{0.391} = 4706$, the total weight of the solution containing 1840 grams of acid. Subtracting from this the weight of the acid, the weight of water is found to be 2866 grams. Since the specific gravity of the water is unity by definition, the sum of the volumes is $2866 + 1000 = 3866$ cc. The percentage of H_2SO_4 by volume on this basis would be $\frac{1000}{3866} = 25.9$ per cent, which is not the correct result. Table XII shows the contraction to be $51 \times 4.706 = 240$ cc. The true volume of the mixture is, therefore, $3866 - 240 = 3626$ cc. and the true percentage of acid by volume is $\frac{1000}{3626} = 27.6$ per cent, as shown in Table XIX.

c. Resistivity

The resistance to the passage of an electric current through the electrolyte varies with the concentration and the temperature. The resistivity is a property of the substance itself. It is the resistance of a specimen one centimeter in length and one square centimeter in cross section. The relation $R = \rho \frac{l}{s}$, where R is the resistance, ρ the resistivity, l the length, and s the cross section, indicates the unit for measuring the resistivity. This may be written $\rho = R\frac{s}{l}\cdot$ Since the area s has the dimensions of length squared, the dimensional formula for resistivity is the product of a resistance and a length. The unit of resistivity is, therefore, the "ohm-centimeter." It is sometimes spoken of as "ohms per centimeter cube."

The electrolytes used in storage batteries are within the range of lowest resistivities of sulphuric acid solutions. It has been known for many years that solutions of about 30 per cent (1.223 sp. gr. at 15° C.) sulphuric acid have minimum resistivity, but only recently has it become known that the proportions of acid and water must be varied slightly to obtain minimum resistivity at other temperatures. Thus, at +30° C. the solution of least resistance contains 31.5 per cent of the acid, but at −25° C. the solution should contain 26.5 per cent. The resistivity of sulphuric acid solutions increases rapidly as the temperature is decreased, particularly when the temperature is below 0° C. (32° F.). Recent determinations[2] of the resistivity are given in Table XIII.

TABLE XIII

RESISTIVITY OF SULPHURIC ACID SOLUTIONS

Temperature		Resistivity in Ohm-Cm.				For Minimum Resistivity	
° C.	° F.	15%	25%	35%	45%	Per Cent	Ohm-Cm.
30	86	1.596	1.180	1.140	1.312	31.5	1.129
25	77	1.689	1.261	1.231	1.422	31.1	1.213
20	68	1.800	1.357	1.334	1.549	30.6	1.310
10	50	2.090	1.606	1.602	1.885	29.8	1.562
0	32	2.51	1.961	1.998	2.371	28.8	1.928
−10	14	.....	2.50	2.60	3.10	27.9	2.48
−20	−4	.....	3.35	3.57	4.31	26.9	3.34
−30	−22	.....	.....	5.29	6.35	....	.....
−40	−40	.....	.....	8.39	9.89	....	.....

The resistivity of the electrolyte is one of the most important factors in determining the resistance of a storage cell. Unless the internal resistance of the cell is small, a considerable portion of the useful energy of the cell is expended within the cell itself.

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[2] Vinal and Craig, *J. Research,* Nat. Bureau of Standards, 13, p. 689, 1934.

d. Freezing Points

The freezing point of the electrolyte varies with its concentration. It is, therefore, often said to vary with the state of charge of the battery. The importance of knowing the freezing points has increased because of the use of storage batteries on automobiles and airplanes, which are often subjected to low temperatures in cold climates and at high altitudes. The freezing points of sulphuric acid solutions were carefully determined many years ago by Pickering.[3] On page 338 of his paper, the whole freezing-point curve from dilute to concentrated solutions is given. There are several maxima and minima in the curve, owing to the hydrates of sulphur trioxide that are formed at the different concentrations.

In Table XIV the freezing points of solutions corresponding to the specific gravities of the first column are given. These values are in accord with the values adopted as standard by the Manufacturing Chemists' Association in this country. The specific gravities are for the solutions at 15° C. and not at the freezing point. For certain concentrations, a considerable error may be made in estimating the freezing point if allowance is not made for the change in specific gravity at the low temperatures. The temperature coefficient of specific gravity for both the Centigrade and Fahrenheit scales, for all concentrations of electrolyte, is given in Table XIX.

TABLE XIV

FREEZING POINTS OF SOLUTIONS OF PURE SULPHURIC ACID

Specific Gravity 15° C.	Freezing Points		Specific Gravity 15° C.	Freezing Points	
	Centigrade	Fahrenheit		Centigrade	Fahrenheit
1.000	0	+32	1.450	−29	−20
1.050	− 3.3	+26	1.500	−29	−20
1.100	− 7.7	+18	1.550	−38	−36
1.150	−15	+ 5	1.600	*	*
1.200	−27	−17	1.650	*	*
1.250	−52	−61	1.700	−14	+ 6
1.300	−70	−95	1.750	+ 5	+40
1.350	−49	−56	1.800	+ 6	+42
1.400	−36	−33	1.835	−34	−29

* Freezing points indeterminate.

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[3] *J. Chem. Soc.*, 57, p. 331, 1890.

The freezing points of solutions of pure sulphuric acid are not exactly the same as the freezing points of electrolyte of the same specific gravity taken from storage batteries. The difference is small. For electrolytes of less than 1.290 sp. gr. the freezing points are slightly higher, and for greater specific gravities the freezing points are lower than for solutions of pure acid. Figure 39 shows the freezing point curves of both the pure acid solutions and the battery electrolyte.

In Fig. 39 there is also shown a series of curves in which the specific gravities of solutions are plotted at every ten degrees between 0° and 60° C. and extrapolated below 0° until they intersect the freezing-point curve. These curves were chosen so that specific gravities of 1.200, 1.225, 1.250, etc., fall on the 25° line. By means of this diagram, the freezing point of any electrolyte may be estimated with reasonable accuracy if the specific gravity and temperature are known. For example: The electrolyte in a battery at −20° C. (−4° F.) is found to be 1.256 sp. gr. This point is located on the diagram, and the nearest oblique line is followed to its intersection with the freezing-point curve of the electrolyte, for which the ordinate is −38° C. (−36° F.). The

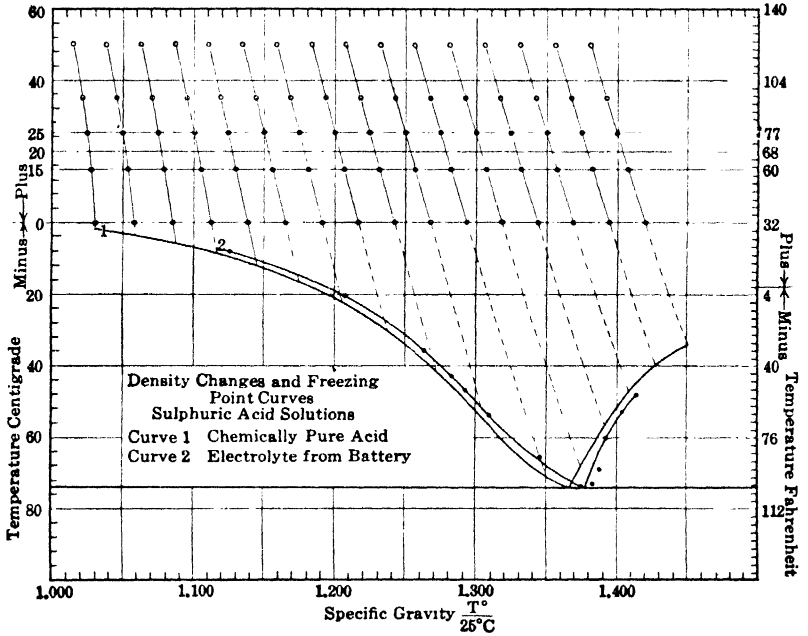

FIG. 39. Freezing-point curve for electrolyte and solutions of sulphuric acid.

temperature can, therefore, fall 18° C. (32° F.) before the electrolyte will begin to freeze.

The lowest freezing point is for solutions having a specific gravity of 1.290. When solutions of lower specific gravity than this freeze, crystals of ordinary ice separate from the solution; for higher specific gravities the crystals are of the tetrahydrate of the acid. Since the lowest freezing points are for concentrations of acid corresponding to the electrolyte of automobile batteries when fully charged, it is apparent that there is no danger of such a battery freezing even under the most severe conditions. If the battery is discharged, however, it will freeze at approximately −10° C. (+14° F.) or even higher. Electrolyte, or acid for preparing it, should be of the proper specific gravity when stored under severe conditions. Electrolyte of from 1.225 to 1.400 sp. gr. will not freeze under ordinary conditions, but nearly concentrated acid of 1.800 sp. gr. freezes at +5° C. (+41° F.). For concentrated acid the freezing point is much lower. At 1.835 it is −34° C. (−29° F.).

e. Vapor Pressure

Sulphuric acid is a powerful drying agent. Concentrated acid readily absorbs water vapor from the air in such quantities that a carboy left unstoppered will soon overflow if nearly filled with acid. Solutions of sulphuric acid have a definite vapor pressure that varies with the concentration and the temperature. The values of the vapor pressure are of theoretical interest in connection with storage batteries, for the same reason as applied to the heat of dilution.

The electrolyte is often said to "evaporate"; most of the water lost from the cells, however, passes off as oxygen and hydrogen during charging. The electrolyte will absorb or give off water vapor according to the relative magnitude of its vapor pressure as compared with that of the surrounding air. If the vapor pressure of the electrolyte exceeds that of the water vapor in the air, evaporation will take place; if it is less, moisture will be absorbed. The simplest method of determining the pressure of water vapor in the air is by some form of dew-point apparatus, or a wet-and-dry bulb hygrometer. The temperatures obtained in such a measurement are referred to suitable tables,[4] in which the corresponding vapor pressures, expressed in millimeters of mercury, are given. For example: On a humid and hot summer day, temperature 95° F. (35° C.) and relative humidity of 87 per cent, the vapor pressure would be 36.7 millimeters; on an average day, tempera-

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[4] *Smithsonian Tables*, 8th ed. revised, p. 236, is a convenient table for use with a ventilated hygrometer.

ture 66° F. (19° C.) and relative humidity of 57 per cent, the vapor pressure would be 9.2 millimeters. These values should be compared with the vapor pressures for solutions of sulphuric acid given in Table XV to determine whether evaporation or absorption of moisture will take place. Such a comparison shows that the electrolyte of specific gravity 1.300 will absorb water in the first case and evaporate in the second case.

TABLE XV

Vapor Pressure of Solutions of Sulphuric Acid

(The vapor pressures are expressed in millimeters of mercury.)

Specific Gravity at 15° C.	Percentage of H_2SO_4	At 0° C. mm.	At 15° C. mm.	At 25° C. mm.	At 35° C. mm.
1.000	0.0	4.6	12.8	23.8	42.2
1.100	14.3	4.2	12.0	21.8	39.0
1.200	27.2	3.6	10.2	18.7	33.8
1.300	39.1	2.6	7.5	13.8	25.0
1.400	50.0	1.6	4.5	8.5	15.4
1.500	59.7	0.8	2.0	4.1	7.3
1.600	68.6	0.2	0.6	1.3	2.6
1.700	77.1	...	0.2	0.4	0.8

Under ordinary conditions, the vapor pressure of the electrolyte is not very different from that of the water vapor in the air. Stationary batteries, which have electrolyte of low specific gravity and open-top cells, will lose water appreciably by evaporation. Automobile batteries, on the other hand, with a higher specific gravity of electrolyte and closed tops, except for a small vent, will lose very little water by evaporation in the strict sense of the word.

Because of the ability of sulphuric acid to absorb moisture, it is evident that, if spilled, it will remain for long periods of time, or in other words it will not "dry up." This makes it difficult to protect painted surfaces, or other surfaces which are not acid-proof, against corrosion. It is necessary to wash off, or, better still, to neutralize and wash off, any electrolyte which may be spilled or become deposited as a result of gassing upon any surface that is liable to injury.

f. Electrochemical Equivalent

According to Faraday's law the transformations taking place at the plates of a storage cell are in the proportion of one gram-equivalent of the substance for the passage of 96,500 coulombs of electricity through the cell. This quantity of electricity is sometimes referred to as the electrochemical constant, and it has been named the faraday.

The equation for the reaction within the cell is:

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

It is apparent that for each gram-equivalent of material transformed at the positive and negative plates, two gram-equivalents of acid are decomposed and two gram-equivalents of water are formed during the process of discharge.

Since the gram-molecular weight of sulphuric acid is 98.076 grams and the valence 2, the gram-equivalent weight is 49.038 grams. One ampere-hour may be defined as one ampere flowing continuously for 3600 seconds and is equal, therefore, to 3600 coulombs. The number of ampere-hours in a faraday is readily computed to be 26.80. From these data the number of grams of acid decomposed by the discharge of one ampere-hour is:

$$2 \times \frac{49.038}{26.80} = 3.660 \text{ g. acid decomposed}$$

Similarly, the number of grams of water formed per ampere-hour of discharge may be calculated. The molecular weight of water is 18.016 and its equivalent weight 9.008, whence

$$2 \times \frac{9.008}{26.80} = 0.672 \text{ g. water formed}$$

In estimating the quantity of acid taking part in any reaction, it is necessary to draw a sharp distinction between the total quantity of acid reacting and the changes in weight taking place in the electrolyte as represented by the change in specific gravity. The reason for this is made apparent by the equation for the reaction given above. Since the decomposition of two equivalents of acid is accompanied by the formation of two equivalents of water, the net change for the passage of one faraday of electricity during discharge is a loss in weight corresponding to the sulphur trioxide, which may be expressed in grams as follows:

$$\underset{H_2SO_4}{-98.076} + \underset{H_2O}{18.016} = \underset{SO_3}{-\ 80.060 \text{ g.}}$$

The minus sign signifies the loss in weight which is manifested in the operation of the cell by the decrease in specific gravity of the electrolyte when discharge takes place. The change in sulphur trioxide content per ampere-hour is

$$2 \times \frac{40.030}{26.80} = 2.987 \text{ g.}$$

When either charge or discharge takes place, there is a change in volume of the electrolyte as well as a change in the weight. In order to make the process clear, it will be well to take an example, solving it completely:

Example. A large stationary cell has a capacity of 4000 ampere-hours at the 8-hour rate of discharge. It contains 618 pounds of electrolyte of specific gravity 1.210 at 25° C. when fully charged. Compute the changes in weight and volume and specific gravity of the electrolyte when 4000 ampere-hours are discharged.

In solving this example, it is convenient to convert the weight of electrolyte to the metric system, as this simplifies the later calculations. 618 pounds = 280.3 kilograms. Table XIX shows that this electrolyte contains 28.9 per cent by weight of H_2SO_4. The amounts of acid and water initially present are, therefore,

$$280.3 \times 0.289 = 81.0 \text{ kg. of acid}$$

$$280.3 - 81.0 = 199.3 \text{ kg. of water}$$

When 4000 ampere-hours are discharged, the amount of acid consumed is

$$3.660 \times 4000 = 14{,}640 \text{ g.} \quad \text{or} \quad 14.64 \text{ kg.}$$

The amount of water formed at the same time is

$$0.672 \times 4000 = 2688 \text{ g.} \quad \text{or} \quad 2.69 \text{ kg.}$$

Comparing the composition of the electrolyte at the beginning and the end, we have

	At the beginning	At the end
Sulphuric acid..............	81.0 kg.	66.36 kg.
Water......................	199.3 kg.	201.99 kg.
Total..............	280.3 kg.	268.35 kg.

The net loss in weight of the electrolyte is therefore 11.95 kilograms. This corresponds to the sulphur trioxide removed, as may readily be seen by multiplying the grams of SO_3 equivalent to the passage of one ampere-hour as given above by the number of ampere-hours.

$$2.987 \times 4000 = 11{,}950 \text{ g.} \quad \text{or} \quad 11.95 \text{ kg.}$$

The next step is to compute the specific gravity of the electrolyte at the end of the discharge.

$$\frac{66.36}{268.35} = 24.7 \text{ per cent of acid in electrolyte at end}$$

Assuming the temperature to be 25°, this corresponds to a specific gravity 1.176 according to Table XIX.

The change in the volume of the electrolyte which accompanies the discharge of this cell is computed from the initial and final weights and specific gravities.

$$\text{Initial volume} = \frac{280.3 \text{ kg.}}{1.210 \text{ sp. gr.}} = 231.7 \text{ liters}$$

$$\text{Final volume} = \frac{268.35 \text{ kg.}}{1.176 \text{ sp. gr.}} = 228.2 \text{ liters.}$$

The decrease in volume is, therefore, 3.5 liters or about 0.88 cc. per ampere-hour.

A table of the ampere-hour equivalents contained in unit volume of solution, for the various concentrations, affords the most convenient means of calculating the changes taking place in the operation of storage cells. This method is more direct than the use of formulas and diagrams which have been previously proposed for this purpose. In Table XVI are given the theoretical ampere-hours on the assumption that all of the acid could be utilized. This is an impracticable condition, since only part of the acid can be used, but the use of the table will appear from several examples. It is necessary to allow for the changes in volume of the solution which occur during charging and discharging. This is easy to do, because the increase in volume of the solution during charge and the decrease during discharge is practically 1 cc. per ampere-hour. This quantity varies slightly with the concentration of the electrolyte. It is a little more than 1 cc. per ampere-hour for acid of 1.300 sp. gr., and about 0.85 for acid of 1.200 sp. gr. For most purposes, however, it is sufficient to assume that it is exactly 1 cc. per ampere-hour.

TABLE XVI

ELECTROCHEMICAL EQUIVALENT OF SOLUTIONS OF SULPHURIC ACID

(Theoretical values per liter calculated for solutions at 25° C., assuming complete utilization of the acid in accordance with the reaction of a storage battery.)

Specific Gravity	Ampere-hours per Liter	Specific Gravity	Ampere-hours per Liter
1.040	17	1.220	100
1.060	26	1.240	110
1.080	35	1.260	120
1.100	44	1.280	130
1.120	53	1.300	141
1.140	62	1.320	151
1.160	71	1.340	162
1.180	81	1.360	173
1.200	90		

Examples. 1. A large stationary cell in a lead-lined tank has a capacity of 4000 ampere-hours at the 8-hour rate of discharge. It contains 618 pounds of electrolyte, specific gravity 1.210 at 25° C. when fully charged. Find the coefficient of utilization of the acid at this rate of discharge.

618 pounds = 280.3 kilograms which, divided by the specific gravity, 1.210, = 231.6 liters. From the table, 1 liter = 95 ampere-hours. 231.6 × 95 = 22,000 the total number of ampere-hours. $\frac{4000}{22,000}$ = 18.2 per cent the coefficient of utilization.

2. A cell of the vehicle type, containing 6.75 pounds of electrolyte, 1.280 sp. gr at 25° C., has a capacity of 220 ampere-hours at the 5-hour rate. What is the coefficient of utilization of the acid? *Answer*, 71 per cent.

3. A storage cell of a tractor battery gave 45 amperes for 5 hours and 42 minutes. The initial specific gravity at 25° C. was 1.269 and the final specific gravity, corrected to 25° after allowing sufficient time for diffusion, was 1.099. How many liters of electrolyte were in the cell?

The total ampere-hours discharged were 45 × 5.7 = 256.5. Letting x represent the number of liters initially present, the number of liters after the discharge was $(x - 0.256)$. The ampere-hour equivalent of the electrolyte is, by Table XVI,

Initial $124.5x$,
Final $43.5(x - 0.256)$.

Whence

$$124.5x - 43.5(x - 0.256) = 256.5.$$
$$x = 3.02 \text{ liters.}$$ *Answer.*

4. A locomotive cell which gives 90 amperes for 5 hours contains 15 pounds of electrolyte of specific gravity 1.280 at 25° C. What will be the final specific gravity after a 5-hour discharge, corrected to 25° after allowing sufficient time for diffusion to take place?

15 pounds = 6.80 kilograms of electrolyte, and this divided by the specific gravity, 1.280, = 5.31 liters.

The total ampere-hour equivalent is 5.31 × 130 = 690
The ampere-hours delivered are 5 × 90 = 450

Subtracting, the ampere-hours remaining are 240

During the discharge the volume of the electrolyte has decreased by 450 cc., so that the final volume of electrolyte is 5.31 − 0.45 = 4.86 liters.

$$\frac{240}{4.86} = 49.4 \text{ ampere-hours equivalent per liter}$$

The table shows this to correspond to 1.112 sp. gr. *Answer.*

5. A cell from an automobile starting and lighting battery, containing 580 cc. of electrolyte, is rated to give 40 ampere-hours at the 5-hour rate. It is required that the specific gravity at the end of a full discharge shall not fall below 1.140 at 25° C. What must the specific gravity be at the beginning of the discharge?

Since the initial volume is 580 cc., the final volume after discharging 40 ampere-hours will be 540 cc. The ampere-hour equivalent of the electrolyte at the end of this discharge will be

$$0.540 \times 62 = 33.5$$

The ampere-hours initially present were

$$33.5 + 40 = 73.5$$

The ampere-hour equivalent per liter initially present was, therefore,

$$\frac{73.5}{0.580} = 127$$

The table shows that this acid was specific gravity 1.274. *Answer.*

6. The electrolyte of a cell of a stationary battery of 280 ampere-hours' capacity has a specific gravity of 1.200 at 25° C. at the conclusion of the charging period. The normal value of the specific gravity in this cell is 1.210. The amount of electrolyte is 40 pounds. How much lead sulphate remains on the plates?

40 pounds of electrolyte = 18.1 kilograms which divided by the specific gravity when fully charged 1.210 = 15.0 liters as the volume initially present. The ampere-hour equivalent for the 1.210 acid is

$$15.0 \times 95 = 1425$$

As a first approximation, it is necessary to assume the volume of electrolyte at 1.200 sp. gr. to be the same. The ampere-hour equivalent of this is

$$15.0 \times 90 = 1350$$

The difference is therefore 75 ampere-hours and the volume of electrolyte at 1.200 is corrected to

$$15.0 - 0.075 = 14.9$$

for which the equivalent is

$$14.9 \times 90 = 1341$$

Since 1 ampere-hour decomposes 3.66 grams of acid, the deficit of acid is

$$(1425 - 1341) \times 3.66 = 308 \text{ g.}$$

$$\frac{H_2SO_4}{PbSO_4} = \frac{98}{303} = \frac{308}{951}$$

Whence there are 951 grams of lead sulphate on the plates. *Answer.*

7. An aviation battery is rated to give 28 ampere-hours at the 5-hour rate. By actual test it was found to give only 24 ampere-hours. The battery contained 210 cc. of electrolyte of specific gravity 1.280 at 25° C. Is this a sufficient amount?

0.210 × 130 = 27.3 ampere-hours, that is, the battery could not give its rated capacity even if the electrolyte could be reduced to water.

g. Viscosity

A knowledge of the viscosity of sulphuric acid solutions is important, because the rate of diffusion of the acid through the pores of the plate is dependent upon it. In this respect the viscosity exerts a powerful influence upon the capacity, but it is seldom referred to in this connection. In the following table, the absolute viscosities expressed in centipoises are given. They have been computed for convenient percentages of sulphuric acid from measurements of Vinal and Craig.[5] The usual range of battery electrolytes lies between 20 and 40 per cent. The viscosity doubles between 25° C. and 0° C. Below zero the viscosity increases more rapidly, and it is at once apparent why the capacity of storage cells falls off so rapidly at low temperatures.

TABLE XVII

VISCOSITY OF SULPHURIC ACID SOLUTIONS

Temperature		Viscosity in Centipoises				
° C.	° F.	10%	20%	30%	40%	50%
30	86	0.976	1.225	1.596	2.163	3.07
25	77	1.091	1.371	1.784	2.409	3.40
20	68	1.228	1.545	2.006	2.70	3.79
10	50	1.595	2.010	2.600	3.48	4.86
0	32	2.160	2.710	3.520	4.70	6.52
−10	14	.....	3.820	4.950	6.60	9.15
−20	− 4	.....	.....	7.490	9.89	13.60
−30	−22	.....	.....	12.200	16.00	21.70
−40	−40	.....	....	......	28.80	.....
−50	−58	.....	.....	......	59.50	.....

The relation of the viscosity to the rate of diffusion is discussed in Chapter V.

3. MEASUREMENT OF SULPHURIC ACID SOLUTIONS

The careful operation of storage batteries requires that the electrolyte should contain the proper amount of sulphuric acid and water. Convenient and accurate means are necessary for measuring the concentration of these solutions. The method most generally used is to measure the specific gravity, or the density of the solution, at some

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[5] *J. Research*, Bureau of Standards, 10, p. 781, 1933.

definite temperature. Other methods include the use of arbitrary scales, such as the Baumé or the Twaddell scales. The concentration may also be expressed as the percentage, by weight or volume, of the sulphuric acid in the solution. This is convenient in preparing solutions of a definite strength. Chemical computations are often facilitated when based on the number of gram-equivalents per liter. For storage or shipping purposes, the concentration as it affects the weight and bulk of the packages is important. This requires the pounds per cubic foot or the kilograms per liter.

Table XIX gives the comparative values of the concentration expressed by these different methods of measurement.

a. Meaning of Specific Gravity and Density

The specific gravity of a solution is the ratio of the weight of the solution to the weight of an equal volume of pure water at some fixed temperature. Density, on the other hand, is the ratio of the mass of the liquid to its own volume at a definite temperature. Density measures a property of the substance itself, but specific gravity depends on properties of two substances. Since specific gravity is based on a comparison with water, for which the density at 4° C. is unity, the values for the specific gravity of a solution and its density are very nearly the same.

The specific gravity of sulphuric acid solutions used for the electrolyte varies appreciably with the temperature. It is, therefore, customary to state the specific gravity thus: specific gravity $\frac{15^\circ \text{ C.}}{15^\circ \text{ C.}}$ or specific gravity $\frac{25^\circ \text{ C.}}{25^\circ \text{ C.}}\cdot$ The temperature above the line is the temperature of the solution, and the temperature below the line the temperature of the water taken as the standard. A specific gravity referred to water at its maximum density (4° C.) is identical with the density of the solution. For a solution at 25° C. this would be written specific gravity $\frac{25^\circ \text{ C.}}{4^\circ \text{ C.}}$, or density $\frac{25^\circ \text{ C.}}{4^\circ \text{ C.}}\cdot$

The difference between the specific gravities and the densities, as measured on the various scales in common use, is at most about four units in the third decimal place. For commercial work in storage batteries, this small difference can generally be neglected. Many of the small and cheap hydrometers used for testing automobile batteries do not indicate the basis of their scale. But research and laboratory work, and the operation of large central station batteries, require a more exact knowledge. In Table XVIII conversion factors to the fourth decimal place are given for the scales in most frequent use. The method of using this table may be seen from the following example: A hydrometer reading density $\frac{20^\circ\text{ C.}}{4^\circ\text{ C.}}$ is used to measure a solution of which the specific gravity $\frac{25^\circ\text{ C.}}{25^\circ\text{ C.}}$ is desired. If the density reading is 1.280, what is the specific gravity?

TABLE XVIII

Conversion of Specific Gravities and Densities *

(The table contains factors which are to be used to multiply the observed reading of specific gravity or density to obtain the difference between two scales of measurement. This difference is to be added to or subtracted from the observed reading, according to the plus and minus signs, to obtain the reading converted to the desired basis of measure.)

Converted from	Converted to						
	Density $\frac{25^\circ\text{ C.}}{4^\circ\text{ C.}}$	Density $\frac{20^\circ\text{ C.}}{4^\circ\text{ C.}}$	Density $\frac{15^\circ\text{ C.}}{4^\circ\text{ C.}}$	Sp. Gr. $\frac{15^\circ\text{ C.}}{15^\circ\text{ C.}}$	Sp. Gr. $\frac{60^\circ\text{ F.}}{60^\circ\text{ F.}}$	Sp. Gr. $\frac{20^\circ\text{ C.}}{20^\circ\text{ C.}}$	Sp. Gr. $\frac{25^\circ\text{ C.}}{25^\circ\text{ C.}}$
Density $\frac{25^\circ\text{ C.}}{4^\circ\text{ C.}}$	0	+0.0001	+0.0002	+0.0011	+0.0012	+0.0019	+0.0029
Density $\frac{20^\circ\text{ C.}}{4^\circ\text{ C.}}$	−0.0001	0	+0.0001	+0.0010	+0.0011	+0.0018	+0.0028
Density $\frac{15^\circ\text{ C.}}{4^\circ\text{ C.}}$	−0.0002	−0.0001	0	+0.0009	+0.0010	+0.0017	+0.0027
Sp. Gr. $\frac{15^\circ\text{ C.}}{15^\circ\text{ C.}}$	−0.0011	−0.0010	−0.0009	0	+0.0001	+0.0008	+0.0018
Sp. Gr. $\frac{60^\circ\text{ F.}}{60^\circ\text{ F.}}$	−0.0012	−0.0011	−0.0010	−0.0001	0	+0.0007	+0.0017
Sp. Gr. $\frac{20^\circ\text{ C.}}{20^\circ\text{ C.}}$	−0.0019	−0.0018	−0.0017	−0.0008	−0.0007	0	+0.0010
Sp. Gr. $\frac{25^\circ\text{ C.}}{25^\circ\text{ C.}}$	−0.0029	−0.0028	−0.0027	−0.0018	−0.0017	−0.0010	0

$$\text{Specific gravity } \frac{25^\circ\text{ C.}}{25^\circ\text{ C.}} = \text{density } \frac{20^\circ\text{ C.}}{4^\circ\text{ C.}} + \left(\text{factor} \times \text{density } \frac{20^\circ\text{ C.}}{4^\circ\text{ C.}}\right)$$

$$= 1.280 + (0.0028 \times 1.280) \doteq 1.284$$

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* **Based on data contained in *Circular* 19, Bureau of Standards.**

Specific gravities of storage-battery electrolytes are usually expressed to the third decimal place, one unit in the last place being called a "point." Thus solutions of 1.285 and 1.270 sp. gr. are said to differ by 15 points. Colloquial expressions, such as "twelve-eighty acid" or "thirteen hundred acid," refer to solutions of 1.280 and 1.300 sp. gr.

The specific gravity of the electrolyte decreases with increasing temperature. The temperature coefficient is not a constant quantity, but varies with the specific gravity. In Table XIX the values of this coefficient per degree Centigrade and per degree Fahrenheit are given for each value of the specific gravity. The coefficient applies strictly to specific gravities referred to water at 15° C., but for practical purposes may be used for the 25° basis also. This coefficient does not, however, convert specific gravities at $\frac{15^\circ}{15^\circ}$ to the $\frac{25^\circ}{25^\circ}$ basis. The familiar rule that there is a change of one point for each 3° F. difference from the standard temperature is correct only for solutions of 1.150 sp. gr. For greater concentrations the correction is larger. At 1.280 sp. gr. it is two points for 5° F., or three points for 4° C. When the temperature of the solution is above the standard temperature, the correction is to be added, and when below, subtracted from the observed specific gravity to reduce this to the correct reading at the standard temperature.

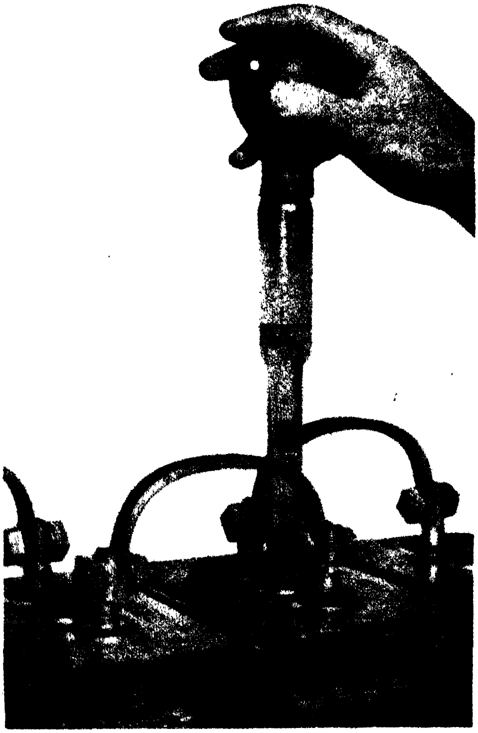

FIG. 40. Use of the syringe hydrometer.

Specific gravities for storage-battery purposes are most conveniently measured by means of hydrometers. These are of several varieties, but all consist of a float of some kind. For stationary batteries, the hydrometer is immersed in the liquid of the cell itself, and in some cases has a recording attachment. Hydrometers for use with portable batteries are usually of the syringe type (Fig. 40), which permits drawing a portion of the electrolyte from the cell into a tube of glass in which the hydrometer is confined. After the reading is completed the solution is replaced in the cell from which it was drawn.

A well-designed hydrometer should be made of smooth, transparent glass, circular in cross section along the axis, with fixed ballast, and a scale on ledger paper with graduation that is correct to within one-half of the smallest division.[6] Flat hydrometers that will float between the plates and jar of stationary cells are also used. The hydrometer should float vertically and indicate the basis of its scale as, for example, specific gravity $\frac{15^\circ \text{C.}}{15^\circ \text{C.}}\cdot$ In making readings of a hydrometer the eye should be level with the surface of the liquid, disregarding the curvature due to the surface tension, as shown in Fig. 41.

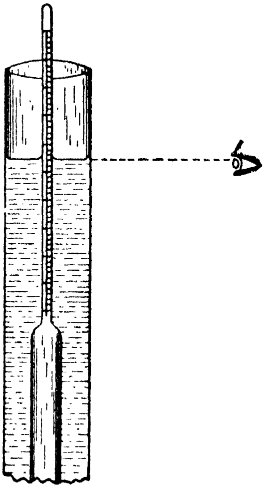

FIG. 41. Proper position of the eye for reading a hydrometer.

Cells in glass or other transparent jars are often provided with built-in "charge" indicators. These are floats which rise or fall with changing specific gravity of the electrolyte. A familiar type comprises several brightly colored balls of wax, which are adjusted to the desired specific gravities corresponding to the respective colors by incorporating with the wax the necessary amounts of a heavy insoluble substance such as barium sulphate. Precautions must be taken to prevent bubbles of gas clinging to the surface of the balls, if they are to operate satisfactorily.

b. The Baumé and Twaddell Scales

The standard Baumé scale, for liquids heavier than water, as used in the United States, is related to the specific gravity by the following equation:

$$\text{Degrees Baumé} = 145 - \frac{145}{\text{Specific gravity } \frac{60^\circ \text{F.}}{60^\circ \text{F.}}}$$

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[6] *Circular* 16, p. 5, Bureau of Standards.

TABLE XIX

MEASUREMENT OF SULPHURIC ACID SOLUTIONS

Specific Gravity, 15° C./15° C.	Specific Gravity, 25° C./25° C.	Temperature Coefficient of Sp. Gr. 15° C.		Per Cent H_2SO_4 by Weight	Per Cent H_2SO_4 by Volume	Baumé Degrees	Twaddell Degrees	Pounds per Cubic Foot	Kilograms per Liter
		Per ° C.	Per ° F.						
1.000	1.000	.....	.....	0.0	0.0	0.0	0	62.4	Approximately equal numerically to the specific gravity; for example, a solution of 1.300 sp. gr. will weigh approximately 1.300 kg. per liter.
1.010	1.009	(.00018)	(.00010)	1.4	0.8	1.4	2	63.0	
1.020	1.019	(22)	(12)	2.9	1.6	2.8	4	63.6	
1.030	1.029	(26)	(14)	4.4	2.5	4.2	6	64.2	
1.040	1.039	(29)	(16)	5.9	3.3	5.6	8	64.8	
1.050	1.049	(33)	(18)	7.3	4.2	6.9	10	65.5	
1.060	1.058	36	20	8.7	5.0	8.2	12	66.1	
1.070	1.068	40	22	10.1	5.9	9.5	14	66.7	
1.080	1.078	43	24	11.5	6.7	10.7	16	67.4	
1.090	1.088	46	26	12.9	7.6	12.0	18	68.0	
1.100	1.097	48	27	14.3	8.5	13.2	20	68.6	
1.110	1.107	51	28	15.7	9.5	14.4	22	69.2	
1.120	1.117	53	29	17.0	10.3	15.5	24	69.8	
1.130	1.127	55	31	18.3	11.2	16.7	26	70.5	
1.140	1.137	58	32	19.6	12.1	17.8	28	71.1	
1.150	1.146	60	33	20.9	13.0	18.9	30	71.7	
1.160	1.156	62	34	22.1	13.9	20.0	32	72.4	
1.170	1.166	63	35	23.4	14.9	21.1	34	73.0	
1.180	1.176	65	36	24.7	15.8	22.1	36	73.6	
1.190	1.186	66	37	25.9	16.7	23.2	38	74.2	
1.200	1.196	68	38	27.2	17.7	24.2	40	74.8	
1.210	1.206	69	38	28.4	18.7	25.2	42	75.4	
1.220	1.216	70	39	29.6	19.6	26.1	44	76.1	
1.230	1.225	71	39	30.8	20.6	27.1	46	76.7	
1.240	1.235	72	40	32.0	21.6	28.1	48	77.3	
1.250	1.245	72	40	33.2	22.6	29.0	50	78.0	
1.260	1.255	73	40	34.4	23.6	29.9	52	78.6	
1.270	1.265	73	41	35.6	24.6	30.8	54	79.2	
1.280	1.275	74	41	36.8	25.6	31.7	56	79.8	
1.290	1.285	74	41	38.0	26.6	32.6	58	80.4	

TABLE XIX—*Continued*

MEASUREMENT OF SULPHURIC ACID SOLUTIONS

Specific Gravity, 15° C. / 15° C.	Specific Gravity, 25° C. / 25° C.	Temperature Coefficient of Sp. Gr. 15° C.		Per Cent H_2SO_4 by Weight	Per Cent H_2SO_4 by Volume	Baumé Degrees	Twaddell Degrees	Pounds per Cubic Foot	Kilograms per Liter
		Per ° C.	Per ° F.						
1.300	1.295	00075	00042	39.1	27.6	33.5	60	81.0	Approximately equal numerically to the specific gravity, for example, a solution of 1.300 sp. gr. will weigh approximately 1.300 kg. per liter.
1.310	1.305	75	42	40.3	28.7	34.3	62	81.7	
1.320	1.315	76	42	41.4	29.7	35.2	64	82.3	
1.330	1.325	76	42	42.5	30.7	36.0	66	82.9	
1.340	1.335	76	42	43.6	31.8	36.8	68	83.6	
1.350	1.345	77	43	44.7	32.8	37.6	70	84.2	
1.360	1.355	77	43	45.8	33.9	38.4	72	84.8	
1.370	1.365	78	43	46.9	34.9	39.2	74	85.4	
1.380	1.375	78	43	47.9	35.9	39.9	76	86.1	
1.390	1.385	79	44	49.0	37.0	40.7	78	86.7	
1.400	1.395	79	44	50.0	38.0	41.4	80	87.3	
1.410	1.405	80	44	51.0	39.1	42.2	82	88.0	
1.420	1.415	80	45	52.0	40.1	42.9	84	88.6	
1.430	1.425	81	45	53.0	41.2	43.6	86	89.2	
1.440	1.435	81	45	54.0	42.2	44.3	88	89.8	
1.450	1.445	82	46	54.9	43.3	45.0	90	90.4	
1.460	1.455	83	46	55.9	44.4	45.7	92	91.0	
1.470	1.465	83	46	56.9	45.5	46.4	94	91.7	
1.480	1.475	84	47	57.8	46.5	47.0	96	92.3	
1.490	1.485	85	47	58.7	47.5	47.7	98	93.0	
1.500	1.495	85	47	59.7	48.7	48.3	100	93.6	
1.510	1.505	86	48	60.6	49.7	49.0	102	94.2	
1.520	1.515	87	48	61.5	50.8	49.6	104	94.8	
1.530	1.525	87	48	62.4	51.9	50.2	106	95.4	
1.540	1.535	88	49	63.3	53.0	50.8	108	96.0	
1.550	1.545	89	49	64.2	54.1	51.5	110	96.7	
1.560	1.554	89	49	65.1	55.2	52.1	112	97.3	
1.570	1.564	90	50	66.0	56.3	52.6	114	98.0	
1.580	1.574	91	50	66.8	57.4	53.2	116	98.6	
1.590	1.584	91	51	67.7	58.5	53.8	118	99.2	

TABLE XIX—*Continued*

MEASUREMENT OF SULPHURIC ACID SOLUTIONS

Specific Gravity, $\frac{15^\circ\text{ C.}}{15^\circ\text{ C.}}$	Specific Gravity, $\frac{25^\circ\text{ C.}}{25^\circ\text{ C.}}$	Temperature Coefficient of Sp. Gr. 15° C.		Per Cent H_2SO_4 by Weight	Per Cent H_2SO_4 by Volume	Baumé Degrees	Twaddell Degrees	Pounds per Cubic Foot	Kilograms per Liter
		Per ° C.	Per ° F						
1.600	1.594	.00092	.00051	68.6	59.7	54.4	120	99.8	Approximately equal numerically to the specific gravity; for example, a solution of 1.300 sp. gr. will weigh approximately 1.300 kg. per liter.
1.610	1.604	93	51	69.4	60.8	54.9	122	100.4	
1.620	1.614	93	52	70.3	61.9	55.5	124	101.0	
1.630	1.624	94	52	71.2	63.1	56.0	126	101.7	
1.640	1.634	95	53	72.0	64.2	56.6	128	102.3	
1.650	1.644	95	53	72.9	65.4	57.1	130	102.9	
1.660	1.654	96	53	73.7	66.5	57.7	132	103.6	
1.670	1.664	97	54	74.5	67.6	58.2	134	104.2	
1.680	1.674	98	54	75.4	68.8	58.7	136	104.8	
1.690	1.684	.00099	55	76.2	70.0	59.2	138	105.4	
1.700	1.694	.00100	55	77.1	71.2	59.7	140	106.0	
1.710	1.704	101	56	77.9	72.4	60.2	142	106.7	
1.720	1.713	102	57	78.8	73.6	60.7	144	107.3	
1.730	1.723	103	58	79.7	75.0	61.2	146	108.0	
1.740	1.733	105	59	80.6	76.2	61.7	148	108.6	
1.750	1.743	107	60	81.5	77.6	62.1	150	109.2	
1.760	1.753	109	60	82.4	78.8	62.6	152	109.8	
1.770	1.763	110	61	83.4	80.2	63.1	154	110.4	
1.780	1.773	110	61	84.4	81.7	63.5	156	111.0	
1.790	1.783	111	62	85.6	83.3	64.0	158	111.7	
1.800	1.793	110	61	86.7	84.8	64.4	160	112.3	
1.810	1.803	109	61	88.1	86.7	64.9	162	112.9	
1.820	1.813	108	60	89.8	88.9	65.3	164	113.5	
1.830	1.823	106	59	91.8	91.4	65.8	166	114.1	
1.835	.....	105	58	93.2	93.0	66.0	167	114.5	
1.840	1.834	.00103	.00057	94.8	94.8	....	168	114.8	

EXPLANATION OF THE TABLE

COLUMN 1. Specific gravities of solutions are given at $\frac{15^\circ\text{ C.}}{15^\circ\text{ C.}}$, which is approximately equal to $\frac{60^\circ\text{ F.}}{60^\circ\text{ F.}}$. Hydrometers which are used for measuring sulphuric acid solutions are frequently standardized at 60° F.

COLUMN 2. Specific gravities of solutions corresponding to those given in Column 1 are given at $\frac{25^\circ\text{ C.}}{25^\circ\text{ C.}}\left(\frac{77^\circ\text{ F.}}{77^\circ\text{ F.}}\right)$.

COLUMNS 3 AND 4. Contain the temperature coefficients to calculate the specific gravity for any temperature t° from the specific gravities given for 15° C. Values are given for both Centigrade and Fahrenheit degrees. They have been calculated from Domke's Tables, *Wiss. Abh. Normal Eichungs Kom.*, 5, p. 75 (1904). Let the required specific gravity at t° be represented by S_t; the specific gravity of the solution at 15° by S_{15} and the temperature coefficient by α, then

$$S_t = S_{15} + \alpha(15^\circ - t^\circ).$$

The temperature coefficient for temperatures other than 15°, which may be taken as standard, varies slightly with the temperature. For solutions of the specific gravities most commonly used in storage batteries, the values given in the table may be assumed to be correct to within 3 per cent for a range of temperature from 0° C. to 45° C. Values in parentheses were obtained by extrapolation.

COLUMN 5. Per cent by *weight* of H_2SO_4 solutions corresponding to those given in Column 1. These were computed from Domke's tables, pp. 131-148.

COLUMN 6. Per cent by *volume* of H_2SO_4 solutions corresponding to those given in Column 1. These were computed from the formula:

$$\text{Per cent by volume} = \frac{d}{1.840} \times \text{per cent by weight}$$

Values of d, the specific gravity of solutions for given percentages of H_2SO_4 by weight, were based on Domke's tables and the computations checked by comparison with Pickering's contraction table. *J. Chem. Soc.*, Vol. 57, p. 148, 1890.

COLUMN 7. Baumé degrees corresponding to the specific gravities given in Column 1 calculated from the formula:

$$\text{Degrees Baumé} = 145 - \frac{145}{\text{Specific gravity }\frac{60^\circ\text{ F.}}{60^\circ\text{ F.}}}$$

COLUMN 8. Twaddell degrees calculated from the formula:

$$\text{Degrees Twaddell} = 200\left(\text{specific gravity }\frac{60^\circ\text{ F.}}{60^\circ\text{ F.}} - 1\right)$$

COLUMN 9. Pounds per cubic foot of solutions having the specific gravities given in Column 1.

COLUMN 10. The kilograms per liter are equal numerically to the specific gravity, if it be assumed that the difference between the specific gravity $\frac{15^\circ\text{ C.}}{15^\circ\text{ C.}}$ and the density $\frac{15^\circ\text{ C.}}{4^\circ\text{ C.}}$ is negligible. For example, the

$$\text{Specific gravity }\frac{15^\circ\text{ C.}}{15^\circ\text{ C.}}\text{ for 38 per cent acid is }1.29027,$$

$$\text{Density }\frac{15^\circ\text{ C.}}{4^\circ\text{ C.}}\text{ for 38 per cent acid is }1.28915$$

Difference 0.00112

The assumption is correct, therefore, to a unit in the third decimal place.

The number 145 is called the modulus. Great confusion has resulted from the variety of values assigned to it.

The Baumé scale is now obsolete in this country for storage-battery work, but it is frequently referred to in foreign books on the subject. The Twaddell scale, extensively used in England, is related to the specific gravity in a more definite way. One degree Twaddell is equal to five units in the third decimal place of the specific gravity, from which it is apparent that the relation may be expressed by the equation:

$$\text{Degrees Twaddell} = \frac{\text{Specific gravity} - 1}{5} \times 1000$$

The use of specific gravities is preferable, in storage-battery work, to any of the arbitrary scales.

4. PREPARATION OF THE ELECTROLYTE

The electrolyte for lead batteries is prepared by diluting pure sulphuric acid with pure water. The acid is ordinarily sold as the concentrated acid of specific gravity 1.835 to 1.840 or partially diluted to 1.400. The latter is more bulky, which is a disadvantage in shipment, but it possesses a marked advantage in being easier to prepare for use. (See p. 95.) When the concentrated acid is diluted, the solution becomes very hot. The acid should always be poured into the water, never the water into the acid, because of the danger to the person making the mixture. Although the amount of heat evolved in either case is the same, the specific heats of water and of concentrated acid are quite different, as was shown in Table XI. A stream of water flowing into the concentrated acid causes the liberation of a great amount of heat, which, because of the low specific heat of the acid, causes a large local rise in temperature. Acid flowing into water cannot cause so great a rise in temperature, because the specific heat of the water is high. The solution should be stirred continually while the acid is being poured into the water, to prevent the heavier acid from flowing to the bottom of the vessel without mixing with the water. Suitable vessels for use in mixing or storing small quantities of the electrolyte are of china, vitreous earthenware, or glass. These are subject to cracking, and lead-lined tanks are preferred, especially for larger quantities. No metallic vessel other than lead should be used.

After diluting the acid, it is necessary to wait until the mixture has cooled before pouring it into the battery, to avoid injury to the plates and separators. The cooling may be hastened by a jet of compressed air, but the air must be pure. The great rise in temperature which occurs when the acid and water are mixed may be avoided altogether by using ice made from distilled water, instead of water. This is because the latent heat of fusion of the ice is approximately equal to the heat liberated by the dilution of the sulphuric acid. The ice, if drained of surplus water, may be added directly to the acid. In an experiment, 220 grams of ice were added to 98 grams of concentrated acid at room temperature. The temperature of the mixture was found to be −2° C. after all the ice had melted. The specific gravity of this mixture at 25° C. was 1.225. Since the latent heat of fusion of the ice is 79.63 gram-calories, the total heat absorbed by the ice was 220 × 79.63 = 17,518 gram-calories. The total heat liberated by the dilution of the acid was, by interpolation of the values given in Table XI, 16,640 gram-calories. The excess of heat absorbed indicates that the solution would be below 0° C., as was observed.

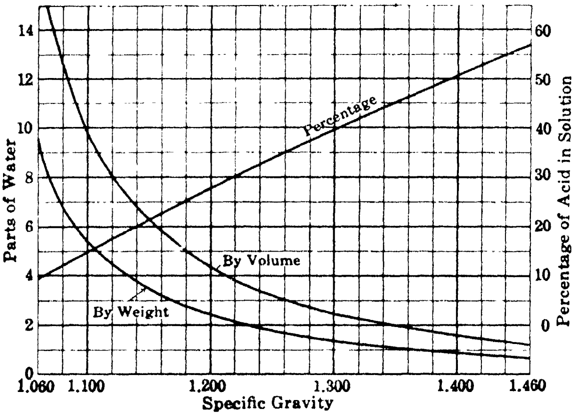

FIG. 42. Preparation of electrolyte of any specific gravity from concentrated acid of 1.835 sp. gr.

To facilitate the preparation of electrolytes of any required concentration, Fig. 42 shows the relative proportions of acid and water necessary. Manufacturers ordinarily furnish information as to the proper strength to be used in any particular battery.

It is often necessary to change the specific gravity of a solution of sulphuric acid by a given amount. The amount of watér or acid which must be added to make the desired change can be calculated easily by using Table XIX. For example: 290 pounds of electrolyte at 25° C. are to be raised from 1.255 sp. gr. to 1.295 sp. gr. How much acid must be added?

By the table, 1.295 would contain 39.1 per cent acid or 60.9 per cent water and 1.255 contains 34.4 per cent acid or 65.6 per cent water.

The excess of water is, by subtraction, 4.7 per cent; or

$$290 \times 4.7 \text{ per cent} = 13.63 \text{ pounds}$$

The amount of acid to be added is

$$\frac{100 \times 13.63}{60.9} = 22.4 \text{ pounds}$$

As another example, 340 pounds of electrolyte at 25° C. of 1.325 sp. gr. are to be reduced to 1.285 sp. gr. How much water is to be added?

By the table, 1.325 contains 42.5 per cent acid and 1.285 would contain 38.0 per cent acid.

The excess of acid is, by subtraction, 4.5 per cent; or

$$340 \times 4.5 \text{ per cent} = 15.3 \text{ pounds}$$

The amount of water to be added is

$$\frac{100 \times 15.3}{38.0} = 40.3 \text{ pounds}$$

5. CHOICE OF SPECIFIC GRAVITIES FOR BATTERY SERVICE

It is a matter of common observation that the specific gravity of the electrolyte in portable batteries is higher than in stationary batteries, but the choice does not depend entirely on space and weight considerations. Chemical reactions, temperature, and the character of service are of importance in determining the proper specific gravity.

The first requirement is that the concentration be sufficient to provide enough acid in a given space within the cell to give the required output. The theoretical number of ampere-hours per liter has been calculated for various concentrations and given in Table XVI. It is not possible, however, to use all the acid in the cell, because the resistance of the cell would increase to a high value and the voltage would fall rapidly if the electrolyte became too impoverished. Space and weight requirements for portable cells do not permit of large quantities of electrolyte. It is evident that high specific gravities are desirable for these, in contrast to the stationary cells for which space and weight are of less importance.

Chemical reactions, occurring within the cell during the time that it is at rest, place a limitation on the concentrations of acid that may be used. Local action (p. 120) increases rapidly when the concentration of the acid is increased. This is particularly true of the negative plate. Another chemical action taking place within the cell is the action of the electrolyte on the separators, which are usually made of wood. These separators are destroyed by too strong acid. The action of 1.300 sp. gr. acid on the separator is much more marked than that of 1.250 and lower concentrations. The performance of batteries that are charged and discharged at frequent intervals, such as starting and lighting batteries or vehicle batteries, is not seriously affected by slight chemical actions resulting in the formation of lead sulphate. Stationary batteries, however, which are less frequently charged, must be free from local action so far as possible.

The chemical reactions within the cell practically limit the higher concentrations to 1.300 sp. gr.

The temperatures to which the battery is subjected in service have an important bearing on the specific gravity. Batteries exposed to low temperatures, such as automobile batteries in cold climates or airplane batteries, require a high density of acid to permit their capacity to be utilized without depleting their electrolyte to so low a specific gravity that freezing occurs. On the other hand, batteries for use in hot climates or on ships passing through the tropics, require a lower specific gravity because of the increased chemical activity at the higher temperatures.

The higher concentrations which are beneficial in increasing the capacity of the positive plates are also detrimental in decreasing the capacity of the negative plates, particularly at high rates of discharge and low temperatures. If the capacity of the battery is limited under such conditions by the negative plates, a slight reduction of the acid concentration will often improve materially the operating characteristics of the battery. The increased capacity of the negative plates more than offsets the proportionally smaller decrease in the capacity of the positives.

The selection of the specific gravity that will produce the best results is necessarily a compromise, involving (1) the limitations of space and weight, (2) the chemical reactions within the cell, (3) the effect of temperature, and (4) the relative capacity of the positive and negative plates under particular operating conditions.

The range of concentrations for different types of batteries when fully charged is approximately as follows:

Stationary batteries	1.200 to 1.225
Truck and tractor batteries	1.270 to 1.280
Starting and lighting batteries	1.270 to 1.300
Ditto in the tropics	1.200 to 1.230
Aviation batteries	1.275 to 1.285
Car-lighting batteries	1.210 to 1.230
Portable railway signal batteries	1.220
Counter cells	1.210 to 1.250

6. PURITY OF THE ELECTROLYTE

The most satisfactory service can only be obtained when the electrolyte is of a high degree of purity. It is necessary, therefore, that both the sulphuric acid and the water which are used in preparing the electrolyte should be pure. Distilled water is much to be preferred to natural water. The impurities which are contained in natural water may be small in amount, but their effect in the storage battery is cumulative because the evaporation which takes place results only in the loss of oxygen and hydrogen which are the constituents of water, leaving the mineral and other impurities in the solution. Natural waters vary considerably in composition from one time of the year to another. The ordinary impurities which natural waters contain are nitrates and other compounds of nitrogen, chlorides, sulphates, bicarbonates, as well as iron, aluminum, silicon, sodium, potassium, magnesium, and calcium. It has been found possible to use natural water for storage-battery purposes in certain localities, but it is not advisable to make this a general rule because of the varying composition of the water in different localities. Distilled water is always to be recommended when it is possible to obtain it. For Edison batteries, distilled water which has been kept in a closed container should be used exclusively. Rain water may be used in lead batteries if not collected from metallic roofs. Impurities found in the electrolyte often are derived from the plates, if the materials used in their manufacture are not pure.

a. Local Action

The discharge of either the positive or negative plates in sulphuric acid solutions results primarily in the formation of lead sulphate. A certain amount of lead sulphate is formed as the result of local action whenever the plates are immersed in any acid solution, even though it be the purest obtainable. Detrimental impurities may (1) corrode the plate, (2) accelerate the formation of lead sulphate, or (3) be deposited in the pores of the plate. In any case the weight of the plate changes and this change affords the most sensitive and exact means we have for estimating the extent of the reaction. This method was devised by Vinal and Ritchie[7] for measurements on positive and negative plates suspended in pure sulphuric acid solutions.

In order to obtain comparable results, it is necessary that the temperature be maintained at a constant value. This was accomplished

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[7] *Technologic Paper* 225, Bureau of Standards; *Chem. and Met. Eng.*, 27, p. 1116; *Electrical World*, 80, p. 1383, 1922.

by immersing the glass jars containing the electrolytes in a large water bath thermostatically controlled at 25° C. (77° F.). This temperature was maintained constant to within about 0.01° C. Two positive plates or two negative plates, suspended on glass hooks, were placed in each jar. As a preliminary step the plates were given several cycles of charge and discharge, following which they were fully charged and then submerged in the electrolytes to be tested. Each jar contained a solution of chemically pure sulphuric acid. The electrolytes were saturated with lead sulphate because the previous work showed this to be necessary.

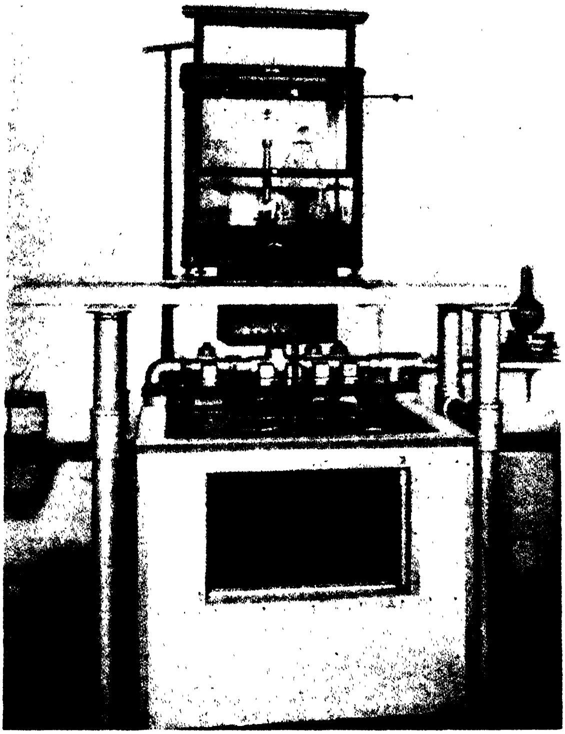

FIG. 43. Apparatus for determining the rate of sulphation of storage-battery plates.

A sensitive balance mounted on a marble slab above the thermostat bath was used for weighing the plates while they were immersed. Any plate could be brought directly under the arm of the balance, as the jars containing them were carried on a revolving frame. The arrangement of the apparatus is shown in Fig. 43.

Since the weighings were made in the electrolyte, a buoyancy correction was necessary. This correction has been calculated on the basis that the materials have the following densities:

Lead		11.3
Lead sulphate		6.3
Lead peroxide	A plates	8.7
	B plates	8.8

The buoyancy corrections are applied to a small difference of two weighings, and hence a slight error in the density of either the solutions or the active materials produces a negligible error in the final result.

Since the molecular weight of lead is 207.21 and that of lead sulphate 303.27, the gain in weight during the transformation of 1 mole of lead to lead sulphate is 96.06 grams; and the relative gain in weight is $\frac{96.06}{207.21}$ times the weight of lead acted upon. There is, of course, a large amount of lead which does not take part in the reaction and which decreases the sensibility of the weighings; but in spite of this fact and the heavy damping resulting from the viscosity of the electrolytes, the balance was sufficiently sensitive to permit an accuracy of a few tenths of a milligram to be obtained.

From the rate of change in weight of the plates, the equivalent loss in ampere-hour capacity can be computed. The valence is 2, and hence a gain in weight of the negative plate of 96.06 grams is equivalent to 2 × 96,500 coulombs. From this the change in weight is computed to be 1.79 grams per ampere-hour.

The effect of temperature and concentration on the rate of sulphation is important. In Table XX are given the measurements made on the negative plates of two manufacturers when the solutions were maintained at constant temperatures of 22°, 25°, and 30° C. The increase in the rate of sulphation from 22° to 25° C. is proportionately greater than from 25° to 30° C.

Both chemical and electrochemical reactions are possible at the negative plate, but the former are probably predominant over the latter during self-discharge. This is indicated by the results for the A plates in 1.150 and 1.400 acid. The gain in weight per hour in the stronger acid is 23 times that in the more dilute. The change in potential of a lead plate as the concentration of the electrolyte is changed from 1.150 to 1.400 sp. gr. acid is less than 0.1 volt, according to the measurements of Gladstone and Hibbert.[8] The resistivity of the more

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[8] *J. Inst. Elec. Eng.*, 21, p. 430, 1892. See also measurements by Crennell and Lea, *J. Inst. Elec. Eng.*, 66, p. 529, 1928.

concentrated electrolyte is higher than for the 1.150 sp. gr. electrolyte. On the basis of Ohm's law, therefore, this marked increase in the extent of the reaction cannot be readily accounted for as an electrochemical reaction.

TABLE XX

EFFECT OF TEMPERATURE ON THE RATE OF SULPHATION OF NEGATIVE PLATES

Specific Gravity $\frac{25°}{25°}$	Gain in Weight, Grams per Hour, Saturated Solutions, for Plates of					
	Manufacturer B at			Manufacturer A at		
	22° C.	25° C.	30° C.	22° C.	25° C.	30° C.
1.150	0.0031	0.0048	0.0056	0.0012	0.0022	0.0022
1.200	0.0073	0.0118	0.0118	0.0016	0.0026	0.0027
1.250	0.0111	0.0178	0.0196	0.0028	0.0036	0.0051
1.300	0.0183	0.0283	0.0325	0.0046	0.0060	0.0082
1.350	0.0270	0.0385	0.0420	0.0122	0.0151	0.0196
1.400	0.0614	0.0906	0.1027	0.0350	0.0460	0.0544

The initial rate of sulphation, particularly in the solutions that were unsaturated with lead sulphate, was somewhat greater than is shown in Table XX. It can easily be computed that the capacity of the plates would be exhausted in a relatively short time if the initial rate of sulphation were to continue indefinitely. The decrease in the rate of sulphation is probably to be attributed to the protection which the lead sulphate affords to the underlying active material and also to the increasing amount of lead sulphate present in the solutions which were initially unsaturated.

Local action at the positive plate is essentially electrochemical, resulting from the difference in potential between the oxide and the lead-antimony alloy of the grid. Metallic impurities are not precipitated by the oxide, and Dolezalek and Finckh[9] have stated that no solubility of the peroxide in solutions of the specific gravities ordinarily used in storage batteries can be detected. The reaction at the positive plate in these experiments is therefore to be regarded as the general expression for the discharge of a cell, with the qualification that the negative electrode may be lead or lead-antimony alloy, depending on the construction of the plate.

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

The lead sulphate formed appears on both the peroxide and the grid.

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[9] *Zeit. f. Anorg. Chem.*, 51, p. 320, 1906.

The gain in weight of the positive plates is not as simply related to the total amount of sulphate formed as in the case of the negatives. The sulphate which forms on the grid or the underlying lead is equal to 96.06 grams for 2 × 96,500 coulombs, but the change in weight of the positive plates because of the formation of sulphate on the peroxide is 64.06 grams for the same quantity of electricity. The difference is accounted for by the loss of 1 mole of oxygen at the peroxide. This means that 160.12 grams of sulphate would be formed on the positive plate if the quantity of electricity flowing were 2 × 96,500 coulombs. The ampere-hour equivalent for the gain in weight resulting from local action is, therefore, 2.99 grams for each ampere-hour. The experimental results for the positive plates in solutions of varying concentration at 25° C. are given in Table XXI for solutions saturated with lead sulphate.

TABLE XXI

GAIN IN WEIGHT, GRAMS PER HOUR, OF POSITIVE PLATES IN SOLUTIONS AT 25° C. SATURATED WITH LEAD SULPHATE

Specific Gravity $\frac{25^\circ}{25^\circ}$	Gain in Weight for Plates of	
	Manufacturer A	Manufacturer B
1.150	0.0128	0.0077
1.200	0.0121	0.0077
1.250	0.0069	0.0047
1.300	0.0053	0.0050
1.350	0.0050	0.0048
1.400	0.0047	0.0049

It will be observed from the results given in Table XXI that the gain in weight of the positive plates decreases as the concentration of the solution increases. This suggests that the plates contained some soluble constituent, the solubility of which increased as the concentration increased, but the data which are available on the solubility of lead peroxide and lead sulphate fail to offer an explanation.

b. Effect of Various Impurities

The importance of obtaining exact information about the effect of impurities in storage-battery electrolytes arises from the detrimental effects which many of them produce on the operating characteristics and life of the storage battery, and such information is necessary as a basis for the preparation of specifications for sulphuric acid to be used in the batteries. Engineers have recognized for a long time the necessity for maintaining a high standard of purity in the electrolyte, but within recent years millions of small batteries have passed into the hands of non-technical users who must depend upon the manufacturers and their subsidiaries for satisfactory service.

Determinations of the effect of many impurities have been made by the method of weighing the plates described above. The following data are taken from the papers[10] by Vinal and Altrup, and Vinal and Schramm. A carefully measured quantity of the impurity was added to the electrolyte before the plates were immersed and simultaneous measurements were made of the rate of sulphation of similar plates in pure solutions, the latter being designated as control experiments. The plates were weighed immediately after placing them in the solutions and at frequent intervals during the first day, because the rate of the reaction was generally the greatest at that time. As the reactions slowed down, weighings were made at less frequent intervals. The concentrations of the impurities are expressed as percentages by weight. An analysis of many control experiments makes possible the computation of the probable error of a single observation. It is important to establish the range of probable error since there are a number of impurities which produce little or no effect, and any definite statement that they do or do not produce effects must be based upon a comparison with normal values for the control experiments to within the limits of the probable error. For negative plates the probable error of a single observation varies from 0.15 gram at 50 hours to 0.60 gram at 500 hours; for positive plates the probable error is somewhat smaller.

Impurities Affecting the Negative Plates Only. These include metals (Table XXII) which are deposited quickly in the metallic state and produce considerable gassing and those chemical compounds which are reduced more slowly at the negative plates and result in little, if any, perceptible liberation of hydrogen. A closed circuit is formed between the lead of the plate and the impurity which is deposited upon it. Lead sulphate is formed in proportion to the quantity of electricity flowing and the plate gains in weight. Hydrogen is deposited on the surface of the metallic impurities. The potential required for the liberation of hydrogen on the various metals varies, but it is usually in excess of the potential of the reversible hydrogen electrode. This excess is referred to as overvoltage. Hydrogen is liberated most easily on metals having a low overvoltage, such as platinum and the other

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[10] *J. Am. Inst. Elec. Eng.*, 43, p. 313, 1924; and 44, p. 128, 1925.

metals of the platinum group. These are therefore the most harmful to the battery. Copper and tin having higher overvoltages are less harmful and those metals having an overvoltage which places them above the discharge potential for hydrogen on lead, such as cadmium, zinc, and mercury, produce little or no effect. In some cases the deposition of hydrogen may result in the formation of other chemical compounds.

TABLE XXII

LOCAL ACTION PRODUCED BY IMPURITIES AFFECTING ONLY THE NEGATIVE PLATES

(Results are expressed as the gain in weight of a single plate in grams at intervals from 50 to 500 hours.)

Impurity	Material Added	Percentage Impurity	Time in Hours					
			50	100	200	300	400	500
None (Control experiments)		....	0.69	1.44	2.68	3.87	5.03	6.08
Platinum	PtCl$_4$	0.00001	0.7	1.4	3.0	4.8	6.8	8.4
		0.00003	13.2	19.3	26.1	29.9	32.4	34.2
		0.00005	27.4	28.1	28.8	29.2	29.3	29.5
Copper	CuSO$_4$	0.008	1.1	2.1	4.0	6.1	8.1	.....
Copper	CuSO$_4$	0.04	7.3	10.7	15.6	19.5	23.5	.....
Silver	Ag$_2$SO$_4$	0.1	13.5	18.6	24.0	.....	.....	.....
Tin	SnSO$_4$	0.1	4.6	7.0	9.4	11.0	12.5	13.9
Tungsten	WO$_3$	0.003	0.3	1.7	5.3	10.0	15.0	20.0
Bismuth	Bi$_2$O$_3$	0.2	4.5	5.8	8.2	.....	.....	.....
Sulphurous Acid	H$_2$SO$_3$	0.05	5.1	6.4	8.3	10.2	11.8	13.6
Sodium Bichromate	Na$_2$Cr$_2$O$_7$	0.05	3.3	5.2	8.4	11.4	14.1	.....
Arsenic *	As$_2$O$_3$	0.001	1.3	2.6	4.8	6.9	8.8	10.9
Arsenic	As$_2$O$_3$	0.10	0.8†	.....	.....	.....	.....	.....
Antimony	Sb$_2$(SO$_4$)$_3$	0.001	3.8	8.8	16.3	.....	.....	.....
Nitrates	HNO$_3$	0.001	1.3	2.0	3.6	.....	.....	.....
		0.004	3.1	4.0	5.2	.....	.....	.....
		0.008	5.3	6.4	7.7	.....	.....	.....
		0.035	23.0	25.3	27.3	.....	.....	.....

* These results are not as reliable as the others.

† At 55 minutes, plates gassing and solution turned brown, test abandoned.

Platinum. Platinum has always been considered one of the most deleterious impurities, but it is not as common an impurity now as formerly, because sulphuric acid is no longer concentrated in platinum vessels. When negative plates are immersed in electrolyte containing even a very minute amount of platinum, gassing begins at once and the plate is rapidly discharged. The presence of 0.0001 per cent of platinum produced such violent gassing that the surface of the plate was apparently blasted off and much of the platinum thereby removed, which accounts for the fact that 0.00003 per cent acting more slowly produced a greater discharge of the plates, as shown in Fig. 44. Negative plates contaminated with platinum are useless.

The curves of Fig. 44 make possible an estimate of the local action in terms of the equivalent current that would be discharged by the plate normally for the same rate of sulphation. The equivalent currents are proportional to the slopes of the lines. The curve for plates in pure acid shows the average equivalent current of the local action to be 0.0059 ampere. With this as a basis, the equivalent currents during the first part of the experiment for the other curves have been calculated to be as shown in the table on p. 128.

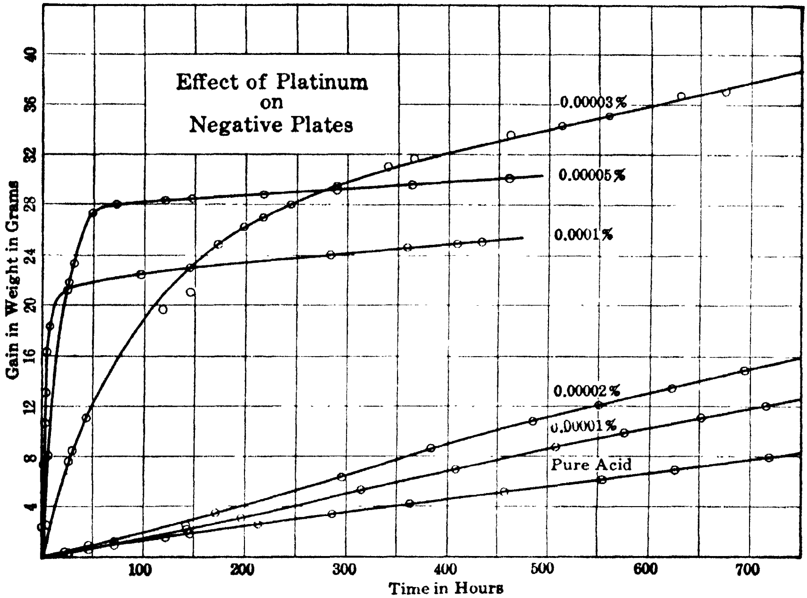

FIG. 44. Local action of plates in solutions contaminated with small amounts of platinum.

By this calculation, a physical meaning is given to the rather vague term "local action."

Platinum Concentration, Per Cent	Current Equivalent of Local Action, Amperes
0.00001	0.0093
0.00002	0.0113
0.00003	0.107
0.00005	0.345
0.00010	1.71

Copper and Silver. Large amounts of copper and silver were added to the solutions as these metals do not produce such marked effects as platinum. A considerable amount of the copper and silver was deposited on the plates as a spongy mass which afterward fell off. The gain in weight of the plates was therefore chiefly lead sulphate. The copper solutions, initially blue, lost color as the copper deposited and an analysis of the electrolyte at the end of the experiment showed only a very small trace of copper remaining. Since the amount of solution to one plate in these experiments was approximately ten times that in a battery under operating conditions, it is apparent that a larger amount of copper or silver was deposited on a single plate than would be the case normally for the same concentration of these impurities. If more plates had been present, these impurities would probably have been deposited more uniformly and so have been more effective. Such impurities as copper and silver cannot be eliminated by changing the electrolyte, but their effect may in some cases be mitigated, as will appear later.

Bismuth. Bismuth trioxide reacts with sulphuric acid to form bismuth sulphate and this, in turn, is reduced at the negative plates to bismuth with the formation of an equivalent amount of lead sulphate. The bismuth is deposited as a brown powder on the plate. Twelve and a half grams of bismuth trioxide were added to the solution of sulphuric acid. This amount is equivalent to 24.4 grams of lead sulphate, but to this must be added the weight of the bismuth deposited in the pores of the plate amounting to 11.2 grams making the predicted increase in weight 35.6 grams. The two plates in the solution actually gained a total of 33.6 grams.

Arsenic and Antimony. Both of these materials affect the negative plates, particularly the latter. The reactions of arsenic and antimony are probably analogous to those of bismuth, as the reduced material becomes visible after a short time. The presence of either antimony or arsenic in the electrolyte may be detrimental for other reasons also.

Traces of arsine and stibine have occasionally been reported in the gas liberated from storage batteries when on charge.

Antimony, when present on the surface of negative plates, is a cause of local action which results in the formation of lead sulphate and the liberation of hydrogen. Jumau [11] recognized this in 1898 and two years later Strasser and Gahl [12] showed that hydrogen is liberated more easily on antimony than on lead, that is, the overvoltage for hydrogen on antimony is less. Within recent years the experiments of Crennell and Milligan,[13] Schubert,[14] and Vinal, Craig, and Snyder [15] have shown that corrosion of the positive grid in normal operation of a battery may supply enough antimony to the negative plates to affect their performance. As a result of each period of charge, antimony from the positive grids is deposited in minute amounts on the negative plates. This freshly deposited antimony is very active, but fortunately for the operation of the battery, successive charges and discharges of the cell cover the antimony previously deposited with lead or lead sulphate and thereby decrease its effect. Old plates contain more antimony in the active material than new plates and they are, therefore, subject to more local action, but the local action is usually not proportional to the amount of antimony carried in the active material. The maximum charging voltage of a cell without antimony (or other materials of low overvoltage for hydrogen) is normally more than for the ordinary cell, because polarization of the negative plates, which are cathodic during charge, is greater when antimony is absent. Maximum cell voltages on charge have been reported from 2.8 to 3.0 volts, but the value in any particular case will depend on current density, resistance and other factors. This excessive voltage has been cited sometimes as a possible cause for corrosion and failure of positive grids which do not contain antimony. This cannot be the correct explanation, however, since the excess voltage is a result of higher polarization of the negative plates while the potentials of the positives are affected little if at all by antimony. This is illustrated in Table XXIII which gives some typical conditions.

Nitrates. Nitric acid added to the electrolyte was reduced at the negative plates and produced a marked increase in the rate of sulphation. Even so small a quantity as 0.001 per cent produced a measurable result. The reduction of nitric acid results in the formation of

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[11] *Ecl. Electr.*, 16, p. 133, 1898.

[12] *Zeit. Elektrochemie*, 7, p. 11, 1900.

[13] *Trans. Faraday Soc.*, 27, p. 103, 1931.

[14] Paper before Nat. Bat. Mfgs. Assn., Apr. 24, 1931.

[15] *J. Research*, Bureau of Standards, 10, p. 795, 1933.

TABLE XXIII

Effect of Antimony on Plate Potentials and Cell Voltages

(Negative grids for these cells were all of the same commercial type.)

Description of Plates	Cycle Number	Per Cent Antimony Found in Active Material	Cell Voltage, in Volts	Plate Potentials, Cadmium Readings	
				Positives, in Volts	Negatives, in Volts
Positive grids, pure lead	1	...	2.61	2.44	−0.15
	50	....	2.79	2.52	−0.24
	115	0.04	2.82	....	−0.25
Positive grids, 7% antimony....	1	....	2.61	2.46	−0.13
	50	....	2.73	2.49	−0.22
	115	0.24	2.59	2.52	−0.06
Positive grids, 10% antimony...	1	....	2.60	2.44	−0.13
	50	....	2.70	2.51	−0.16
	115	0.46	2.52	2.52	0.00
Positive grids, pure lead with new negative plates..........	..	....	2.64	2.49	−0.13
Same, 0.03% antimony added to the electrolyte...............	...	....	2.53	2.50	0.00
Positive grids, pure lead negatives after 2 years in service...	....	....	2.51	2.49	0.00

lead sulphate and ammonium sulphate. In the static tests, nitric acid was without effect on the positive plates, but this would not be the case in a battery in actual operation. The grids of the pasted plates would then be attacked. The use of nitrates as forming agents has been referred to previously.

Impurities Affecting the Positive Plates Only. These are chiefly organic compounds such as starch, dextrose, sucrose, and extracts from wood separators.

The effects of acetic acid in storage batteries may appear to be contradictory, as they are not proportional to the amount of acetic acid present. Under some conditions, 1 per cent (or more, if the temperature is not too high) may be added to cells without deleterious effects, but under other conditions much smaller amounts will quickly destroy the positive plates. Experiments have shown that positive plates whose grids are adequately protected by a covering of lead peroxide are relatively immune to the action of acetic acid, but portions of the grid which are bare or covered with lead sulphate are readily attacked. The difficulty in studying this problem lies in determining small amounts of acetic and other volatile organic acids in the presence of large amounts of sulphuric acid. Craig[16] has, however, developed a satisfactory method recently for determining acetic and formic acids in battery electrolytes.

Electrolytic effects of acetic acid and other materials yielding acetate ions occur during charging. Acetic acid, as an impurity in the electrolyte has little effect on the rate of sulphation of plates standing in the electrolyte (see Table XXIV), but it has a very corroding effect on lead and lead alloys when these are made anodic.

Schreiner[17], without discussing storage batteries, has shown that anodic oxidation of acetic acid in sulphuric acid solutions occurs as follows:

$$\underset{\text{(acetic acid)}}{CH_3COOH} \rightarrow \underset{\text{(glycolic acid)}}{CH_2OHCOOH} \rightarrow \underset{\text{(glyoxylic acid)}}{CH(OH)_2COOH}$$

$$\rightarrow \underset{\text{(oxalic acid)}}{COOHCOOH} \rightarrow \underset{\text{(carbon dioxide)}}{2CO_2}$$

This represents the condition when the grids are fully protected by lead peroxide. Tests on cells fulfilling this condition showed that acetic acid, added to the electrolyte initially, is eliminated.

When grids are subject to attack, lead acetate is formed. This is soluble and increases the lead ions with the result that considerable lead sulphate is deposited. The acetate ion, CH_3COO^-, migrates to the anode, which in this case is the positive plate of the battery, and attacks the lead repeatedly. Because the density of lead sulphate is less than that of lead, expansion occurs and the plate is said to "grow," while at the same time the grid loses its mechanical strength and ultimately disintegrates.

It is characteristic that the attack of acetic acid occurs in confined places, as between the grid and the active material. This is illustrated in Fig. 45. The acetic acid is less likely to attack the outer rim of the grid because this is covered, presumably, with lead peroxide. If the active material has pulled away from the grid, or if there are void spaces, or if formation is incomplete, areas are present which are subject to attack by acetic acid. When this occurs, the process is likely to continue.

[16] *J. Research*, Bureau of Standards, 6, p. 169, 1931.

[17] *Zeit. Elektrochem.*, 36, p. 953, 1930.

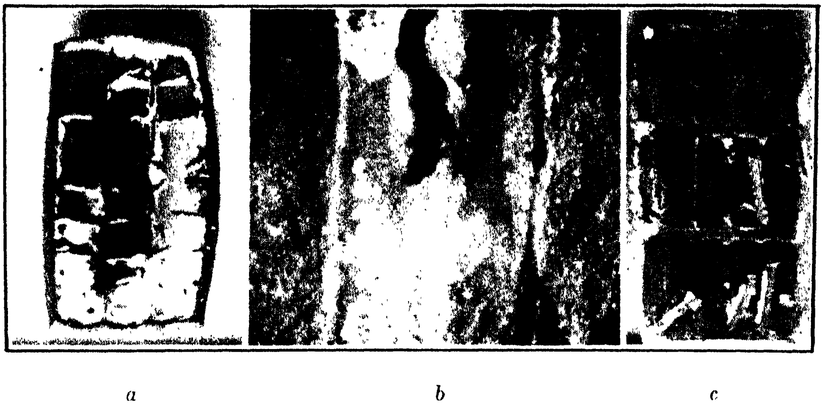

FIG. 45. Effect of acetic acid on positive grid. (*a*) and (*c*), grids destroyed by acetic acid; (*b*), magnified image of surface between grid and positive-active material of a plate readily attacked by acetic acid, showing voids and sulphate spots.

Ethyl alcohol (C_2H_5OH) appears at first sight to be a most unlikely impurity to associate with the electrolyte of a storage battery, but a surprising number of inquiries have been made as to the effects that it produces. Alcohol finds its way into automobile batteries either as

TABLE XXIV

LOCAL ACTION PRODUCED BY IMPURITIES AFFECTING ONLY THE POSITIVE PLATES

(Results are expressed as the gain in weight of a single plate at intervals from 50 to 500 hours.)

Impurity	Percentage of Impurity	Time in Hours					
		50	100	200	300	400	500
None	(Control experiments)	0.34	0.51	0.66	0.86	1.05	1.15
Acetic acid	0.1	0.4	.....	.....	.....	.....	.....
	1.0	.....	0.9	1.6	.....	.....	.....
	3.0	.....	.....	.....	2.4	3.3	.....
Separator extracts (treated)	...	3.2	5.2	7.7	9.4	.....	.....
Separator extracts (untreated)	...	8.9	13.5	18.6	21.1	.....	.....
Dextrose	1.0	23.2	26.3	27.2	.....	.....	.....
Sucrose	1.0	23.6	26.7	27.6	.....	.....	.....
Invert Sugar	2.0	23.6	26.4	26.8	.....	.....	.....
Starch	0.5	11.5	20.3	25.1	.....	.....	.....
Tannic Acid	0.10	0.6	1.1	1.9	2.6	.....	.....

the result of a mistake when water should have been added or because of the impression that it will prevent freezing. Laboratory experiments have shown that alcohol, which is oxidized to acetic acid at the positive plates when the battery is charged, produces corroding effects similar to acetic acid.

Extracts from separators of cedar and cypress in both the treated and untreated condition were made with sulphuric acid solutions of 1.250 specific gravity. The effects which they produced led to experiments with other organic materials. The quantitative effects of materials affecting the positive plates are given in Table XXIV.

Impurities Affecting Both Positive and Negative Plates. These include several metals which may be present in the electrolyte in two states of oxidation and chlorine.

Iron. Iron is perhaps the most common impurity. It is oxidized at the positive plates and reduced at the negative plate, resulting in the discharge of both. Experimental results on the effect of iron are given in Table XXV.

When iron in the ferrous condition is added to the solution it is oxidized by the active material of the positive plates to ferric sulphate, accompanied by the formation of lead sulphate and water. The following equation for the reaction is assumed:

$$PbO_2 + 2FeSO_4 + 2H_2SO_4 \rightarrow PbSO_4 + Fe_2(SO_4)_3 + 2H_2O \qquad (1)$$

The lead sulphate which is formed permits an accurate calculation to be made of the extent of the reaction from the gain in weight of the plates. The gain in weight of the positive plates must, however, be calculated as $PbSO_4 : (PbSO_4 - PbO_2)$, because the plate gains the sulphate radical SO_4 as the result of the reaction but loses simultaneously two oxygen atoms for each molecule of lead sulphate which is formed. The reaction expressed by equation (1) proceeds to completion if sufficient time is allowed. That is to say, all the ferrous sulphate is oxidized to the ferric condition, and beyond this point the rate of formation of lead sulphate is essentially the same as for plates in pure acid solutions. The results of these experiments showed that the curves representing data obtained from the iron solutions become parallel to those for the pure acid solutions after about 150 hours. We may, therefore, calculate the amount of lead sulphate which should be formed and compare it with the amount determined by the weighings. Such a comparison is made in Table XXVI.

Since the reaction expressed in equation (1) came to a definite termination, this afforded an excellent opportunity to determine what the effect of introducing negative plates into the solution would be. This

TABLE XXV

LOCAL ACTION PRODUCED BY IMPURITIES WHICH AFFECT BOTH THE POSITIVE AND NEGATIVE PLATES

(Results are expressed as the gain in weight of a single plate in grams at intervals from 50 to 500 hours.)

Impurity	Material Added	Percentage of Impurity	Time in Hours					
			50	100	200	300	400	500
		(Positive Plates)						
None	(Control experiments)	.. ..	0.34	0.51	0.66	0.86	1.05	1 15
Iron	$FeSO_4$....	0.012	0.7	0 9	1.1	1.3	.....	.....
		0.08	1 5	1.8	2.2	2.3	.....	.....
		0.4	5 6	6 8	7.2	7.5	.....	.....
Manganese	$MnSO_4$	0.08	2.9	3 7	4.4	5 0	.....	.....
		0.4	8.4	10.6	14 4	18.4	.....	.. ..
Chlorine	HCl	0.5	5.5	7.1	8 2	11 9	13 5	.....
	NaCl	1.00	23.7	25.4	26 0	26 2	.....	.....
		(Negative Plates)						
None	(Control experiments)	.....	0.69	1.44	2.68	3.87	5.03	6.08
Iron	$Fe_2(SO_4)_3$	0 012	1.2	2.0	3.4	4.6	5.8	7.0
		0.08	6 3	8.0	9.5	10.8	12.2	13.6
Manganese	$KMnO_4$	0.04	2.2	3.0	4.3	5.6	.....	.....
		0.40	3.1	4.0	5.3	6.7	.....	.....
Chlorine	HCl	0.02	0.6	1.3	2.7	.....	.....	.....
	NaCl	1.00	22.0	27.1	30.2	32.7	.....	.....

TABLE XXVI

COMPARISON OF CALCULATED AND OBSERVED VALUES FOR POSITIVE PLATES IN SOLUTIONS CONTAINING IRON

Amount of Iron Added		Equivalent Ferrous Sulphate, Grams	Calculated Equivalent Lead Sulphate, Grams	Observed Amount of Lead Sulphate, Grams
Per Cent	Grams			
0.4	22.5	61.2	61.2	60 2
0.08	4.5	12.2	12.2	11.8
0.012	0.675	1.8	1.8	3.4

case represents the condition of a battery containing both positive and negative plates. One charged negative plate was immersed in each solution at the conclusion of 360 hours. These plates were not in electrical contact with the positive plates. The reduction of the iron to the ferrous condition began immediately and the product in turn was reoxidized by the positive plates, accompanied by a further discharge. Curves showing the observations which were made are given in Fig. 46, the experiment being continued until 820 hours had elapsed. Iron has a destructive corroding action on the positive plates, particularly those of the Planté variety, because it increases the rate of sulphation.

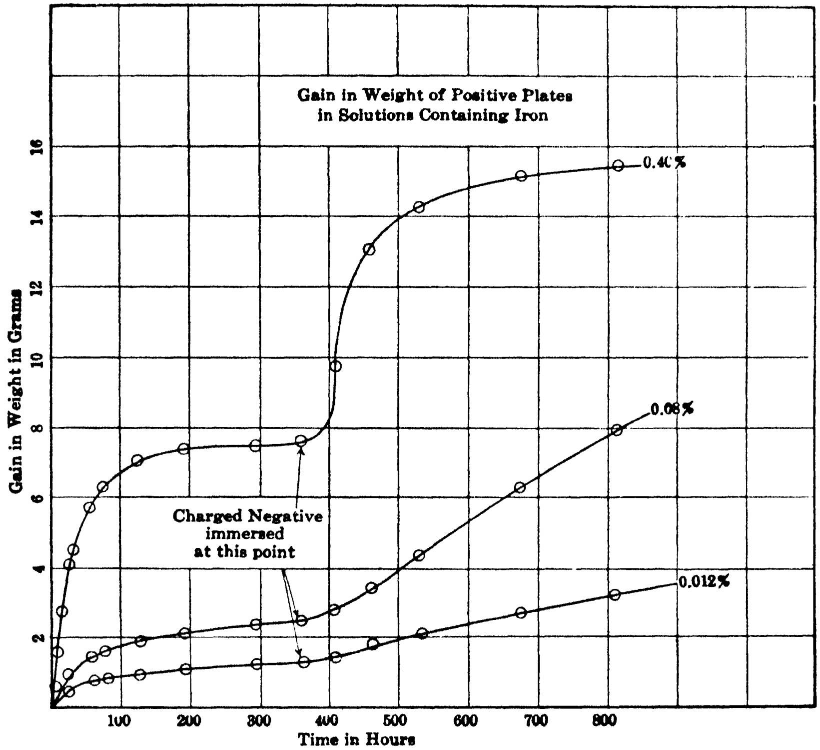

FIG. 46. Effect of iron in producing local action at the positive plate.

The action of iron on the negative plates is much more pronounced than on the positives, and the local action produced is in excess of the amount which would be calculated from the reduction of the ferric sulphate. The effect is probably the result of two simultaneous reactions, which may be represented by the following equations:

$$Pb + Fe_2(SO_4)_3 \rightarrow PbSO_4 + 2FeSO_4 \qquad (2a)$$

$$Pb + H_2SO_4 \rightarrow PbSO_4 + H_2 \qquad (2b)$$

The amounts of iron added to the solutions were 4.5 grams and 0.675 gram. These are equivalent to 16.1 grams and 2.4 grams of ferric sulphate. On the basis of equation (2*a*) these amounts will account for 12.2 and 1.8 grams of lead sulphate, respectively.

Table XXV shows the gain in weight of the plates in terms of the sulphate, SO_4, taken from the electrolyte. This gain in weight calculated to lead sulphate, $PbSO_4$, is in excess of what may be accounted for by the reduction of the iron salt from the ferric to the ferrous condition. This indicates that the presence of iron accelerates the reaction between sulphuric acid and lead, as represented by equation (2*b*).

In the early stages of the experiment, when considerable ferric iron was present, this reaction was greatly accelerated. When 150 hours had elapsed, this accelerating effect of the iron seems to have died out. After 150 hours sulphate was being formed at a slightly greater rate on the plates in the solutions to which iron was added than in the pure acid. This effect is probably to be accounted for by the well-known slow spontaneous reoxidation of the ferrous sulphate by the air and its subsequent reduction by the negative plates during the long time that the experiment lasted.

Our knowledge of the reaction of iron in the storage battery has been extended by Lea and Crennell,[18] who have found that in addition to the discharge of the plates as a result of local action some permanent loss of capacity occurs which they attribute to adsorption of iron by the lead peroxide of the positive plates. They deny that iron accelerates the sulphation of negative plates as mentioned above, claiming that the self discharge of both positive and negative plates follows the simple theory of oxidation and reduction. However, Jumau [19] has stated that the effect of iron is greater on negative plates than on positives. His results support those of Vinal and Altrup. Lea and Crennell found that a definite tendency exists for iron to accumulate at the bottom of the cell. This may afford an explanation for the difference in condition occasionally observed between the upper and lower portions of positive plates.

Manganese. The experimental results obtained when negative plates were immersed in solutions containing manganese are shown in Table XXV. It is at once apparent that the effects produced are not

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[18] *Trans. Faraday Soc.*, 23, p. 269, 1927.

[19] *Étude résumé des accumulateurs électriques*, p. 93, 1924.

proportional to the amounts of manganese added. The reason for this is a reaction between the sulphuric acid and the potassium permanganate, which is independent of the reaction at the plates. The reaction between the permanganate and the 1.250 sp. gr. acid may be expressed by the equation:

$$4KMnO_4 + 6H_2SO_4 \rightarrow 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2 \quad (3)$$

This is a slow reaction that may be demonstrated by a simple laboratory test, several hours being required to collect enough of the oxygen to make a satisfactory test. During the experiments the gas (oxygen) given off appeared in small amounts over the entire surface of the liquid. It was not localized at the plates.

The reactions which take place at the plates, in contradistinction to the above reaction, which occurs whether the plates are present or not, results in decolorizing the permanganate and in the formation of lead sulphate and manganese dioxide. The reactions are not fully understood, but the following equation, which is in accordance with the observed facts, is believed to represent the reaction:

$$2KMnO_4 + 4H_2SO_4 + 3Pb \rightarrow K_2SO_4 + 2MnO_2 + 3PbSO_4 + 4H_2O \quad (4)$$

There are probably several intermediate reactions which take place before the end products are reached. A sludge which fell to the bottom of the jar was tested and found to be hydrated manganese dioxide. Possibly some of the manganese was converted into manganese sulphate. No gassing was visible at the plates.

Manganese was added to the solutions in which the positive plates were immersed, as manganous sulphate, $MnSO_4$. The solutions were initially colorless but began to show a purple coloration almost immediately after contact with the positive plates. This indicated the formation of permanganic acid, $HMnO_4$, probably according to the equation:

$$5PbO_2 + 2MnSO_4 + 3H_2SO_4 \rightarrow 2HMnO_4 + 5PbSO_4 + 2H_2O \quad (5)$$

Although manganese may be thrown out of solution as relatively insoluble manganese dioxide, a small amount of manganese persisting in the solution as permanganate has a strong and destructive oxidizing action on organic matter, including both wood and rubber. The action occurs particularly at points where the organic matter is pressed into direct contact with lead peroxide of the positive plates. Small amounts of manganese are probably more destructive to the tightly packed elements of the present storage batteries than to those of earlier years in which there was a wider separation of the plates. A few hundred thousandths of a per cent of manganese in the electrolyte have been found destructive.

Manganese causes wood separators to become bleached and thin; the ribs are destroyed and the web becomes perforated. If separators damaged in this way are dried, the side which was next to the positive plates usually has a characteristic silvery appearance. Rubber separators also are eaten away in a manner to shorten the useful life of the cell.

The characteristic pink to purplish coloration produced when the battery is on charge is a definite symptom of the trouble, but it cannot be readily observed when the cells are in opaque cases.

There are several possible sources of manganese in a storage battery. The sulphuric acid used in preparing the electrolyte may contain small amounts, but acid free from manganese in harmful quantities is obtainable. Material of the case is a more likely source. Sometimes the covers and bridges contain more manganese than the side walls. Iron and manganese often are found together in case material. Such material should be avoided.

Other Impurities Affecting Both Plates. Hydrochloric is similar to nitric acid in its property of being a solvent for lead. Hydrochloric acid attacks both the sponge lead of the negative plate and the lead peroxide of the positive plate. Chlorine gas is liberated at the latter.

Ammonia may be present in the electrolyte as a result of absorption of ammonia gas by the electrolyte, or it may come from the use of ammonium sulphate in preparing the paste for pasted plates, or from the reduction of nitric acid. It exerts some forming action on the positive plate and has been said to be a cause of self-discharge of both positive and negative plates. Tests have shown, however, that ammonia may be present in the electrolyte to the extent of even 50 parts in 100,000 without the battery losing more than 8 per cent in capacity while standing during a period of four weeks following full charge.

Combinations of Impurities. Kugel[20] found that combinations of impurities such as tungsten and copper produced local action at the negative plates exceeding the effects of either of these materials singly. He advanced the theory that the polarization of the copper is decreased by the presence of the tungsten. Scarpa[21] has given a similar explanation that the presence of the tungsten lowers the overvoltage, permitting the liberation of hydrogen on the surface of the copper. In either case the local currents between the lead and the copper would be in-

[20] *Elektrotech Zeit.*, 13, pp. 8 and 19, 1892.

[21] *L'Elettrotecnica*, 6, p. 317, 1919.

creased. Tungsten is an unusual impurity but furnishes an interesting example, as shown in Fig. 47. The more recent work of Vinal and Schramm[22] has revealed other combinations more likely to occur that result in the rapid discharge of the negative plates. These combinations all include copper as one constituent, the others being mercury, molybdenum, zinc, arsenic, and antimony, for which the detailed results are given in Table XXVII. The harmful effect of copper in a battery, therefore, depends more on the combinations with other impurities than on the effect produced by the copper alone.

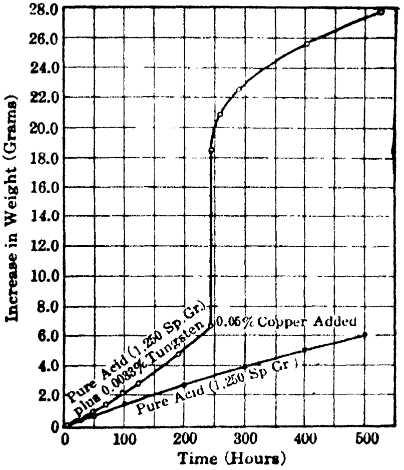

Fig. 47. Effect of a combination of copper and tungsten on negative plates.

TABLE XXVII

Local Action Produced by Combinations of Impurities Affecting the Negative Plates

(Each experiment was started with the first named impurity and then copper was added at the time shown.)

Combination	Material Added	Percentage of Impurity	Time of Adding Cu (hours)	Time in Hours					
				50	100	200	300	400	500
None (Control experiments)				0.69	1.44	2.68	3.87	5.03	6.08
Tungsten	WO_3	0.003	246	1.1	2.4	5.4	23.1	25.6	26.7
Copper	$CuSO_4$	0.05							
Mercury	Hg_2SO_4	0.01	145	0.8	1.7	31.6	31.8	31.0	31.2
Copper	$CuSO_4$	0.05							
Molybdenum	MoO_3	0.01	145	1.1	2.0	30.5	.....	32.4	40.0
Copper	$CuSO_4$	0.05							
Zinc	ZnO	0.01	145	1.2	1.6	24.0	33.7	33.2	.....
Copper	$CuSO_4$	0.05							
Arsenic	As_2O_3	0.001	145	1.0	2.0	23.2	25.8	28.0	29.2
Copper	$CuSO_4$	0.05							
Antimony	$Sb_2(SO_4)_3$	0.001	145	3.6	8.8	28.0	38.5	38.0	36.0
Copper	$CuSO_4$	0.05							

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[22] *Loc. cit.*

Some local action is produced by the gases, oxygen and hydrogen, which are produced when the cells are on charge. The oxygen oxidizes the active materials of the negative plate, and the hydrogen reduces some of the lead peroxide of the positive plate. The extent of the reaction caused by these gases, when the electrolyte is saturated with them at the end of a charge, is small compared with the total capacity of the battery, but probably accounts in part at least for the fact that the most rapid rate of loss of charge is observed immediately after the charging period.

c. Limits for Impurities in Sulphuric Acid

Specifications for sulphuric acid, both in the concentrated form and when diluted for use in storage batteries, differ very greatly as to the amount of the various impurities which are considered allowable. In Table XXVIII are given figures which are taken from the Federal Specifications OA111 and WB131b. If the amount of the impurities allowed by specifications is made too small, a serious difficulty may arise in finding acid sufficiently pure to meet them. On the other hand, the specifications must limit the impurities to such amounts as are still within the limits for satisfactory operation of the batteries.

It is assumed that when the concentrated acid is diluted to a specific gravity of 1.400 (50 per cent) with pure distilled water, the percentage of impurities in the diluted solution will be approximately halved. There is no hard and fast rule for electrolytes in batteries. The limits given in Table XXVIII are about what may be expected in the case of new batteries when fully charged. Some impurities tend to accumulate as the age of the battery increases, but not all of them remain in the electrolyte. Platinum, silver, copper, arsenic, and antimony deposit on the negative plates; nitrates are reduced to ammonia; chlorides are eliminated as chlorine, in part at least, during charge; manganese is precipitated as manganese dioxide, but enough can remain in the electrolyte to do damage to organic materials; iron and ammonia remain in solution and are likely to increase with time.

d. The Reduction of Sulphation

Frequent attempts have been made to reduce the sulphating action of sulphuric acid on the plates of storage batteries by the addition of various substances. Chief among these has been sodium sulphate, which is frequently sold under the name of Glauber salts. Schoop,[23] as far back as 1895, expressed the opinion that the use of sodium sul-

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[23] "Das Sekundar Element," *Encyklopädie der Elektrochemie*, IV, Part 2, p. 133, 1895.

TABLE XXVIII

PURITY OF SULPHURIC ACID AND SOLUTIONS FOR BATTERY USE
(Specific gravities are at 60° F.)

	Calculated as	Maximum Limits, Per Cent (Except as Noted)		
		Sp. Gr. 1.835	Sp. Gr. 1.400	Sp. Gr. 1.280 (In New Battery)
Per cent H_2SO_4, not less than	....	93.19	50.0	36.8
Organic matter	....	*	*	*
Fixed residue	....	0.03	0.015	....
Suspended matter	...	....	....	Lead compounds only
Iron	Fe	0.005	0.003	0.012
Sulphurous acid	SO_2	0.004	0.002	....
Arsenic	As	0.0001	0.00005	0.00005
Antimony	Sb	0.0001	0.00005	0.00050
Manganese	Mn	0.00002	0.00001	0.00002
Nitrates	NO_3	0.00050	0.00030	....
Ammonia	NH_4	0.00100	0.00050	0.00600
Chloride	Cl	0.00100	0.00050	0.01200
Copper	Cu	0.00500	0.00300	0.00500
Zinc	Zn	0.00400	0.00200	....
Selenium	Se	0.00200	0.00100	....
Platinum †	Pt	<0.00002	<0.00001	<0.00001

* To pass test, see Chapter IX.

† Platinum should always be less than the limits specified as these are dependent on sensitivity of the test.

phate was not beneficial. Its use appears to have originated with some experiments made in England by Preece. Neither is sodium sulphate a satisfactory substance for the removal of the sulphation from the plates. For this purpose Schoop advocates the use of sodium bisulphate, $NaHSO_4$, in place of the acid solution. When this is used, the acid electrolyte is poured out from the battery before the sodium bisulphate solution is added. It has been found possible in some cases, however, to simplify this treatment for the removal of sulphation by merely pouring out the acid electrolyte and filling the cells with distilled water. Lead sulphate is more soluble in water than in solutions of sulphuric acid as shown in Table XXXIII. The cells are then put on charge at a low rate, provided they do not gas excessively, or at a current density which will maintain the voltage at the terminals of the cell at 2.3 volts, or less. If low-current densities are used, considerably more time is required for the reduction of the lead sulphate. High-current densities, on the other hand, raise the temperature of the cell, particularly when the internal resistance is high, because of the presence of lead sulphate; they may also result in hard gassing. While the water treatment may not be the best in all cases, it has been found satisfactory, particularly in the case of batteries of the starting and lighting type. Excessive sulphation and the water treatment are discussed in Chapter VI.

e. Solid Electrolytes

Various attempts have been made to solidify the electrolyte in storage cells in order to eliminate spilling, and for other reasons. Materials which have been used in the past for making the electrolyte viscous have included albumen, starch, burnt clay, pumice, cellulose, soap, fatty acids, plaster of Paris, asbestos, sand, water glass, and fuller's earth. Of these various substances, water glass is perhaps the most suitable. The solidification of the electrolyte is brought about by the formation of silicic acid. The ratio of sodium oxide, Na_2O, to silica, SiO_2 varies somewhat and the commercial silicate contains more silica than is indicated by the formula, Na_2SiO_3. The reaction for the silicate and sulphuric acid may be represented by the following formula:

$$Na_2SiO_3 + xH_2O + H_2SO_4 \rightarrow SiO_2 \cdot (x + 1)H_2O + Na_2SO_4$$

It is necessary that both the acid and the water glass should be pure. Chlorides are perhaps the most common impurity occurring in the water glass. The time of setting before solidification takes place, and the stiffness of the jelly afterwards, are regulated by the proportions of the acid and the water glass. When thickening of the mixture begins, the final setting process occurs within a very few minutes. This mixture represents an interesting time reaction. If the mixture is made from dilute solutions, as, for example, sulphuric acid of specific gravity 1.275 and water glass of specific gravity 1.210, the greater the percentage of water glass in proportion to the acid, the more quickly the jelly sets and the more solid it becomes. The hard jellies are resonant.

Jelly electrolytes may be made from mixtures of concentrated sulphuric acid and dilute solutions of water glass or from dilute solutions of the acid and somewhat more concentrated solutions of the water glass. The time of setting is shortened by increasing the percentage of water glass and by using stronger acid, but if the percentage of water glass is too great crystals will form as soon as the two liquids are poured together and these crystals will make the jelly cloudy and granular. It is possible to prepare the jelly as a clear, translucent, bluish mass which varies in consistency from a thick liquid to a fairly hard, resonant solid. The time of setting for various combinations is shown in Fig. 48. The curves are numbered from 1 to 11 and represent

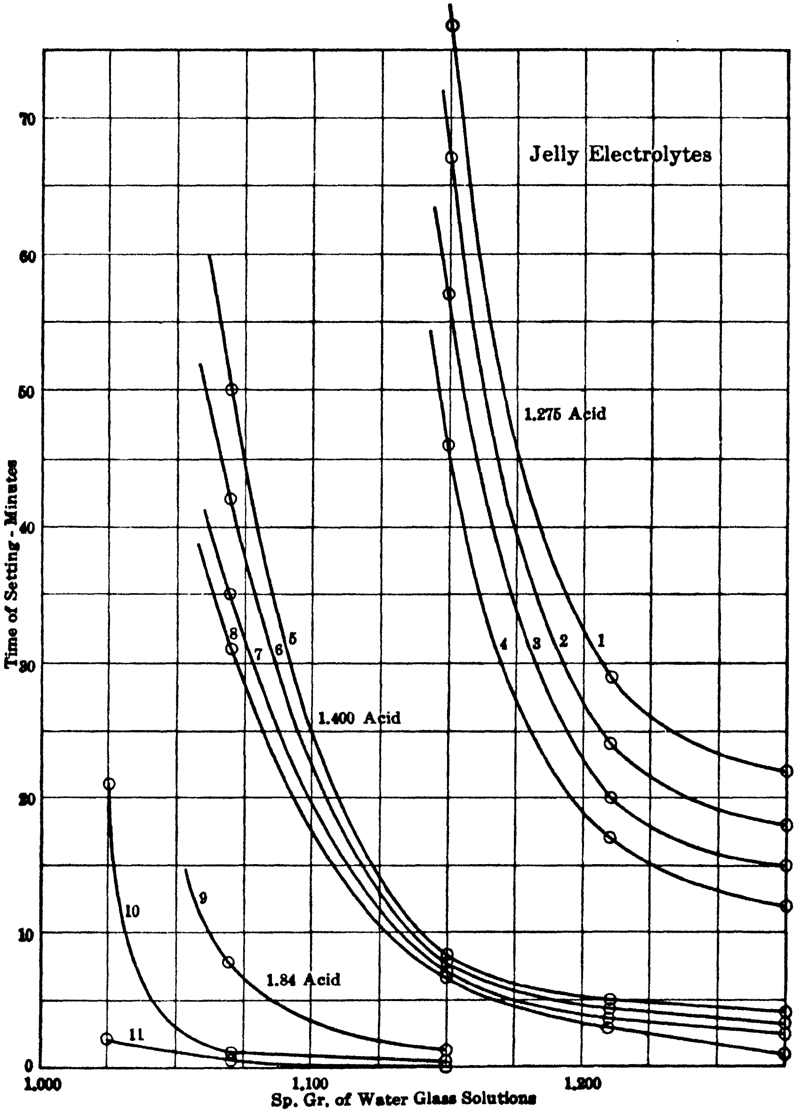

FIG. 48. Preparation of jelly electrolytes from solutions of sulphuric acid and water glass.

different proportions of the water glass and acid solutions measured by volume. These are as follows:

Curve 1, 5 parts 1.275 acid to 1 part of water glass
Curve 2, 4 parts 1.275 acid to 1 part of water glass
Curve 3, 3 parts 1.275 acid to 1 part of water glass
Curve 4, 2 parts 1.275 acid to 1 part of water glass

Curve 5, 5 parts 1.400 acid to 1 part of water glass
Curve 6, 4 parts 1.400 acid to 1 part of water glass
Curve 7, 3 parts 1.400 acid to 1 part of water glass
Curve 8, 2 parts 1.400 acid to 1 part of water glass

Curve 9, 1 part 1.84 acid to 4 parts of water glass
Curve 10, 1 part 1.84 acid to 3 parts of water glass
Curve 11, 1 part 1.84 acid to 2 parts of water glass

Batteries containing jelly electrolytes do not have as good electrical properties as those with the ordinary electrolyte. The internal resistance is higher and the capacity lower. They do not last well in service; and in spite of the many attempts to use this material, no battery of which the author has knowledge has stood the test of time.

Since the jelly formed by the action of the water glass and the acid has a tendency to crack away from the plates of the storage battery, Schoop[24] has advocated the addition of paper stock, cellulose, or asbestos to the mixture to serve as a binder. In preparing this material for use, the water glass is poured into the acid and thoroughly mixed. The binding material is then added, and the mixture allowed to stand until thickening of the solution is observable. When this point comes, it is necessary to pour the electrolyte into the cells immediately, as it is impossible to do so after solidification has actually taken place. When the electrolyte is prepared in this manner, it will not stick to the plates. Gas bubbles, which are formed at the plates during the process of the charging, will have an opportunity to escape between the plate and the layer of solid electrolyte. A layer of fluid electrolyte is desirable between the solid electrolyte and the surface of the plate. This facilitates the reactions within the storage battery and increases the capacity. Schoop obtained a patent[25] on jelly electrolytes in 1889. His experiments were further described in 1890.[26]

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[24] *Loc. cit.*

[25] *Elektrotech. Zeit.*, 10, p. 473, 1889.

[26] *Electrician*, 25, p. 253, 1890.

The use of sodium silicate for the preparation of solid electrolytes has been periodically rediscovered a number of times during recent years. Its use, however, dates back probably fifty years. A clear and detailed description of its preparation has been given by Schoop in the reference previously mentioned.

f. "Patent" Electrolytes

Within the past few years, a considerable number of special electrolytes for use in storage cells, particularly of the starting and lighting type, have appeared. For the lack of a better designation for these electrolytes, they have been commonly referred to as patent electrolytes. Very few of them, however, are patented, and for the most part their composition is not revealed by the manufacturers. From the tests and experiments which have been made on this class of substances it may be stated that few, if any, of them have any real merit. They fall naturally into three classes, the first of which includes those consisting merely of ordinary sulphuric acid solution, of approximately customary densities, sold under trade names at fancy prices and with extravagant claims. The second class of these electrolytes contains substances, such as sodium sulphate, which are supposed to decrease the sulphation of the plates within the battery. The third class is that containing various corrosive agents such as bichromates, nitrates, and similar substances.

One of the most common claims made for electrolytes of this type is that the electrolyte is capable of charging the battery within a very short period of time or in a few minutes. It is sometimes stated that the electrolyte is "charged." This is obviously not the case. It is true that any battery may be partially charged by an electric current within a few minutes, but by the term charged we generally understand that the battery is fully charged. It is obviously impossible that the battery should be charged instantaneously or in a short time. The reactions taking place within the battery are in accordance with Faraday's law, irrespective of the particular substances which the electrolytes may contain.

If the electrolyte be poured out of a discharged battery and a more concentrated electrolyte then added, a small additional capacity may be obtained from the remaining active materials of the plates, and so, in the absence of exact measurements, the battery may appear to be charged; but the addition of a strong electrolyte to obtain a little more capacity is analogous to beating an exhausted horse.

7. PROPERTIES OF ALKALINE ELECTROLYTES

The electrolyte for the alkaline storage batteries, in which the electrodes are nickel oxide and iron, is a solution of potassium hydroxide in water. To this solution, as used in the Edison batteries, is added a small amount of lithium hydroxide. The lithium hydroxide has a beneficial effect on the operation of the cells but is not necessary for the fundamental reactions which occur. The use of the lithium hydroxide is based on the results of experiment rather than on theoretical considerations. The lithia is considered essential for long life of the Edison battery, since a new battery without it has a falling life curve, but when the lithia is present the curve rises slowly for a considerable time before it begins to fall.

The concentration and chemical composition of the alkaline electrolytes, considered as a whole, do not change during the periods of charge and discharge. The measurement of the specific gravity is, therefore, of less importance than for sulphuric acid electrolyte used in the lead batteries. Occasional measurements of the specific gravity should be made, however, because there is a gradual weakening of the electrolyte, accompanied by a decrease in capacity of the battery to the point at which renewal is required.

The alkaline electrolytes for Edison cells are distinguished as "First Fill Electrolyte," "Refill Electrolyte," and "Renewal Electrolyte." The first is a 21 per cent solution of potassium hydroxide in water with 50 grams of lithium hydroxide to the liter of solution. The second is also a 21 per cent solution of potassium hydroxide with x[27] grams of lithium hydroxide. The last is a 25 per cent solution of potassium hydroxide with 15 grams of lithium hydroxide per liter. The uses of these solutions are indicated, in a general way, by their names. The initial filling of the cells at the factory is done with the "First Fill Electrolyte" with extra dry lithium hydroxide added according to the type of cell, to provide the correct amount per unit of the positive active material. The second kind of electrolyte is used mostly in export batteries, which after formation are shipped dry. The refill electrolyte is also used to replace losses caused by spillage, or when it is necessary to replace the electrolyte because of impurities. The third or "Renewal" electrolyte is used when the previous solution has reached the low limit of specific gravity. It is more concentrated than the first fill, in order to compensate for the dilution caused by the old electrolyte held in the pores of the plates.

[27] The amount of lithia is made approximately equal to the quantity found after formation in the original electrolyte.

Before these electrolytes are placed in the cells, their normal specific gravities are as follows:

	Potassium Solutions, Sp. Gr. at 60° F.
First-fill electrolyte	1.228 to 1.230
Refill electrolyte	1.212 to 1.216
Renewal electrolyte	1.248 to 1.250

When the electrolyte has decreased in the course of service to a specific gravity of 1.160, it should be renewed. In determining when this limiting value is reached, certain precautions must be taken. The electrolyte must be adjusted to the proper level and thoroughly mixed by giving the battery a full charge, and the sample which is taken must be free from gas bubbles at the time that the specific gravity is measured. Correction must be made for temperature if the measurements are made at other than the standard temperature of 60° F. Normally the electrolyte will require renewal two or three times during the useful life of the battery. Operating a battery containing electrolyte of lower specific gravity than the limit mentioned above will produce sluggishness, loss of capacity, and rapid breakdown in heavy service. Since these difficulties may also be caused by the presence of impurities in the electrolyte, a chemical analysis of the electrolyte or the water used for flushing the cells may sometimes be necessary.

Sufficient renewal electrolyte should be procured when the results of careful measurements indicate that renewal is necessary. When it is available, the battery should be discharged at the normal rate to zero voltage and then short-circuited in groups of not more than 5 cells for 2 hours. The old electrolyte is to be poured out while the battery is vigorously shaken to rinse the plates. It may be necessary to handle the cells separately, if they are large. Water should not be used for rinsing the plates. As each cell is emptied, the new electrolyte should be added immediately, and when all are filled the battery should be put on charge at the normal rate for 15 hours, A and B types, or 10 hours for type G cells. During this operation observations of the temperature ought to be made at intervals, and if the battery should reach the limits set for normal operation (115° F.) the charge should be interrupted until the battery has cooled.

Potassium hydroxide is variously called potassium hydrate, caustic potash, and potassa. It is a white solid substance which is very deliquescent and easily soluble in water. It dissolves the skin and many other organic substances. Potassium hydroxide, both in the solid state and in solution, absorbs carbon dioxide from the air. It is necessary to protect the solution in the battery, by gas valves in the vent plugs, from contamination by carbon dioxide. These valves are designed to prevent the ingress of gas, but to permit the ready escape of gas generated within the cell. Potassium hydroxide may be prepared electrolytically from potassium chloride. Lithium hydroxide is obtained in solution by the action of lime on a solution of lithium carbonate. The solution is colorless and is very caustic. Crystals of lithium hydrate contain only 54 per cent lithium hydroxide.

a. Properties of Potassium Hydroxide Solutions

The data which are given in Table XXIX are for pure solutions of potassium hydroxide without the addition of the lithium hydroxide.

TABLE XXIX

PROPERTIES OF POTASSIUM HYDROXIDE SOLUTIONS

Per Cent	Density $\frac{15^\circ \text{C.}}{4^\circ \text{C.}}$	Resistivity		Viscosity 18° C. Centipoises	Freezing Point, ° C.	Specific Heat, Calories	Grams of KOH per Ml of Solution
		At 18° C., Ohm-Cm.	Temperature Coefficient				
1	1.008	....	......	1.08	− 1	0.98	0.0101
5	1.045	5.40	0.0186	1.17	− 3	.92	.0522
10	1.092	3.20	.0187	1.30	− 8	.87	.1092
15	1.140	2.34	.0190	1.48	−15	.83	.1710
20	1.188	2.00	.0196	1.72	−24	.80	.2376
25	1.239	1.86	.0206	2.05	−38	.77	.3097
30	1.290	1.84	.0220	2.50	−59	.74	.3870
35	1.344	1.96	.0240	....	....	.71	.4704
40	1.399	2.20	.0267	....	....	.69	.5596
45	1.456	2.56	.0298	....	....	....	.6552
50	1.514	....	......	....	....	....	.7570

The amount of the latter which is added is relatively small and the electrolytes are, therefore, represented sufficiently well by the properties of the pure solutions for which accurate information is available. The percentage composition is given for densities at 18° C., since most of the original material is given on this basis. To correct the observed results at any temperature to the standard temperature, one unit in the third decimal place is to be added for each two degrees Centigrade or three degrees Fahrenheit if the temperature is above the standard temperature, or subtracted, if below it. These corrections are approximately the same as for the acid electrolyte used in the lead batteries.

b. Resistivity of Electrolyte

The resistivity of the alkaline electrolyte varies with the concentration, the temperature, and the amount of lithium hydroxide added to the solution. The electrical resistance depends on the resistivity, the length of the path, and the cross-sectional area through which the current flows, according to the equation $R = \rho\frac{l}{s}$ where R is the resistance, l the length, s the cross section, and ρ the resistivity. The unit of resistivity is the ohm-centimeter, which was explained in connection with the resistivity of sulphuric acid solutions on page 97. The resistivity of solutions of pure potassium hydroxide at 18° C. (64.4° F.) is given in Table XXIX. The resistivity of the solutions actually used is slightly higher than the figures given in the table, because of the addition of the lithium hydroxide. The percentage increase in the resistivity of a 21 per cent solution of potassium hydroxide containing 50 grams of lithium hydroxide per liter was determined by Turnock[28] to be 21 per cent. Smaller amounts produce effects shown in Table XXX. The addition of the lithium hydroxide increases the capacity of the cells, as stated on page 146, but it drives back the ionization of the potassium hydroxide according to the law of mass action and decreases the conductivity of the solution. By plotting the results given in Table XXIX, it will be seen that the shape of the resistivity-concentration curve for potassium electrolyte is somewhat similar to the resistivity curve for sulphuric acid. Minimum resistivity is attained at a concentration corresponding to a density of 1.270.

TABLE XXX

PERCENTAGE INCREASE IN RESISTIVITY AND CAPACITY USING 21 PER CENT SOLUTION OF POTASSIUM HYDROXIDE WITH LITHIUM ADDED

Grams of LiOH, per Liter	Per Cent Increase * in Resistivity	Per Cent Increase * in Capacity
10	7.1	5.1
20	11.4	7.3
30	15.4	9.3
40	18.5	10.5
50	21.0	12.0

* Turnock, *loc. cit.*

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[28] *Trans. Am. Electrochem. Soc.*, 32, p. 405, 1917.

c. Freezing Points

The freezing points of potassium hydroxide solutions without lithium are given in Table XXIX.

d. Concentration Limitations

As in the case of lead batteries, there are rather definite limitations to the concentration of solutions which can be used successfully in the alkaline cells. Below 1.200 the resistivity begins to increase rapidly, which would impair the electrical output. The cells tend to become sluggish in a weak solution and fail to give their rated capacity. For several reasons, therefore, the lower permissible limit of density has been set at 1.160 for Edison batteries. High concentrations, on the other hand, are also detrimental because of the increased solubility of the iron electrode which becomes noticeable at the higher temperatures. High concentrations, that is, above 1.270, result in increased resistivity. Aside from the matter of cost, therefore, the proper density of the potassium hydroxide electrolyte is the result of compromise and it is fixed within rather narrow limits.

e. Effect of Impurities

Carbonates formed in the electrolyte as a result of the absorption of carbon dioxide from the air or introduced in the water used for flushing the cells are detrimental to the operating characteristics of the battery. Carbonates, when present, result in increasing the resistivity of the solution. The maximum permissible limit is usually stated to be 50 grams of carbonate per liter of electrolyte. The presence of carbonates has been assigned as one of the causes of sluggishness, but no quantitative data are available on this point.

Acid radicals are said to be detrimental to the positive plates. It is quite obvious that the density or specific gravity of the alkaline solutions should not be measured with the same hydrometer that is used to measure acid solutions, unless it is washed entirely free from acid. Good practice requires a separate hydrometer for each kind of electrolyte.

Metallic impurities more positive than iron would deposit on the active material of the negative plate and tend to produce local action. In such a case the iron would be oxidized and hydrogen would be liberated at the surface of the impurity. The detrimental effects of these impurities are mitigated in many cases by several factors. If the overvoltage for hydrogen discharge at the surface of the impurity is in excess of the potential for the discharge of hydrogen on the iron itself, local action cannot occur. Many metals form insoluble hydroxides in the alkaline electrolytes and these will not be effective in producing local action.

Iron is very nearly insoluble in the electrolyte under normal operating conditions but may be present in the electrolyte if it is too concentrated or at too high a temperature. Iron in the electrolyte affects the positive plate resulting in a loss of capacity. At high temperatures hydrogen may be produced as a result of a reaction between iron and the electrolyte. Such a reaction may even occur slowly between iron and water as has been found in studies of the soil corrosion of iron pipes.

f. Modifications of the Electrolyte

The principal modification of the potassium hydroxide solutions used in alkaline batteries is the addition of lithium hydroxide, mentioned above, for use in Edison batteries. Vail[29] mentions efforts to make the electrolyte unspillable. A viscous mixture of sodium metasilicate and sodium hydroxide was used. This should not be confused with the formation of a gel sometimes employed in lead-acid batteries. In any kind of battery, whether of the lead-acid or alkaline type, the diffusion of the electrolyte is an important factor. It is hardly to be expected, therefore, that the batteries could operate as satisfactorily with a viscous or solid electrolyte as with the ordinary solutions.

8. SHIPPING THE ELECTROLYTE

The electrolyte for storage batteries is classed as a corrosive liquid by the regulations[30] of the Interstate Commerce Commission. The regulations require compliance with certain rules relating to the containers, the method of packing, and the labels. Concentrated acid may be shipped in tank cars, drums, or carboys. The tank cars range in capacity from 60,000 to 160,000 pounds and are usually arranged with piping for blowing the acid out by compressed air. To avoid contamination of the acid by the iron, it is highly important that the acid be concentrated and that the tank be completely filled and tightly sealed. Dilute acid, sometimes called "electrolyte," and ranging in specific gravity up to about 1.400, can be shipped only in glass carboys. The term "carboy" does not denote a container of definite capacity.

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[29] *Soluble Silicates in Industry*, p. 140, 1928.

[30] *Regulations for the Transportation of Explosives and Other Dangerous Articles, by Freight and Express.*

The carboy is a glass bottle having a capacity of 10 to 13 gallons. Usually a carboy holds about 180 pounds of concentrated acid. The glass of the carboy is protected from breakage by a box packed with straw or other material.

The electrolyte for the nickel-iron batteries is shipped in steel containers. The smaller amounts, up to 22 pounds, are contained in cans similar to the containers for the cells. Larger amounts of 50 to 1100 pounds are shipped in steel drums.

Rebates are usually allowed for the return of the drums and carboys when they are empty.

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CHAPTER IV

THEORY OF REACTIONS, ENERGY TRANSFORMATION, AND VOLTAGE

1. ELEMENTARY THEORY OF ELECTRIC CELLS

The simplest form of cell may be made of a strip of copper and one of zinc immersed in water acidulated with sulphuric acid. If the zinc is sufficiently pure to be free from local action, there will be no visible effect until the zinc and copper are connected by a wire. The strips are, however, at different potentials with respect to each other, and when they are connected by a wire a current of electricity will flow in the wire. As this action progresses the strip of zinc will pass into solution and bubbles of gas will form at the copper electrode and collect on its surface. This gas is hydrogen which is formed from the electrolyte. The electric current flows from the copper strip through the wire to the zinc strip, and from the zinc strip through the electrolyte to the copper.

As the action of this cell progresses, the sulphuric acid of the electrolyte is gradually replaced by zinc sulphate which is formed at the dissolving zinc electrode. This diminishes the voltage of the cell. A greater decrease, however, is caused by the collection of gas bubbles on the copper. Both effects produce "polarization." Such a cell is of little practical importance.

The Daniell cell, devised in 1836, is a modification of the foregoing and possesses important advantages since it eliminates the decrease in voltage caused by polarization. This cell consists of a strip of copper immersed in a solution of copper sulphate and a zinc strip in a solution of zinc sulphate, the two liquids being separated by a porous diaphragm to prevent mixing. As the action of this cell progresses the zinc electrode dissolves, forming more zinc sulphate, and the copper electrode is increased by the deposition of copper from the electrolyte. The Daniell cell will be referred to in the pages that follow, as occasion may require, since because of its relative simplicity as compared with other types it is useful in explaining parts of the theory.

a. Ions and Electrons

The current is transported through the electrolyte by particles of molecular size that carry electrical charges. These are called "ions," a term that was originated by Faraday more than a hundred years ago. The ions are formed from the electrodes or from the substance that is dissolved in water to make the electrolyte. When zinc sulphate, for example, is dissolved in water, a spontaneous decomposition of a certain proportion of the zinc sulphate molecules takes place. The products are zinc ions and sulphate ions. This process is called "electrolytic dissociation." The zinc sulphate in the molecular state is electrically neutral, but as the molecules dissociate, positive and negative charges in equivalent amounts appear on the ions. In general, the metallic ions and hydrogen ions carry the positive charges; the non-metallic elements and radicals carry the negative charges. The sign of the charges has been ascertained by the direction in which the various ions move when between electrodes of opposite polarity, as in a simple electrolytic cell.

It was found many years ago that ions of substances that are divalent carry twice the charge of the ions formed from monovalent substances. Trivalent and tetravalent ions have, respectively, three and four times the charge of the monovalent ions. Within recent years the electron theory has given an explanation of the magnitude of these charges.

The electron is conceived to be a discrete and definite charge of negative electricity. One or more electrons, moving around a nucleus of equivalent positive charge are a part of each atom. In this respect atoms may be likened to miniature solar systems. The electrons move in orbits at several levels which are fixed by energy relations. Thus, copper, lead, hydrogen, and the other elements differ from one another in the number and motion of their respective electrons. The number of electrons in the outer level of an atom is important in determining whether the atom may give up or receive one or more electrons and thereby become an ion having a positive or negative charge. There is one electron for monovalent reactions, two for divalent reactions, and so on for trivalent and the higher valencies. As long as an element has its normal number of electrons it is electrically neutral, but if it loses one or more electrons it exhibits a positive charge equivalent in magnitude, but opposite in sign, to the negative charge or charges that it has lost. An atom or molecule thus becomes a positive ion. On the other hand, the gain of one or more electrons is manifested by negative charges. Since the electron is a definite quantity of electricity, it is easy to understand why the charges carried by the ions are simple multiples of a unit charge.

Recent researches have shown the relation between the electrons and the dissociation process, so that we may write an equation for the ionization of such a substance as zinc sulphate, as follows:

$$ZnSO_4 \leftrightarrows Zn^{++} + SO_4^{--}$$

The metallic ion, Zn^{++}, differs from the zinc atom both physically and chemically. Compared with an atom, it lacks two electrons; it is in solution; it moves under the influence of a potential gradient; and, finally, it has a marked tendency to attract and combine with oppositely charged ions. Probably the ions of opposite charges are combining and being formed continuously, but the proportion present at any time is determined by equilibrium conditions. A state of equilibrium is reached when the number forming during any specified interval of time is exactly equal to the number combining during the same interval. The equilibrium conditions which determine the proportion of the various ions present at any time depend on several factors. The nature of the dissolved substance and the solution pressure of the electrode (see p. 156) are of first importance. Some substances dissociate to a greater degree than others. The percentage of the molecules that dissociate also depends on the concentration of the solution. The more dilute the solution the greater will be the percentage dissociation, until 100 per cent, or complete dissociation, is reached; but this does not mean that more ions are present in dilute solutions than in those more concentrated. The presence of other dissolved substances and the flow of an electric current also affect the equilibrium condition.

Ions of the same kind are identical in their properties. No difference is observable between the zinc ions formed from a zinc electrode and those formed by the dissociation of zinc sulphate. The hydrogen ions in a storage battery all behave in the same way, irrespective of whether they came from dissociated molecules of water or sulphuric acid. The same is true of the lead ions, which can be derived from the lead sulphate or from the negative plate.

The motion of an electric charge constitutes an electric current. The motion of an ion in the electrolyte, or of an electron in a wire, is a transfer of a definite amount of electricity from one point to another The actual amount of electricity transported by a single electron or a monovalent ion is very small. Its value has been found to be

$$1.592 \times 10^{-19} \text{ coulomb}$$

The number of ions required to transport one ampere flowing for one second (one coulomb) is, therefore, enormously great. It is preferable to deal in magnitudes more easily comprehended. As a unit there has been chosen the aggregate charge carried by a number of ions equal in weight to the number of grams representing the atomic or molecular weight of the ion, which for convenience is designated as a "gram-ion." If the ion in question is monovalent, the total charge is 96,500 coulombs; if divalent, the charge is twice this amount, and so on. This is further discussed under Faraday's law on page 162.

In a storage battery there are many kinds of ions present to carry the current. The sulphuric acid dissociates by two steps into hydrogen ions H^+ and sulphate ions SO_4^{--}, there being more of the former. There may be also ions of the composition HSO_4^- from the initial step in the dissociation process. The water present contributes hydrogen ions, H^+, and hydroxyl ions, OH^-. A few lead ions, including both the divalent and the tetravalent states, are present. These are Pb^{++} and Pb^{++++}. According to some theories, there are also lead-peroxide ions, PbO_2^{--} The lead and lead peroxide ions are relatively unimportant in carrying the current because there are few of them, but they are of great importance in fixing the potential differences between the plates and the electrolytes, as will be shown.

b. Potential Differences

The differences of potential that exist between the electrodes and the electrolyte are conveniently explained by Nernst's conception of solution pressures. By this theory, it is assumed that all metals have a tendency to send their ions into solution, but it is observed that the metals which are easily oxidized, such as zinc or lead, have this tendency to a greater degree than gold or platinum which cannot be easily oxidized. Zinc and lead are therefore said to have greater solution pressures than gold or platinum. When a strip of zinc is immersed in a solution of zinc sulphate, as in the Daniell cell, zinc ions carrying positive charges are thrown into the solution. The strip of zinc becomes negatively charged because of an excess of electrons that remain after the departure of the positively charged ions from its surface. This reaction cannot continue indefinitely, since the positive charges of the ions in solution repel the positively charged ions leaving the surface of the zinc. The latter are also held back by the attraction of the negatively charged zinc strip. The magnitude of the charges on the strip of zinc and of the surrounding electrolyte increases as more and more zinc ions are formed, until a state of equilibrium is eventually reached when the solution pressure of the metal is balanced by the electrostatic forces. This prevents the further formation of zinc ions. Figure 49 shows diagrammatically the double layer of charges. The ions which pass into the solution from the strip of zinc increase the osmotic pressure of the zinc ions which were formed from the zinc sulphate when it was dissolved in the water. As the tendency of the osmotic pressure is to deposit ions upon the strip of zinc as atoms of zinc, it is evident that the solution pressure of the zinc is opposed by the osmotic pressure of the zinc ions in the solution. When the solution pressure of the metal is equal to the osmotic pressure of the ions in solution, equilibrium is reached.

The copper electrode of the Daniell cell is immersed in a solution of copper sulphate. At this electrode the reaction produces a different result from that observed at the zinc electrode. The solution pressure of the copper is very small as compared with the osmotic pressure of the copper ions in the electrolyte. The result is a deposition of copper ions upon the surface of the strip of copper. When these ions are deposited their deficiency in electrons is imparted to the copper electrode. The electrode thereby acquires a positive charge, and the solution becomes negatively charged because of the excess of negative ions that remain. These negative ions are the sulphate ions that were formed by the dissociation of the copper sulphate. A double layer is again formed, as shown in Fig. 50. The equilibrium condition is reached when the electrostatic forces prevent the further deposition of copper ions on the electrode.

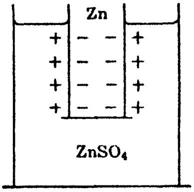

FIG. 49. Zinc in a solution of zinc sulphate becomes negatively charged.

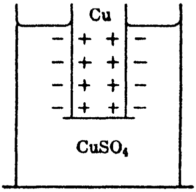

FIG. 50. Copper in a solution of copper sulphate becomes positively charged

Other theories have been proposed to account for the potentials of the electrodes, and various objections have at times been raised to the theory of Nernst. Nernst's theory, however, gives a mental picture of the process that is easily comprehended.

c. The Convention as to Positive and Negative Potentials

The result of practical importance that arises from the formation of the zinc ions at the zinc electrode and the deposition of copper ions at the copper electrode is the potential difference between the electrodes and the electrolyte. When the strip of zinc is immersed in a solution containing one gram-ionic weight of zinc ions, the electromotive force at the surface of contact between the solution and the zinc attains an equilibrium value of about 0.76 volt in a direction corresponding to the passage of current from the metal into the solution. The actual potential of the zinc with respect to the solution is negative. The copper, on the other hand, in a similar solution of copper ions, has a potential difference of 0.34 volt in a direction corresponding to the passage of the current from the solution to the metal. The copper is positive with respect to the solution. If a closed circuit between the zinc and the copper is formed, and at the same time the electrolytes are brought into contact through a porous diaphragm that will permit the passage of ions without allowing the two solutions to mix, a cell having a voltage equal to the algebraic difference of the potentials of the two electrodes with respect to the solution is formed. In the case of the Daniell cell, the combined voltage is $0.34 - (-0.76) = 1.10$ volts, neglecting the small potential difference that exists at the surface of contact between the solutions.

The polarity of the cell is defined by the polarity of the individual electrodes with respect to the electrolyte and, therefore, their potential relations to each other. In the Daniell cell the positive is the copper, although this is sometimes called the electronegative metal. Much confusion has arisen because of the lack of a standard terminology in this respect. The convention as here given has been adopted as standard by a number of organizations, including the American Electrochemical Society,[1] the International Congress of Pure and Applied Chemistry, 1922, and the Bureau of Standards. In dealing with the storage battery, in which the current flows in opposite directions when on charge and on discharge, there is further chance for confusion. Fortunately, however, the brown peroxide plates are so universally called the positives, and the gray, metallic sponge-lead plates, the negatives, that this terminology may be considered fully standardized. When the storage cell discharges, the peroxide plate is the positive in the same sense as the copper electrode of the Daniell cell.

d. The Electrochemical Series

Lists of the elements arranged in the order of increasing potentials have been given by many authorities, but these differ somewhat both as to the order of the elements and the values assigned for their potentials. Single-electrode potentials are always measured in connection with

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[1] *Trans. Am. Electrochem. Soc.*, 36, p. 3, 1919.

some standard electrode. The hydrogen electrode is generally chosen as the standard and its single potential is stated arbitrarily to be zero. Although the hydrogen electrode is the standard, its use is not always convenient or possible. Other kinds of electrodes which are used with storage batteries are described in connection with the measurement of plate capacities in Chapter V.

A selected list of elements, with the approximate values of their potentials on the hydrogen scale, is given in Table XXXI. Metals following lead, such as copper, silver, and platinum, are the elements that deposit on the negative plates of storage batteries; but the elements that precede it will not be deposited under ordinary circumstances. The position of the various elements with reference to lead has a bearing on the effects they produce when present as impurities in the electrolyte. This is discussed in Chapter III.

TABLE XXXI

ELECTRODE POTENTIALS

(Calculated for electrochemical reactions of elements immersed in solutions containing 1 gram-ion per liter. The potentials are expressed as the potential of the electrode minus the potential of the solution.)

Element	Valence	Potential in Volts
Potassium	1	−2.92
Sodium	1	−2.71
Calcium	2	−2.50
Magnesium	2	−1.55
Manganese	2	−1.00
Zinc	2	−0.76
Iron	2	−0.44
Cadmium	2	−0.40
Nickel	2	−0.22
Tin	2	−0.14
Lead	2	−0.12
Iron	3	−0.04
Hydrogen	1	0.00
Antimony	3	+0.10
Copper	2	+0.34
Copper	1	+0.52
Mercury	2	+0.80
Silver	1	+0.80
Platinum	4	+0.86
Gold	3	+1.36

A more complete list of the elements, showing the probable order in the electrochemical series, is as follows:

> Potassium, sodium, barium, strontium, calcium, magnesium, aluminum, manganese, zinc, iron, cadmium, cobalt, nickel, tin, lead, hydrogen, antimony, bismuth, arsenic, copper, mercury, silver, palladium, platinum, gold, silicon, tantalum, tellurium, carbon, boron, tungsten, molybdenum, vanadium, chromium, iodine, bromine, chlorine, fluorine, nitrogen, sulphur, oxygen.

In using the list of elements, the order cannot be considered to hold true in all cases. The order depends somewhat on the nature, concentration, and temperature of the solutions. Usually any metal will displace from solution the others which follow, and it will be displaced by those that preceded. Secondary reactions may interfere, however.

e. The Flow of Current

When the terminals of a cell are connected through an external circuit by a wire, the current that flows is proportional to the potential difference of the electrodes and inversely proportional to the resistance of the whole circuit, including the resistance of the battery as well as that of the external circuit. This is in accordance with Ohm's law.

The Migration of Ions. The flow of current is continuous throughout the entire circuit. The current in the wire is believed to consist of a stream of electrons flowing from the anode, negatively charged with respect to the solution, to the cathode. In the solution the current is carried by ions both positively and negatively charged, traveling in opposite directions toward their respective electrodes. The positively charged ions, called "cations," move to the cathode which in the Daniell cell is the copper. The negatively charged ions, called the "anions," migrate to the anode. It is obvious that at the surface of the electrodes where one form of conduction meets the other, exchanges of electrons between the electrodes and the ions in the solution must take place, if the electric current is to flow continuously. The reactions which involve both the current carrying ions and electrons on the one hand and the chemical composition of the electrodes and electrolyte on the other are called electrochemical reactions.

Across any imaginary surface that may be drawn in the solution, the current is carried by the ions, each kind of ion carrying its proportionate share. The ions that are the most numerous and travel the fastest carry a greater amount than the others, but all take part. At the electrodes, however, the actual transfer of current from the solution to the electrode is usually through the medium of only one kind of ion. Suppose that a zinc ion, having left the anode and traveled only part way to the cathode, meets and reacts with a sulphate ion that has traveled in the opposite direction, from the cathode. The ions neutralize each other and change into the molecular state, but the result is the transfer of two charges (the ions are divalent) from one electrode to the other. Few, if any, of the ions actually travel the entire distance from one electrode to the other.

To continue the relatively simple case of the Daniell cell for the sake of illustration, it may be supposed that the solution pressure of the zinc driving the positively charged zinc ions into the solution leaves free negatively charged electrons which give to the zinc its negative charge. When a connection is made by a wire to the copper electrode, a path is provided for the electrons to flow to the positively charged copper. The motion of the electrons is opposite to the direction in which the current is said to flow. The departure of the electrons from the zinc disturbs the state of equilibrium between it and the electrolyte, and more zinc ions are thrown into the solution. Coincident with this, additional electrons are liberated in the zinc and they follow on through the wire after the others as long as the circuit remains closed. Two electrons, each with one negative charge, are freed, with the formation of each zinc ion. This process is represented by the ionic equation:

$$\mathrm{Zn} - 2\ominus = \mathrm{Zn}^{++} \tag{1}$$

The electrons, reaching the copper terminal after their passage through the wire, neutralize an equivalent number of positive charges, thereby disturbing the equilibrium of this electrode and permitting the further discharge of copper ions. Two electrons neutralize two positive charges and permit the deposit of one ion of copper, which gives up its charges. This fact is represented by the equation:

$$\mathrm{Cu}^{++} + 2\ominus = \mathrm{Cu} \tag{2}$$

The zinc cations move toward the cathode, carrying their share of the current through the electrolyte. Probably most of them combine with the sulphate anions moving in the opposite direction to form zinc sulphate according to the equation:

$$\mathrm{Zn}^{++} + \mathrm{SO}_4{}^{--} = \mathrm{ZnSO}_4 \tag{3}$$

The relative motion of the electrons, anions, and cations is shown in Fig. 51.

In the solution around the cathode there are several different kinds of ions carrying positive charges and, therefore, several different reactions are possible. The transfer of positive charges is accomplished under ordinary circumstances, however, by the discharge of only one kind of ion. The factors which determine the preferential reaction are the relative electrolytic potentials and the relative concentrations of the ions. When each electron of the stream of electrons moving from the anode to the cathode through the wire reaches the cathode, it reduces the positive potential of the cathode by a small amount, and ions having the highest equilibrium potential, deposit. In the case of the Daniell cell these are the copper ions, Cu^{++}.

The unequal speeds of the ions produce concentration differences in the region of the electrodes, which have an important effect upon the performance of a battery. In a storage battery this effect is in addition to the actual consumption of the acid as it combines with the active materials of the plates when current is produced. During the discharge, hydrogen ions leave the region of the anode and migrate toward the cathode, while the sulphate ions go in the opposite direction. The speed of the hydrogen ions is greater than that of the sulphate ions, which is a fortunate circumstance in the operation of the lead storage battery, as otherwise the amount of acid required for the operation of the positive plate would be much larger than is actually the case.

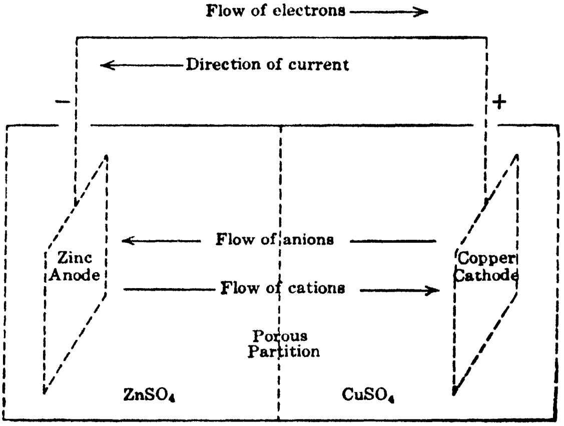

Fig. 51. Relative flow of the ions, electrons, and the direction of the current in a Daniell cell.

Faraday's Law of Electrolysis. In 1834 Faraday formulated his fundamental law of the relation between the amount of electrochemical action and the quantity of electricity passing through the cell. Many experiments since that time have proved the validity of this law, which is of the greatest importance in discussing the storage battery.

The first part of Faraday's law states that the chemical effects produced at the electrodes by the passage of an electric current are in direct proportion to the magnitude of the current and the time that it flows, that is, to the quantity of electricity. This law establishes a relationship between the output of a battery and the amount of active materials which it contains. It therefore denies the possibility of drawing current from the battery indefinitely (perpetual motion), or of charging it by merely changing the solution. Not all the materials within a battery may be used for the production of electric current, because of practical limitations, but interesting comparisons on the basis of Faraday's law may be made for the various types and kinds of batteries.

The second part of Faraday's law states that quantities of various substances, which are liberated or consumed by the action of the electric current, are in all cases proportional to the equivalent weights. This part of the law enables the experimenter to determine with exactness the amount of lead, or lead peroxide, or sulphuric acid which takes part in the reaction when a specified amount of electricity is passed through the cell. The quantity of electricity which liberates one gram-equivalent weight is the same for all substances. It is equal[2] to 96,500 coulombs (see p. 6). This quantity has been named the "faraday" and it is the fundamental constant of electrochemistry. Lead has an atomic weight of 207.21 and a valence of 2, whence the gram-equivalent weight of lead which takes part in the reactions when one faraday of electricity is passed through the solution is $\frac{207.21}{2} = 103.60$ grams.

2. THEORY OF THE LEAD-ACID CELLS

a. Review of the Early Theories

A number of theories have been proposed to account for the reactions taking place in the lead-acid batteries. The controversies which have arisen over these theories have been acrimonious, but the so-called "double-sulphate" theory, which will be described in detail, is now generally accepted. Before this is discussed, a brief résumé of the principal theories which have been proposed will be given.

The first theory, in point of time, is the so-called *oxidation and reduction theory*. This was the original theory of Planté. He believed the lead peroxide to be reduced to lead at the positive plate and the lead

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[2] Vinal and Bates, *Sci. Paper* 218, Bureau of Standards.

of the negative plate to be oxidized during the process of discharge. He recognized the formation of lead sulphate during this reaction, but considered it to be accidental.

According to the *occluded-gas theory* the negative plates were supposed to occlude hydrogen, and the positive plates oxygen, during the process of charging. The water was believed to be the real electrolyte, sulphuric acid being added merely to make it conduct. The formation of lead sulphate at the plates was considered a secondary action and an unmitigated evil. This idea has been perpetuated to the present time and forms the basis of much advertising of solutions to eliminate sulphation.

The *double-sulphate theory* was first proposed by Gladstone and Tribe in 1882.[3] Their theory met with violent opposition but it has survived to the present day. They discovered that lead sulphate was formed at both plates as part of the process of discharge. They also discovered that the electrolyte became more dilute during the discharge, but Frankland [4] is believed to have been the first to suggest utilizing the change in specific gravity to indicate the state of charge of the battery.

The *persulphuric acid theory* was developed subsequently to the double-sulphate theory. It was claimed that persulphuric acid and hydrogen peroxide were formed during the charge and that the electromotive force of the cells depended on these. In 1878 Berthelot had found that persulphuric acid can be formed by electrolysis of sulphuric acid solutions and that hydrogen peroxide accompanies it. Persulphuric acid is formed when moderately strong sulphuric acid is electrolyzed between platinum electrodes at a high-current density. These are not the conditions which obtain in the storage battery; the specific gravity of the electrolyte is low and the electrodes are more soluble than platinum plates. For these and other reasons it does not seem likely that persulphuric acid in appreciable amounts is formed during the normal operation of storage batteries. Persulphuric acid is known to be destructive to the plates and, if any considerable amount of it were to be formed, the period of useful service of a storage battery would undoubtedly be short.

According to a still more recent theory, elaborated by Féry,[5] which may be termed the "*higher-oxide*" *theory*, the active material of the positive plate is an oxide higher than the peroxide, and on discharge this is reduced to lead peroxide by hydrogen. The reaction at the nega-

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[3] *Nature*, 25, p. 221, 461; 26, p. 251, 343, 602; 27, p. 583, 1882–3; *Electrician*, 9, p. 612, 1882.

[4] *Proc. Royal Society*, 35, p. 67, 1883.

[5] *Rev. gen. de l'elec.*, 1, p. 10, 1917; 19, p. 296, 1926.

tive plate during discharge is supposed to result in the formation of a lower sulphate, such as Pb_2SO_4, which is spontaneously converted to the ordinary lead sulphate. Jumau[6] has shown, however, that Féry's determinations of the change in weight of the plates when corrected for buoyancy of the electrolyte afford a striking confirmation of the double-sulphate theory.

Only the double-sulphate theory, in support of which there is abundant experimental evidence, has survived to the present time. The discussions in this book are based entirely on the double-sulphate theory, which is described in detail.

3. THE DOUBLE-SULPHATE THEORY

The double-sulphate theory is most conveniently stated by the equation for the reaction.

$$PbO_2 + Pb + 2H_2SO_4 \rightleftarrows 2PbSO_4 + 2H_2O \qquad (4)$$

From left to right this equation represents discharge, and from right to left, charge. The significance of the term "double sulphate" lies in the fact that lead sulphate is formed at both the positive and negative plates during the process of discharge.

a. Reasons for Believing in Its Correctness

Although the double-sulphate theory of reactions in lead storage batteries has been generally accepted, its validity has been challenged occasionally because of disagreement between certain experimental results and the requirements of the theory. Proof of the theory rests (1) on the identification of the materials, (2) on the quantities of these involved in the reactions, and (3) on the thermodynamic relation of the electrical energy produced to the chemical energy of the chemical reactions.

Gladstone and Tribe observed the formation of lead sulphate at both positive and negative plates during discharge and its subsequent oxidation at positive plates and reduction at negative plates during charge. MacInnes[7] and others have found that PbO_2 is the substance produced by anodic oxidation of lead and that the oxide so formed has the same chemical composition and electrical potential as the active material of the positive plates. More recently Mazza[8] and Barrett[9]

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[6] *Rev. gen. de l'elec.*, 20, p. 235, 1926; *Trans. Am. Electrochem. Soc.*, 53, p. 245, 1928.

[7] *Ind. Eng. Chem.*, 14, p. 421, 1922; *Trans. Am. Electrochem. Soc.*, 37, p. 641, 1920.

[8] *Atti. accad. Lincei*, 4, p. 215; 5, p. 117, 688, 1927.

[9] *Ind. Eng. Chem.*, 25, p. 297, 1933.

have employed the X-ray spectrograph to identify the materials of the plates. They found battery plates in the charged condition to consist of lead peroxide (positives) and lead (negatives). In the discharged condition lead sulphate was found in both plates in addition to the original materials. On the other hand, Riesenfeld and Sass,[10] using X-rays, concluded that a basic sulphate is the normal product at the positive plates. It would seem that the X-ray method should provide an unequivocal answer. The difference in opinion is, therefore, surprising.

Many experiments have been made to determine the consumption of H_2SO_4 per faraday. Some of these have shown two equivalents of acid to be used per faraday, as required by the double-sulphate theory, but others have indicated smaller amounts, with the result that the validity of this theory has been denied. One of the difficulties in making experiments of this kind lies in determining the amount of acid in the cell. The free electrolyte can be measured easily, but to this must be added the electrolyte in the pores of the plates and in the separators. The porosity of the plates changes during discharge and thus makes corrections uncertain. If the plates are washed or dried prior to the experiment, their condition is not normal. More than a score of publications in support of, or in opposition to, the double-sulphate theory are reviewed in a recent paper by Vinal and Craig.[11] These earlier papers will not be discussed here.

A more accurate method of determining the amount of acid in the cell and the quantity of it taking part in the reaction was described by Vinal and Craig in the paper mentioned above. Their method is called the "method of mixtures." In principle it is based on the fact that, if to a solution of known concentration, but unknown weight, a carefully measured portion of water or of another solution differing in concentration is added, and the concentration of the resulting mixture is determined, the exact weight of both the original and the final solution can be calculated. It is not necessary to dismantle the cell or to interfere with its operation. This method enabled the authors to measure not only the equivalents of acid consumed, but also the equivalents of water which are formed.

The application of the method is illustrated by the following example. The mixture is made within the cell itself, care being taken to equalize the acid throughout the cell. Evidence of complete equilization of the acid is obtained when successive readings of electromotive force and density are constant. The concentrations in the following example are expressed as weight fractions.

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[10] *Zeit. Elektrochemie*, 39, p. 219, 1933.

[11] *J. Research*, Bureau of Standards, 14, p. 449, 1935.

Initial concentration of electrolyte.................. 0.22783
Acid added, concentration 0.59820
Weight added 117.684 g.

Concentration of resulting mixture.................. 0 33447
Let y equal weight of electrolyte after mixing

$$\frac{0.33447y - (0.59820 \times 117.684)}{y - 117.684} = 0.22783$$

Whence.................................y = 408.73
Deduct for sample removed................ 60.66

Net weight of electrolyte available.......... 348.07 grams

A similar method was used to determine the weight of electrolyte at the end of the discharge.

The cell used in these experiments contained eleven small pasted plates. All the grids were pure lead which reduced local action to a minimum. Each plate was provided with a long lug which extended through the cover, connections being made outside the cell in order to provide the best insulation. Beginning with the eighth experiment the cell was kept under a sealed bell jar to prevent evaporation of water which amounted otherwise to about 0.5 gram per day.

No preliminary assumptions regarding the correctness or applicability of any theory of chemical reactions in the battery are necessary. The number of equivalents of acid consumed or water formed as a result of the cell discharging a measured number of coulombs was measured directly. Let w and w' represent the weight of electrolyte at the beginning and at the end of discharge, respectively; let p and q be the weight fractions similarly; also, let c represent the coulombs of electricity discharged and F the value of the faraday, 96,500 coulombs. The equivalent weights of sulphuric acid and water are, respectively, 49.04 and 9.01 grams. All these quantities are known or can be measured. The number of equivalents of acid consumed per faraday is equal to:

$$\frac{F}{c}\,\frac{(pw - qw')}{49.04} \tag{5a}$$

The number of equivalents of water formed per faraday is equal to:

$$\frac{F}{c}\,\frac{(pw - qw') - (w - w')}{9.01} \tag{5b}$$

The experimental results as given by the authors in two tables have been combined into one, Table XXXII.

It is apparent that two equivalents of acid are consumed per faraday and that two equivalents of water are formed at the same time. These

TABLE XXXII

EQUIVALENTS OF ACID CONSUMED AND WATER FORMED PER FARADAY DURING DISCHARGE OF THE LEAD STORAGE BATTERY

Experiment	Date	Discharge Data		Percentage of H_2SO_4 (by Weight)		Weight of Solution		Equivalents per Faraday	
		Time	Coulombs	Start	Finish	Start	Finish	H_2SO_4	H_2O
	1934	*Hours*				*Grams*	*Grams*		
1	Mar. 9	10.42	45,252	35.53	24.82	......	311.2	2.04	.....
2	Mar. 20	7.81	34,992	36.60	29.17	358.77	330.60	1.96	2.05
3	Mar. 27	8.00	35,833	28.061	18.933	341.78	307.65	2.07	1.06
4	Apr. 6	8.83	39,116	30.885	21.684	358.71	324.73	2.03	1.75
5	Apr. 13	4.83	31,232	32.518	25.607	364.20	337.88	2.01	1.92
6	Oct. 5	10.60	42,088	28.21	17.89	355.33	317.20	2.03	1.36
7	Oct 17	5.84	23,130	42.714	38.246	......	345.92	2.02	......
8a	Oct. 31	5.03	19,786	20.951	15.850	347.73	......	2.03	......
8b		5.80	22,316	15.850	8.898	....	284.98*	2.01	......
9	Nov. 23	5.75	22,638	41.24	36.72	360.85	340.28	2.07	1.56
10	Nov. 30	19.87	44,173	33.948	23.584	351.22	315.14	2.00	2.14
11	Dec. 7	6.73	31,237	33.447	26.276	348.07	323.13	1.99	2.25
12	Dec. 27	13.42	38,152	31.141	22.298	359.09	326.87	2.01	1.89
					Mean of all			2.02	1.78
					Mean of last four			2.02	1.96
					Average deviation			±0.03	±0.19

* Between the two discharges 18.62 grams of electrolyte were removed for density determinations

are precisely the requirements of the double-sulphate theory. It is apparent also that the results given in the Table XXXII are independent of the concentration of the electrolyte, the extent of the discharge and the rate of the discharge. No evidence of the formation of basic sulphate was found and no spontaneous change in the final products of the reaction was observed after the discharge was discontinued. The double-sulphate theory of Gladstone and Tribe is supported, therefore, to the exclusion of the other theories which have been proposed.

Thermodynamic transformations, which are discussed in later sections, afford further proof of the double-sulphate theory.

b. Reactions at the Positive and Negative Plates

Although the double-sulphate theory states that lead sulphate is formed at each plate during the discharge, and gives us an equation for calculating the performance of the cell, it leaves us in the dark about the actual processes that go on at the positive and negative plates. It does not tell how the substances are formed, or explain their relation to the transfer of electricity through the cell.

Figure 52 is a diagram which shows in detail the probable processes that result in final products of discharge, according to the double-sulphate theory. At the negative plate the process is relatively simple; the solution pressure of lead causes it to throw lead ions into solution (see p. 156). These are in the divalent state, carrying two positive charges. Coincident with the departure of each of the positive lead ions from the surface of the electrode, the electrode itself acquires two negative charges. The lead ions react with sulphate ions, which have charges of equal magnitude but opposite sign, forming lead sulphate. This is so nearly insoluble in the electrolyte that it immediately precipitates out of the solution and is deposited on the electrode.

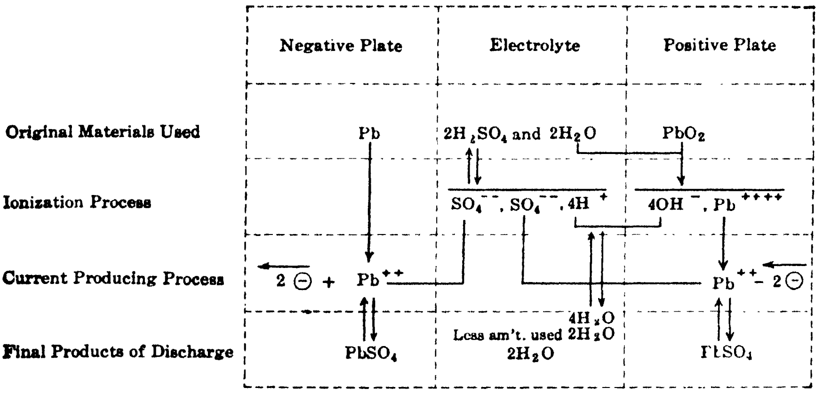

FIG. 52. Discharge reactions.

Reactions occurring at the positive plate are not so well understood. They may be explained, however, in several ways. The tetravalent-ion theory, which seems the most probable, was proposed by Le Blanc[12] many years ago. Lead peroxide, although insoluble in appreciable amounts in sulphuric acid under ordinary conditions, may pass into solution to a limited extent when the current flows. Small amounts of it, in combination with water, ionize into tetravalent lead ions and monovalent hydroxyl ions, according to the equation:

$$PbO_2 + 2H_2O \rightleftarrows Pb(OH)_4 \rightleftarrows Pb^{++++} + 4OH^- \qquad (6)$$

The current-producing process is associated with potential differences at the electrodes that depend, first, on the equilibrium potentials

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[12] *Lehrbuch der Elektrochemie*, 1st ed., p. 223, 1895.

for the ionic reactions and, second, on the ionic concentrations. At the positive electrode the ionic reaction is

$$\mathrm{Pb^{++++}} + 2\ominus \rightarrow \mathrm{Pb^{++}}$$

and for this the potential difference is about +1.75 volts on the basis of potentials in Table XXXI. Ionization of the electrolyte occurs substantially as follows:

$$\mathrm{H_2SO_4} \rightleftarrows \mathrm{H^+} + \mathrm{HSO_4^-}$$

and

$$\mathrm{H_2SO_4} \rightleftarrows 2\mathrm{H^+} + \mathrm{SO_4^{--}}$$

As a last step in the process of discharge, the combination of lead and sulphate ions takes place, with the formation of lead sulphate which, being practically insoluble in the electrolyte, deposits as a solid substance on the plates. This reaction is represented by equation (7):

$$\mathrm{Pb^{++}} + \mathrm{SO_4^{--}} \rightleftarrows \mathrm{PbSO_4} \tag{7}$$

These reactions are shown diagrammatically in Fig. 52. It should be noted that four molecules of water are really formed for each two molecules of sulphuric acid consumed, but, as two molecules of water are used up at the same time, the net change is the production of two molecules of water, which is in accordance with the equation for the double-sulphate theory (4).

The single potential of the positive plate is given by the formula:

$$E_p = 1.75 + \frac{RT}{2F} \log_e \frac{[\mathrm{Pb^{++++}}]}{[\mathrm{Pb^{++}}]} \tag{8}$$

The concentrations of the ions inclosed in the brackets are small quantities for which no directly measured values are available. R in this equation is the gas constant, T, the absolute temperature and F, the faraday.

Similarly, the potential of the negative electrode is obtained. The reaction in this case is

$$\mathrm{Pb} - 2\ominus \rightarrow \mathrm{Pb^{++}}$$

for which the equilibrium potential value (Table XXXI) is −0.12 and the single potential

$$E_n = -0.12 + \frac{RT}{2F} \log_e [\mathrm{Pb^{++}}] \tag{9}$$

The electromotive force of the cell is the difference between these two single potentials and is given by the expression

$$E = E_p - E_n = 1.75 + 0.12 + \frac{RT}{2F}\log_e\frac{[\mathrm{Pb}^{++++}]}{[\mathrm{Pb}^{++}]^2} \qquad (10)$$

Since $R = 8.32$, $T = 291°$, and $F = 96{,}500$, equation (10), after changing to common logarithms, becomes:

$$E = 1.87 + \frac{0.058}{2}\log\frac{[\mathrm{Pb}^{++++}]}{[\mathrm{Pb}^{++}]^2} \qquad (11)$$

The values of the ionic concentrations vary with the concentration of the electrolyte, and it is to be expected, therefore, that the voltage of the cell will vary with the concentration of the electrolyte, as will be shown to be the case in a later section.

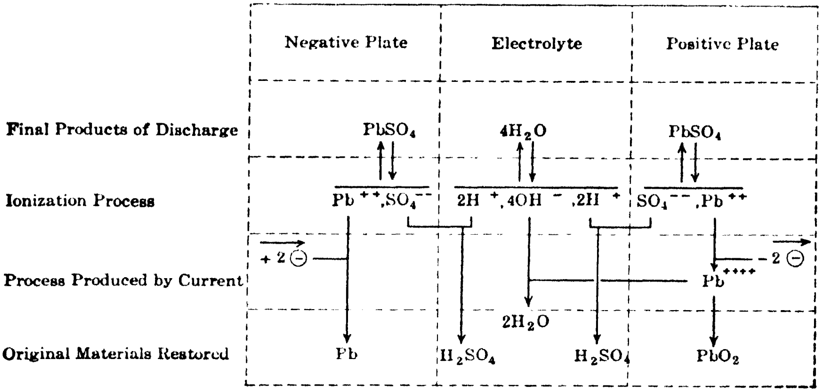

FIG. 53. Charge reactions.

The charging process is shown diagrammatically in Fig. 53. Starting with the products of discharge, the lead sulphate at both electrodes passes into solution and ionizes. The water also is ionized as rapidly as equilibrium conditions permit. The divalent lead ions at the negative plate, which is now the cathode, take up two electrons, neutralizing their charges, and then are deposited as lead in the solid state. The divalent lead ions at the positive plate or anode are forced by the charging current to give up two electrons, which changes them to the tetravalent state. Each of these ions may then unite with two oxygen ions, through an intermediate step, to form lead peroxide, which is deposited upon the plate. The sulphate ions formed at each plate unite with two hydrogen ions, with an intermediate step, forming sulphuric acid at each plate.

Lead sulphate, which plays such an important role in the chemical reactions of the lead storage battery, is very sparingly soluble in the sulphuric acid electrolyte. The amount in solution under equilibrium conditions is so small that accurate measurements of it are difficult to make. This probably accounts for the meager data which have hitherto been available. Within the past few years diphenylthiocarbazone, commonly called dithizone, has been introduced as a sensitive reagent for lead. This organic reagent is sensitive to less than one-millionth of a gram of lead when used with a spectrophotometer or with a photronic cell and a suitable color screen. A dithizone solution in chloroform is normally green, but when in contact with an aqueous ammoniacal solution containing an excess of lead it becomes a bright cherry red. Craig and Vinal [13] have used this reagent to determine the solubility of lead sulphate in sulphuric acid solutions up to 50 per cent H_2SO_4. The solutions were stirred continuously for several days, after which the samples were drawn through fritted-glass filters and evaporated in quartz dishes. The lead sulphate residues, after evaporation, were taken up in nitric acid solutions and carried through a titration process with both aqueous and organic phases present. The results are contained in Table XXXIII, which also includes a determination of the solubility of $PbSO_4$ in water, taken from other sources. Lead sulphate is ten times as soluble in water as in 0.5 per cent sulphuric acid. The effect of the acid in depressing the solubility is a good illustration of the common-ion effect, but the solubility increases again in stronger acid to a maximum at 10 per cent acid. At higher acid concentrations the solubility decreases again, probably as a result of changes in the equilibrium between the sulphate and bisulphate ions of the acid solution.

4. ENERGY TRANSFORMATIONS

A storage cell of any kind stores electrical energy by virtue of the chemical reactions taking place at the electrodes. Electrical energy is not stored as electrical energy, but as chemical energy. During the charging process the electrical energy is converted into chemical energy, and when the cell is discharged at a later time this chemical energy is reconverted into electrical energy. The law of the conservation of energy governs these transformations. The energy cannot be created from nothing, nor can it be annihilated; therefore, the electrical energy which the cell can supply bears a definite relation to the amount of chemical energy which it contains. We cannot determine the total

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[13] *J. Research*, 22, p. 55, Bureau of Standards, 1939.

TABLE XXXIII

SOLUBILITY OF LEAD SULPHATE IN SOLUTIONS OF SULPHURIC ACID

Concentration of H_2SO_4			Weight of $PbSO_4$ per Liter	
Per Cent	Molarity 25°	Specific Gravity $\frac{25°}{25°}$	At 25° C., Milligrams	At 0° C., Milligrams
0.0	0.00	1.000	45.0	28.0
0.5	0.05	1.003	4.60	2.06
1.0	0.10	1.006	4.91	2.10
5.0	0.52	1.033	6.15	2.46
10.0	1.08	1.067	6.68	2.86
15.0	1.68	1.102	6.28	2.63
20.0	2.32	1.140	5.18	2.21
25.0	3.00	1.179	3.76	1.76
30.0	3.72	1.219	2.75	1.27
35.0	4.48	1.260	2.02	0.84
40.0	5.30	1.303	1.52	0.53
45.0	6.16	1.348	1.23	....
50.0	7.10	1.395	1.08	....

amount of chemical energy of the cell, but it is possible to determine the change in chemical energy which occurs as the cell is charged or discharged and, by relating this to the electrical measurements, the electrochemical theory of the storage cell may be developed. This theory includes the theory of the chemical reactions and the theory of the energy transformations.

Chemical reactions in general are accompanied by the evolution or absorption of heat in varying amounts, depending on the nature of the reaction. The heat of reaction expresses the difference between the heat content of the reacting substances and that of the products of the reaction. If heat is liberated, the reaction is said to be "exothermic," but if heat is absorbed the reaction is "endothermic." For each reaction the amount of heat liberated or absorbed per gram molecule depends on the initial and final states and may be called the heat of reaction.

The heat of reaction of the lead-acid storage cell as it would occur in a calorimeter depends on the heat of formation of each of the constituents. Basic data can be found in such books as the *International*

Critical Tables, or in the more recently published book (1936), *Thermochemistry of Chemical Substances* by Bichowsky and Rossini. In calculating the heat of the reaction thermochemically, we shall choose as a starting point a dilute solution of sulphuric acid, having the proportions of one mole of acid to 200 moles of water. The heats of formation of the various constituents are written beneath the respective symbols in the equation:

$$\begin{array}{ccccc} PbO_2 & + 2(H_2SO_4 + 200H_2O) & + Pb \rightleftarrows & 2PbSO_4 & + \quad 402H_2O \\ 65{,}000 & 2(211{,}500) & 0 & 2(218{,}500) & 2(68{,}370) \end{array}$$

The heats of formation are values at 18° C. From these numerical values the heat of reaction, Q, is 85,740 calories. To convert this to the equivalent at 25° C., at which temperature most of the electrical measurements have been made, a correction factor is computed on the basis of the heat capacities of all the constituents. This amounts to − 45.4 calories per degree for the whole reaction as expressed by the equation. The heat of the reaction then becomes 85,420 calories at 25° C.

The solution is the variable factor and values for the heat of reaction for other concentrations will differ by changes of the heat of formation of H_2SO_4 and H_2O in the respective concentrations. Considered from a purely chemical point of view, the changes in the heat of formation of sulphuric acid solutions from one concentration to another vary by the amount of heat liberated as the solutions are diluted. Eventually a point is reached where no more heat is liberated and the solution is infinitely dilute and its volume infinitely great. The pressure is assumed to be constant. Values of the relative apparent molal heat content at 25° C. are given in Table XXXIV. On the other hand, if we start with a given solution and add a small quantity of the solute, the heat change per mole is the partial [14] or differential heat effect. The relative partial molal heat contents are also given in Table XXXIV. At infinite dilution these are zero and the heat of reaction in the cell is precisely the same as the thermochemical or calorimetric heat of reaction.

To calculate the heat of reaction for a state of infinite dilution of the sulphuric acid, we must deduct from the value above the relative apparent molal heat content for the solution $H_2SO_4 \cdot 200H_2O$. As shown in Table XXXIV this is 5.41 kilocalories or 5410 calories per mole. Two moles are involved, whence 85,420 − 10,820 = 74,600 calories as the heat of reaction at infinite dilution. This applies to either the thermometric or the battery reaction and is a convenient

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[14] See *Thermodynamics*, by Lewis and Randall, p. 89.

value from which to calculate the heat of reaction of a battery at any other concentration of the solution.

From a practical standpoint we wish to know the heat of reaction for the battery at finite and useful concentrations of the electrolyte. The discharge reaction involves the consumption of acid represented by a term on the left of the equation and the formation of water on the right side of the equation. With due regard for algebraic signs, the heat of reaction then equals the heat of reaction at infinite dilution, 74,600 calories plus twice the sum of the relative partial molal heat contents of the acid and the water. The factor two comes from the use of two moles each of acid and water for each mole of lead peroxide.

Table XXXV, which is based on the work of Craig and Vinal,[15] gives in parallel columns the heat of reaction calculated from thermochemical data and from the best available electrical data. The two are entirely independent sources of information, but the agreement of the results is remarkable throughout the range of acid concentrations from 3 to 40 per cent. In the battery the calories, representing the heat of reaction, are one form of energy. If only heat energy were involved, this would mean that the battery would become very hot, but this is obviously not the case. The cell may even cool during discharge. These apparently contradictory facts are reconciled by the knowledge that the change in energy of the reacting materials, which has been calculated as calories, is transformed into electrical energy when the battery discharges. It does not appear as heat.

As an example, we may choose $n = 400$ which was the condition for which values were reported long ago by Tscheltzow [16] and Streintz [17] as 88,600 and 87,000, respectively.

Heat of reaction ($n = \infty$)...............	74,600 cal. per mole
Relative partial molal heats, acid (×2)...	11,276
water (×2)...	2
Heat of reaction ($n = 400$)...............	85,878

The water factor becomes more important at higher concentrations as shown in Table XXXIV.

A comparison of the heats of reaction of the lead storage battery calculated from thermochemical data and electrochemical data is given in Table XXXV. The method of computing the values from electro-

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[15] *J. Research*, 24, p. 475, Bureau of Standards, 1940. Much of the discussion of this subject has been taken from this paper.

[16] *Compt. rend.*, 100, p. 1458, 1885.

[17] *Wied. Ann.*, 53, p. 698, 1894.

TABLE XXXIV

RELATIVE APPARENT MOLAL HEAT CONTENT OF SULPHURIC ACID SOLUTIONS

(Values are in kilogram calories.)

Concentration of Solution		Relative Apparent Molal Heat Content H_2SO_4*	Relative Partial Molal Heat Content*	
n, Moles H_2O	Per Cent H_2SO_4		H_2SO_4	H_2O
∞	0	0.00	0.000	0.000
25,600	0.02	1.54	2.234	0.000
6,400	0.08	2.90	3.725	0.000
1,600	0.34	4.04	4.811	-0.000_5
400	1.34	5.02	5.638	−0.001
200	2.65	5.41	5.842	−0.002
100	5.16	5.62	5.888	−0.003
50	9.82	5.78	6.065	−0.006
25	17.88	6.07	6.681	−0.024
15	26.63	6.55	7.896	−0.090
10	35.25	7.30	9.632	−0.233
5	52.13	9.45	13.282	−0.766
3	64.47	11.66	16.089	−1.477
1	84.48	16.72	21.451	−4.731
0	100.00	23.54	23.540	. . . . .

* The convention as to algebraic signs of these quantities requires some explanation. In this book a positive sign has been used to indicate that energy is liberated when the reaction, expressed by the thermochemical equation, is from left to right. In the paper referred to, from which Table XXXIV is taken, the contrary convention has been followed. That is, a positive sign indicates an increase in heat content of the solutions. Values given in Table XXXIV should have the signs reversed for the computations given here. Since the symbol for the acid appears on the left side of the equation (page 174), a negative value would mean that the quantity should be added to the net value on the right side. The negative sign for the water, which appears in the table, becomes a positive sign and, since the symbol for water is on the right side of the equation, this is also added. Both acid and water, therefore, contribute to increase the heat of reaction for all concentrations above infinite dilution.

chemical data will appear after a brief discussion of the thermodynamic relationships between electromotive force, temperature, and heat of reaction.

5. ELECTROMOTIVE FORCE

a. Relation of Electromotive Force to Temperature

The Gibbs-Helmholtz Equation. The maximum useful work which the cell can deliver is the quantity of electricity (current × time) expressed in coulombs, multiplied by the electromotive force. This is

TABLE XXXV

Comparison of the Heats of Reaction of the Lead Storage Battery Calculated from Thermochemical and Electrochemical Data

Concentration of Solutions			Heat of Reaction at 25° C., Thermochemical Kilogram-Calories	Heat of Reaction at 25° C., Electrochemical (Electrode Measurements) Kilogram-Calories
n Moles of H_2O to 1 Mole of H_2SO_4	Molality	Per Cent H_2SO_4		
400	0.1388	1.34	85.88	85.65
200	0.2775	2.65	86.29	86.24
100	0.5550	5.16	86.38	86.23
80	0.6937	6.37	86.43	86.43
60	0.9251	8.32	86.61	86.62
50	1.110	9.82	86.74	86.75
40	1.388	11.98	87.02	87.01
30	1.850	15.36	87.52	87.58
25	2.220	17.88	88.01	88.13
20	2.775	21.40	88.88	89.12
15	3.700	26.63	90.57	90.88
12	4.626	31.20	92.59	92.68
10	5.550	35.25	94.33	94.35
8	6.937	40.49	96.88	96.85

Average difference ± 0.11 per cent

sometimes called the free or available energy, to distinguish it from the total energy as represented by the heat of the reaction. The available energy will be designated by W.

By the first law of thermodynamics, the change in the total energy of cell Q, considered as a system, is equal to the sum of the external work W, done by the system, and the heat evolved, q. This is expressed by the equation:

$$Q = W + q \tag{12}$$

The heat of the reaction, Q, is measured in calories. The calorie is also called the gram-calorie. This unit of heat energy may be converted into its electrical equivalent of energy, by the following relation: 1 calorie (20° C.) = 4.183 volt-coulombs.

The available energy of the cell, W, is naturally expressed in volt-coulombs. The quantity q will be positive or negative, according as W is less or more than Q. In the case of the lead storage battery, W exceeds Q, and therefore q must be subtracted from W. The significance of this is that the cell has a tendency to cool on discharge, or must absorb heat from the surroundings if its temperature is kept constant.

It is a well-known fact that the electromotive force of any kind of voltaic cell varies more or less with the temperature. The change in electromotive force per degree change in temperature for a lead-acid storage cell is so small that for practical purposes it may be neglected, but it is of importance from a theoretical point of view. Before attempting to determine the actual magnitude of the temperature coefficient, we shall derive,[18] from theoretical considerations, the celebrated Gibbs-Helmholtz equation, which shows the relation of the energy transformations, electromotive force, and temperature. It will then be possible to make comparisons of the observed quantities with those calculated from thermodynamic reasoning.

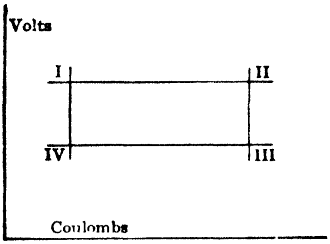

Fig. 54. Cyclic process.

Let it be assumed that a storage cell of the lead-acid type has an electromotive force of E when the absolute temperature is T, and that the cell is in equilibrium with its surroundings. It is also assumed that a quantity of electricity, designated by e, may be passed through the cell either as a charge or discharge, and that the cell may be kept at a uniform temperature (isothermal process) or completely insulated to prevent the transfer of heat (adiabatic process) as we may desire.

The following cyclic process is to be carried out:

I. Let the initial state of the cell be described by the electromotive force E and the temperature T, at the point marked I on the diagram (Fig. 54). Then let a quantity of electricity, e, pass through the cell in the discharging direction while the temperature is held constant at T by furnishing a small amount of heat as required by the term q in the equation above. The current must be small during this process, so that irreversible heat effects due to the ohmic resistance of the cell may be neglected. The work, in volt-coulombs, done by the cell during this part of the cycle is $W_1 = Ee$.

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[18] *Theory of Thermodynamics*, by Buckingham, p. 140.

II. When the quantity of electricity, e, has passed through the cell, let the isothermal process be changed momentarily to adiabatic, during which time the temperature of the cell will fall by an infinitesimal amount δT, becoming $T - \delta T$. The electromotive force becomes $E - \left(\frac{\partial E}{\partial T}\right) \delta T$, where $\left(\frac{\partial E}{\partial T}\right)$ is the temperature coefficient when no current is flowing.

III. Let the quantity of electricity, e, pass through the cell in the charging direction while the temperature is held at $T - \delta T$. The amount of work done on the cell during this process is $W_3 = \left[E - \left(\frac{\partial E}{\partial T}\right)\delta T\right]e$.

IV. When the quantity of electricity, e, has passed through the cell, let the isothermal process be changed to adiabatic while the temperature of the cell increases by the amount δT, which restores the cell to its original temperature. The total external work done by the cell during the cycle is

$$W_1 - W_3 = Ee - \left[E - \left(\frac{\partial E}{\partial T}\right)\delta T\right]e = e\left(\frac{\partial E}{\partial T}\right)\delta T = \delta q$$

The adiabatic processes are infinitesimal in length and are negligible.

Considering, for a moment, the cell as a purely chemical apparatus, we shall suppose chemical reactions to take place in amount and direction equivalent to the discharge of one coulomb. The heat of this reaction is to be measured in volt-coulombs and designated by Q'. For a discharge equivalent to e coulombs, the heat of the reaction will be $Q'e$. The electrical energy of the corresponding reactions at temperature T is equal to Ee. The difference in these two quantities gives at once the amount of heat supplied by the constant temperature reservoir at temperature T during the first step of the cyclic process. This is sometimes called the latent heat of the cell q. It is equal to the difference between the electrical energy and the heat of the reaction:

$$q = Ee - Q'e$$

According to Carnot's cycle, the ratio of the amount of heat converted into useful energy (which in this case is electrical) to the amount of heat received by the system when held at the upper temperature during the cyclic process, is related to the absolute temperature according to the equation.

$$\frac{\delta q}{q} = \frac{\delta T}{T}$$

Substitution of the values for δq and q may now be made in this equation

$$\frac{e\left(\frac{\partial E}{\partial T}\right)\delta T}{Ee - Q'e} = \frac{\delta T}{T}$$

or

$$T\left(\frac{\partial E}{\partial T}\right) = E - Q'$$

the relation of Q' to Q when measured in calories for n faradays is

$$\frac{96{,}500nQ'}{4.183} = Q$$

and the final equation becomes

$$\frac{Q}{23{,}070n} = E - T\left(\frac{\partial E}{\partial T}\right) \tag{13}$$

This is the celebrated Gibbs-Helmholtz equation applied to a reversible electric cell. It shows that the term q in equation (12) is proportional to the absolute temperature and the temperature coefficient of the electromotive force. This equation correlates heat of reaction, electromotive force, and temperature coefficient. It was used to compute the electrochemical heat of reaction shown in the last column of Table XXXV.

b. Variation of the Electromotive Force with Acid Concentration

The electromotive force, or open-circuit voltage, as it is often called, varies with the concentration of the sulphuric acid contained in the cell. The reasons for this are apparent from the discussion of the heat content of the constituents of the cell. The effect of changing the acid concentration on the potentials of the plates may be seen by considering the equations which were given on page 171. The product of the concentration of the hydrogen and hydroxyl ions is equal to a constant, K.

$$[\mathrm{H}^+]\,[\mathrm{OH}^-] = K$$

If the percentage of sulphuric acid in the electrolyte is changed, an increase in the specific gravity means an increase in the concentration of the hydrogen ions and a corresponding decrease of hydroxyl ions. Applying this to equation (6) on page 169, an increase in acidity causes the reaction to proceed to the right, and equilibrium conditions require an increase in the concentration of the tetravalent lead ions in proportion as the hydroxyl ions decrease. Equation (8) for the potential of the positive plate shows that the potential increases as the concentration of the tetravalent lead ions increases. Coincident with the increase in concentration of the hydrogen ions there is an increase in concentration of the sulphate ions. Equilibrium conditions for equation (7) on page 170 show that this condition must be accompanied by a decrease in the concentration of the divalent lead ions. This also results in increasing the potential of the positive plate, as equation (8) shows. Turning now to the potential of the negative plate, by equation (9) it is apparent that a decrease in the concentration of divalent lead ions, accompanying an increase in concentration of the electrolyte, results in a smaller value for the potential of the negative plate; but, as this is to be subtracted from the potential of the positive plate to obtain the voltage of the cell, the effect is in the same direction as for the positive plates. Experiments by Dolezalek[19] have shown that for an increase in acid strength from 6 to 16 per cent, the increase in potential of the positive plates is 0.06 volt and the decrease in potential of the negative plates for the same change in concentration is only 0.004 volt. The change in voltage of the cell is, therefore, the sum of these values, or 0.064 volt. It is at once apparent that the positive plates are much more sensitive to the changes in concentration of acid than the negatives. Considering the cell as a whole, as in equation (10), it is found that the voltage increases as the concentration of the tetravalent lead ions increases and as the square of the concentration of the divalent lead ions decreases. The observed facts are in agreement with the theory, but reliable data are lacking as to the magnitude of the concentrations of the ions upon which a computation of the quantitative effects can be based.

Many measurements of the relation of acid concentration to electromotive force have been made, but it is difficult to compare the results, because the earlier experimenters have employed various means of expressing the acid concentration and the electrical measurements are subject to uncertainty. An effort was made to calculate the various determinations reported in the literature to a uniform basis, and these were tabulated in earlier editions of this book. Newer and more reliable data are now available on batteries and on electrodes from which

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[19] *Theory of the Lead Accumulator*, p. 80.

the electromotive force of the batteries can be calculated. A critical and perhaps somewhat arbitrary selection of the earlier values has been made. Table XXXVI contains a group of determinations on batteries and another group of measurements on electrodes for corresponding acid concentrations. The mean values of the former are in close agreement with those of the latter group. In the last column of the table the mean of all measurements included in the table is given as representing the best data on the relation of electromotive force to acid concentration. The value of such data is twofold. From the theoretical standpoint, it is necessary for calculations based on thermodynamic theory, and from the practical standpoint it is of use in fixing the conditions of floating batteries.

c. Temperature Coefficient of Electromotive Force

By the temperature coefficient is meant the differential change in electromotive force, or open-circuit voltage, of the cell with change in temperature of the cell. This should not be confused with the change in capacity of the cell which is caused by change of temperature. The coefficient is conveniently expressed as the change in voltage per degree change in temperature. It is positive within the working range, that is, a rise in temperature is accompanied by a rise in voltage. The coefficient is constant or very nearly so, which means that the same values for the change in voltage per degree change in temperature may be expected for a given concentration, regardless of the actual temperature of the cell.

A critical review of the temperature coefficients for different acid concentrations, Table XXXVII, has been made as in the case of the electromotive force data. The temperature coefficients are more difficult to determine accurately, but it is important that they should be known for theoretical reasons as well as for more practical matters of battery operation. Three sets of determinations on batteries are given in the table. The mean values agree reasonably well with the mean of three sets of determinations on electrodes. As the most probable values, the mean values of all are given in the last column. The temperature coefficients for acid concentrations below 4.3 per cent are negative, but this is below the operating range of storage batteries. For all concentrations above 4.3 per cent the coefficient is positive and reaches a maximum value at approximately 21 per cent (1.150 sp. gr.).

Having the necessary data on electromotive force and temperature coefficient, the heat of the reaction for different concentrations of electrolyte may be calculated from electrochemical measurements, using

TABLE XXXVI

Electromotive Force of the Lead Storage Battery as a Function of the Acid Concentration

(All values in volts.)

Sp. Gr. 25° C./25° C.	Per Cent H_2SO_4	Determinations on Storage Batteries					Calculated from Electrode Measurements				
		Dolezalek Calculated to 25° C.	Thibaut Calculated to 25° C.	Vinal and Altrup at 25° C.	Craig and Vinal at 25° C.	Mean	Harned and Hamer at 25° C.	Vosburgh and Craig at 25° C.	Craig and Vinal at 25° C.	Mean	Mean of All
1.020	3.05	.....	(1.833)	.....	1.855	1.855	1.855	1.856	....	1.855	1.855
1.030	4.55	.....	(1.851)	.....	1.876	1.877	1.878	1.878	1.882	1.879	1.878
1.040	6.04	.....	(1.867)	1.890	1.892	1.892	1.895	1.893	1.896	1.895	1.893
1.050	7.44	1.906	(1.879)	1.903	1.905	1.905	1.908	1.909	1.908	1.908	1.907
1.100	14.72	1.963	(1.941)	1.956	1.962	1.960	1.960	1.962	1.961	1.961	1.961
1.150	21.38	2.012	(1.944)	2.000	2.005	2.005	2.005	2.006	2.007	2.006	2.006
1.200	27.68	2.054	2.043	2.045	2.050	2.048	2.050	2.049	2.051	2.050	2.049
1.250	33.80	2.098	2.094	2.091	2.098	2.095	2.097	.....	2.094	2.095	2.095
1.280	37.40	2.125	2.126	2.119	2.128	2.125	2.127	.....	2.121	2.124	2.125
1.300	39.70	2.143	2.148	2.138	2.148	2.144	2.147	....	2.140	2.144	2.144

Notes: 1. All emf values have been read from curves for the percentages given in column 2, for which equivalent specific gravities at 25° C are given in column 1.

2. Dolezalek's values in column 3 have been calculated to 25° C. and corrected for the difference between his value for the Weston cell and the value in use now.

3. Values in parenthesis, column 4, were omitted in taking the mean values.

4. Determinations in column 6 were made on cells containing pure lead grids; other cells are believed to have contained lead-antimony grids.

5. Electrode measurements are based on combining values of the separate electrode potentials, experimentally determined.

6. References: Dolezalek, *Theory of the Lead Accumulator*, p. 55, 1904; Thibaut, *Zeit. f. Elektrochem.*, 19, p. 881, 1913; Vinal and Altrup, this book, 1st ed., p. 166, 1924; Harned and Hamer, *J. Am. Chem. Soc.*, 57, p. 33, 1935; Vosburgh and Craig, *J. Am. Chem. Soc.*, 51, p. 2009, 1929; Craig and Vinal, *J. Research*, 24, p. 475, Bureau of Standards, 1940.

TABLE XXXVII

CHANGE IN ELECTROMOTIVE FORCE OF THE LEAD STORAGE BATTERY WITH TEMPERATURE

(Values of $\frac{\Delta E}{\Delta T}$ are in millivolts per degree Centigrade.)

Sp. Gr. $\frac{25^\circ \text{ C.}}{25^\circ \text{ C.}}$	Per Cent H_2SO_4	Determinations on Storage Batteries				Calculated from Electrode Measurements				Mean of All
		Dolezalek 0° to 24° C.	Thibaut 15° to 50° C.	Craig and Vinal 0° to 40° C.	Mean	Harned and Hamer 0° to 40° C.	Craig and Vinal 0° to 40° C.	Vosburgh and Craig 20° to 40° C.	Mean	
1.020	3.05	......	−0.06	......	−0.06	.....	......	−0.06	−0.06	−0.06
1.030	4.55	......	+0.02	......	+0.02	......	+0.03	+0.01	+0.02	+0.02
1.040	6.04	−0.04	+0.08	+0.10	+0.05	......	+0.08	+0.06	+0.07	+0.06
1.050	7.44	+0.06	+0.13	+0.15	+0.11	+0.08	+0.10	+0.10	+0.09	+0.10
1.100	14.72	+0.34	+0.26	+0.29	+0.30	+0.19	+0.23	+0.21	+0.21	+0.25
1.150	21.38	+0.36	+0.29	+0.33	+0.33	+0.22	+0.26	+0.24	+0.24	+0.28
1.200	27.68	+0.31	+0.28	+0.30	+0.30	+0.22	+0.25	+0.22	+0.23	+0.26
1.250	33.80	+0.24	+0.25	+0.22	+0.24	+0.20	+0.22	......	+0.21	+0.23
1.280	37.40	+0.19	+0.22	+0.19	+0.20	+0.20	+0.19	......	+0.20	+0.20
1.300	39.70	+0.16	+0.20	+0.18	+0.18	+0.17	+0.16	......	+0.17	+0.17

NOTES: 1. Values in column 5 are for cells with pure lead grids. Range of temperatures is indicated approximately.
2. The temperature coefficient is zero for an acid concentration of about 4.3 per cent H_2SO_4.
3. For references see Table XXXVI.

the Gibbs-Helmholtz equation (13) given on page 180. These values for the heat of the reaction are contained in Table XXXV where they are compared with the results of thermochemical calculations.

Reversible and Irreversible Heat Effects. If a storage cell of the lead-acid type be placed in a calorimeter which will permit the making of accurate measurements of heat evolved or absorbed during charge or discharge, it will be found that the cell absorbs a small amount of heat from its surroundings during discharge and gives out a similar amount during charge. This means that on discharge the cell delivers more useful work than is represented by the heat of the chemical reactions taking place in it, and that correspondingly more energy is required to charge it. Stated in another way, it means that the cell on discharge draws heat energy from its surroundings and converts it into useful work. Several names have been proposed for the heat liberated or absorbed during the charge or discharge of the cell, but none of them has come into common use. One of these is "reversible heat," which distinguishes this heat from the irreversible heat which is generated in the cell during its operation owing to the ohmic resistance. The latter is proportional to the square of the current. The reversible heat effect is directly proportional to the current and time, because it is dependent on the extent of the electrochemical action. Another name which has been proposed is the "latent heat" of the cell, suggested by the analogy of the heat energy liberated or absorbed when water freezes or ice melts. A third proposal has been to call it the "Helmholtz heat," to distinguish it from that due to the I^2R loss within the cell, for which the name "Joule heat" has been sometimes used. This reversible heat effect has been designated by q.

All the determinations of the temperature coefficient mentioned above were made directly on the voltage changes accompanying a change in temperature. There is another, but indirect, method that can be used, since it was shown above that the reversible heat absorbed during discharge and liberated during charge is dependent on the temperature coefficient multiplied by the absolute temperature. When 2 faradays pass through the cell,

$$q = (23070 \times 2)\, T \frac{dE}{dT}$$

Streintz[20] has made such a measurement, using an ice calorimeter to determine the heat liberated. He could separate the reversible from the irreversible heat effects, since the former is positive on charge and negative on discharge, while the latter is positive in both cases. The

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[20] *Wied. Ann.*, 49, p. 565, 1893.

latter depends on the square of the current and the resistance. Streintz therefore obtained the following equations from which to calculate the value of q for unit time.

$$\text{Total heat effect, discharge } h = I^2R - qI,$$

$$\text{Total heat effect, charge } h' = I^2R + qI;$$

whence,

$$q = \frac{1}{2I}(h' - h)$$

By making I the same on charge and discharge and keeping it a small quantity, so that there would be a negligible difference in the resistance of the cell, he obtained two values of the coefficient at the specific gravity 1.155, which were 0.000345 and 0.000326.

6. THEORY OF THE NICKEL-IRON CELLS

It is generally agreed that the reactions taking place in the nickel-iron cells consist of the transfer of oxygen from one plate to another. When the cells discharge, oxygen is taken from the nickel or positive plate and added to the iron or negative plate. During charge the reverse action takes place. The electrolyte as a whole does not appear to change in composition or density; but there are, nevertheless, important changes in the electrolyte within the pores of the plates.

a. Equations for the Reaction

Although the general character of the reactions is known, the exact nature of the reacting substances and the chemical formulas for them are in some doubt. The process is not as well understood as in the case of the lead-acid cells.

Much of the available theoretical material is based on the researches of Zedner, Foerster, Herold, and Schoop, but many other experimenters have contributed to it. A great variety of equations to represent the reactions have been proposed. Some of these represent certain phases of the operation of the cells, but none of them represents the complete reactions in a single equation as is the case with the lead-acid cells.

The active material of the positive plate is an oxide of nickel or a combination of such oxides. Two oxides of nickel are generally recognized: NiO and NiO_2. It has been supposed that the oxides of nickel form solid solutions. Ni_2O_3 and Ni_3O_4, however, are sometimes regarded as mixtures of NiO_2 and NiO. Besides these oxides, there are two hydroxides, nickelous hydroxide, $Ni(OH)_2$, and nickelic hydroxide, $Ni(OH)_3$.

When the positive plate is charged the proportion of oxygen to nickel is increased. Foerster[21] has found that nickel peroxide, NiO_2, is the primary product of the electrolytic oxidation process and determines the charging potential. The nickel peroxide combines as soon as it is formed with unchanged nickelous oxide to give an intermediate product which approximates Ni_2O_3. Towards the end of the charge, however, the available supply of nickelous oxide becomes much decreased and nickel peroxide begins to accumulate in the plate. The nickel peroxide is not stable and it passes over to a lower state of oxidation, while oxygen is given off and the potential of the plate decreases by more than a tenth of a volt. The peroxide is believed to be present in a solid solution in the active material, since the potential of the plate falls gradually during a period of several days. The open-circuit voltage of the nickel-iron cell when freshly charged is about 1.48 volts and after standing for some time about 1.35 volts.

This spontaneous reaction has certain interesting consequences, as shown by a study of the performance of cells of the nickel-iron type. The decomposition of NiO_2 is accompanied by the liberation of oxygen, which causes the popping of the caps for a considerable time after charging has ceased. The discharge of the cell soon after the completion of the charge will show a slightly greater average voltage and capacity than a similar discharge after one or more days. This is an important point to recognize in testing nickel-iron batteries, since differences in procedure will produce variations in voltage, watt efficiencies and capacities. There is abundant experimental evidence to show that little gas escapes from the cells if they are put on discharge soon after the termination of the charge, as compared with the amount of gas which escapes if the cells stand idle. This indicates that the oxygen which escapes spontaneously can be made use of. It also explains why the "noon-hour boost" for motive power cells in heavy service is so effective in making them "lively," aside from the mere number of ampere-hours that are added to their capacity. Lastly an explanation is offered for the well-known fact that the rate of loss capacity of the nickel-iron cell is considerably more during the first two days after charging than subsequently. It is often stated that a partially discharged nickel-iron battery will lose less charge proportionately, when standing idle, than one fully charged.

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[21] *Elektrochemie Wässeriger Lösungen*, 3rd ed., p. 270, 1922.

In passing from the fully charged to the discharged condition, the oxygen content of the materials decreases from an amount somewhat greater than that indicated by the formula Ni_2O_3 to an amount equivalent to Ni_3O_4 or less.

Crennell and Lea[22] have concluded, as a result of their critical study of the theories of alkaline cells, that the main part of the discharge is provided by a reduction of the hydrated sesquioxide to a lower state of oxidation and the simultaneous formation of ferrous oxide at the negative plates. Since the products of the discharge are hydrated to a different degree than in the charged state, small changes in the concentration of the electrolyte do occur. Foerster[23] has shown that the density of the solution is slightly higher after discharge than before. The difference is so small, however, that it may easily escape detection by the ordinary syringe-hydrometer measurements. Crennell and Lea give as the equation for the complete cell reaction:

$$Ni_2O_3,\ 6H_2O + Fe + 3H_2O \rightleftarrows 2NiO,\ 9H_2O + FeO$$

The discharged material of the negative plate may be given, however, as ferrous hydroxide.

Roeber[24] proposed the formula

$$NiO_2 + Fe \rightleftarrows NiO + FeO$$

which is delightfully simple. On the basis of this formula he developed theoretical discussion of the changes which occur in the electrolyte at the two electrodes during charge and discharge.

Kammerhoff[25] and others have quoted the equation for the Edison cell as follows:

$$2Ni(OH)_3 + Fe \rightleftarrows 2Ni(OH)_2 + Fe(OH)_2$$

It is probable that both the iron and nickel oxides in the alkaline solution are hydrated, and this equation is referred to by Allmand as the usual equation. Foerster, in referring to this equation, states that the nickel-iron cell is not independent, theoretically, of the electrolyte. Practically, however, the cell is independent of the electrolyte and this equation has much to recommend it.

Foerster[26] writes the equation for the complete cell, neglecting the initial decomposition of NiO_2,

$$Fe + Ni_2O_3,\ 1.2H_2O + 1.8H_2O \rightleftarrows Fe(OH)_2 + 2Ni(OH)_2$$

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[22] *Alkaline Accumulators*, p. 94, 1928.

[23] *Zeit. f. Elektrochem.*, 14, p. 285, 1908.

[24] *Electrical World*, 37, p. 1105, 1901.

[25] *Der Edisonakkumulator*, p. 13, 1910.

[26] *Loc. cit.*

Although some authors have stated definitely that Ni_2O_3 is a proven compound, such is not the view of the Edison Company. From a final product of charge which contains at least a portion of NiO_2, a stable state is reached at a ratio of oxygen to nickel which approximates Ni_4O_7. The transition is gradual and this suggests a solid solution or mixture of NiO with a higher oxide, probably the peroxide, NiO_2. To say this, however, involves the assumption that all the higher oxide which is formed is not in solid solution with NiO and that some excess of NiO_2 which is less stable is therefore formed.

b. Reactions at the Plates

Just as in the case of the lead battery, the general equation for the reaction does not tell the whole story of the reactions at the separate plates.

Many years ago Roeber[27] developed a theory for the processes at the individual plates, based on his assumed equation for the cell reaction:

$$NiO_2 + Fe \rightleftarrows NiO + FeO$$

The electrolyte, potassium hydroxide, is dissociated into K^+ ions and OH^- ions. Both of these are monovalent and one gram-ion is therefore equivalent to 96,500 coulombs. During discharge K^+ ions are set free at the nickel electrode. Each K^+ ion takes from the electrode one electron, and the potassium atom immediately reacts with water and one oxygen atom taken from the nickel peroxide, to form potassium hydroxide. The reaction may be represented by the equation:

$$NiO_2 + 2K^+ + H_2O \rightarrow NiO + 2KOH - 2\ominus$$

but we may just as easily write the equation for the reaction by starting with Ni_2O_3 as the active material. This equation shows that the solution becomes more concentrated at the positive plate during discharge, the opposite of what happens in the lead cell.

At the negative plate the discharge of OH^- ions occurs, oxygen is given up to the iron, and water is formed. The equation may be written:

$$Fe + 2OH^- \rightarrow FeO + H_2O + 2\ominus$$

Comparing this equation with that given above, it is seen that the water consumed at the positive plate is restored by the action at the negative, and the two molecules of potassium hydroxide formed at the

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[27] *Electrical World*, 37, p. 1105, 1901.

positive plate just balance the two that disappear. The net result is, therefore, the reduction of the nickel oxide and the oxidation of the iron by equivalent amounts. The electrolyte does not appear to change.

The restoration of the active materials to the charged state is brought about by the passage of an electric current through the cell in the opposite direction to that of the discharge, as in the case of the lead-acid batteries. Hydroxyl ions, OH^-, now are liberated at the nickel plate, and potassium ions at the negative plate. The charging reactions may be written as follows:

Positive plate $NiO + 2OH^- \rightarrow NiO_2 + H_2O + 2\ominus$

Negative plate $FeO + 2K^+ + H_2O \rightarrow Fe + 2KOH - 2\ominus$

During charge, the solution becomes more dilute at the nickel plate and more concentrated at the other, but the two effects balance and the electrolyte as a whole appears to remain constant in composition.

It is possible to construct a diagram, showing the probable reactions at the plates, as has been done for the lead-acid batteries. Foerster[28] gives such a diagram, and a slightly different diagram, based on Crennell and Lea's equation,[29] was published in an earlier edition of this book (2nd ed., p. 179). Both of these assumed the principal reaction to involve the oxide Ni_2O_3. As the more recent researches of the Edison Storage Battery Co. have indicated that a definite compound of this composition is doubtful and that the active material of the positive plate stabilizes at a ratio of oxygen to nickel approximating Ni_4O_7, which is probably a solid solution or mixture of NiO_2 and NiO, the following diagrams for charge and discharge reactions are based on NiO_2, the characteristic product of charging reactions. It must be noted, however, that the following diagrams (Fig. 55), prepared and published by the Edison Co., probably do not represent the complete reactions, nor do they indicate the hydrated state of the active materials which probably exists. The highest electromotive force, immediately after charging, is characteristic of the peroxide, but this falls eventually over an extended time to a more stable value of about 1.35 volts per cell, the cell being on open circuit. This change depends on the potential of both positive and negative plates, but the greatest change is at the positives, and it is accompanied by evolution of oxygen. Such diagrams as those given in Fig. 55 suggest the mechanism of the reactions, but they cannot be regarded as the only or necessarily correct explanation of what occurs at the individual plates.

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[28] Foerster, *Elektrochemie Wässeriger Lösungen*, 3rd ed., p. 270

[29] Crennell and Lea, *Alkaline Accumulators*, p. 99.

Certain irreversible effects, resulting in the liberation of gas during the charging period, occur in the nickel-iron batteries as in the lead storage battery. Gassing of the negative plate begins soon after charging commences. Hydrogen is liberated and plays a most important role in the operation of the battery, since it makes the iron active in spite of its tendency to become passive in an alkaline solution. A liberal proportion of the hydrogen is probably absorbed by the iron. The necessity for the liberation of hydrogen at the negative plate is the explanation of the saying, familiar among battery service men, that if the battery does not gas it is not taking the charge. The rate of liberation of the gas is dependent on the amount of the current flowing, and therefore the rate of charging can affect the subsequent output of the battery. During the latter part of the charging period, oxygen is also liberated, the amounts changing slowly to two parts of hydrogen to one of oxygen as the end of the charge is reached. This means, of course, that at the end the charging current is merely electrolyzing the water present in the cell.

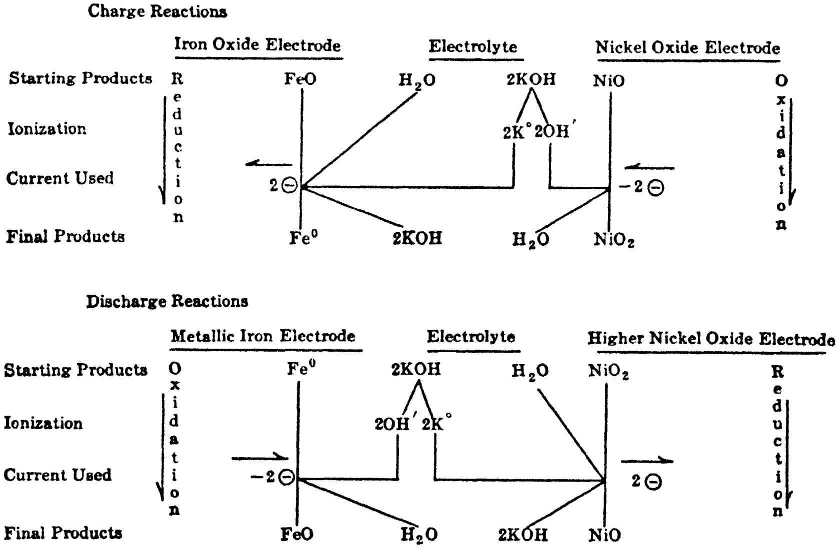

FIG. 55. Charge and discharge reactions, Edison cells.

Schoop[30] has made an interesting series of experiments on this type of cell, with electrodes suspended from the arm of a balance so that changes in weight could be measured as the cells discharged. He found

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[30] *Electrochem. Ind.*, 2, pp. 272 and 310, 1904.

changes in the volume of the active material to occur during charge and discharge. His experiments showed that the active material of the positive plate decreases in volume during discharge and increases during charge. Because of this change in volume the active material of positive plates in the Edison batteries is enclosed in tubes reinforced by iron rings. Changes in volume at the negative plate are smaller under normal operating conditions and therefore of less importance.

c. Secondary Discharge Reactions

The capacity of the alkaline cells is ordinarily limited by the positive plates. When the knee of the discharge curve has been reached the practical capacity of the battery has been exhausted. Beyond this there is some evidence of second stage reactions which occur at lower voltages.

Positive plates containing graphite show a second stage reaction occurring at a potential lower by about 0.5 of a volt than that corresponding to the first stage. This effect has been ascribed to oxygen absorbed by the graphite as it has not been observed in the case of positive plates which do not contain graphite.

If a second stage reaction occurs in the negative plates, it is not important, because the capacity of alkaline batteries is normally limited by the positive electrode. The presence of ferric iron in the active material of the negative plate is detrimental, the plates losing capacity. Edison found that the presence of mercury was very beneficial in stabilizing the capacity of these plates and in preventing reactions of the second stage.

d. Relation of Voltage to Concentration

Since the electrolyte, considered as a whole, does not change, it might be supposed that the electromotive force of the nickel-iron cell would be independent of the concentration. Such is very nearly the case. The researches of Foerster have shown that the reactions are not entirely independent of the electrolyte, however, and he has found changes of a few millivolts in the voltage of the cells when the specific gravity of the electrolyte is varied through limits wider than are ever found in practice. The effect of changing concentration on the voltage is therefore negligible.

e. Temperature Coefficient of Electromotive Force

The information contained in the literature on the temperature coefficient of voltage is conflicting. Schoop[81] quotes Foerster as saying

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[81] *Loc. cit.*

that it is 0.0007 volt per degree. Thompson and Richardson,[32] on the other hand, found by experiment a temperature coefficient averaging +0.00024 volt per degree C. at the concentrations ordinarily employed, but with values of the coefficient that were higher for low concentrations, and lower for the higher concentrations.

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[32] *Trans. Am. Electrochem. Soc.*, 7, p. 114, 1905.

CHAPTER V

CAPACITY

1. METHODS OF RATING STORAGE-BATTERY CAPACITY

a. Ampere-Hour and Watt-Hour Capacity

The capacity of a storage battery may be expressed in two ways, either as the ampere-hour capacity or as the watt-hour capacity. The ampere-hour capacity is a measure of the electrochemical reactions taking place within the cell in accordance with Faraday's law. In this sense the term capacity means the quantity of electricity which the battery is able to deliver. The watt-hour capacity, on the other hand, is a measure of the energy or ability to do work. The relation of the ampere-hour capacity to the watt-hour capacity is a simple one. The watt-hour capacity is obtained by multiplying the ampere-hour capacity by the average value of the voltage during the discharge period. In stating the capacity of any battery, it is necessary to specify the rate at which the battery is to be discharged, the temperature and the final or cut-off voltage. It will be shown in this chapter that these three factors affect the capacity to a marked degree, apart from the effect of other factors which involve the design or condition of the battery.

The ampere-hour capacity of storage batteries is more often stated than the watt-hour capacity. It is simpler to measure; but a more probable reason for its almost universal use is the fact that in nearly all applications of storage batteries, the current requirement is an important and controlling factor. The torque exerted by a motor, the heating of a lamp filament, or the intensity of the field within a solenoid are proportional to the current. In such instances the current becomes a primary consideration and it is necessary to know the ampere-hour capacity. If the ampere-hour capacity and the number of cells in any battery are known, an approximation of the watt-hour capacity, sufficient for ordinary purposes, can be made immediately, since the nominal voltage of the lead-acid type of battery is 2 volts per cell and of the nickel-iron type 1.2 volts per cell.

b. Time and Current Ratings

Batteries may be rated for ampere-hour capacity in several different ways. That most commonly adopted is the so-called time rating, by which the capacity of the battery is stated to be a certain number of ampere-hours which can be delivered within a specified time. For example, stationary batteries are rated at eight hours, and starting and lighting batteries are rated at twenty hours. Current ratings consist in specifying the capacity which may be obtained at some particular current. The time rating is to be preferred to the current rating because the time rating makes the capacities of different sizes of batteries comparable, whereas a current rating irrespective of the size of the battery imposes a less severe tax on the larger sizes and their capacity appears more than proportionately greater. A practical example of this is furnished in the case of starting and lighting batteries for automobiles. These have been rated in the past at 5 amperes; that is to say, the capacity of the battery was expressed as a certain number of ampere-hours which the battery was capable of delivering at a current of 5 amperes. A battery of this type whose cells contain seven plates has one-half the number of positive plates that a thirteen-plate battery would have, and the capacity of the former may naturally be assumed to be one-half the capacity of the latter, provided the details of structure, materials, and discharge are comparable. A comparison of the capacities of two such batteries at the 20-hour or any other time rate of discharge shows the ratio of capacities to be 1 : 2, but at the 5-ampere rate the capacities may be in the ratio 1 : 2.6.

The test current is easily found from the time rating. It is equal to the quotient of the rated capacity of the battery by the time.

c. Fluctuating and Intermittent Ratings

The ampere-hour capacity of the battery is most easily ascertained when the current is constant during the period of discharge. In this case the ampere-hours are equal to the product of the current in amperes by the time in hours. If the current fluctuates with time, it is necessary to determine the integral

$$C = \int_0^t I dt$$

This can be obtained most conveniently by plotting the current as a function of the time and integrating the curve. The capacity C is that obtained during a discharge lasting for a time t. In general t will be determined by the falling voltage of the cell, but it may be chosen as a purely arbitrary quantity.

Intermittent discharges often constitute the normal service that a battery may be called on to render. Intermittent ratings, however, are seldom provided. Some years ago isolated plant batteries, in addition to having a continuous discharge rating of 8 hours, had a second rating which was intermittent, covering a period of 72 hours. This is no longer standard practice.

d. Choice of Final Voltages

The entire theoretical capacity of a battery cannot be obtained, for several reasons. The electrolyte does not diffuse into the pores of the plates with sufficient rapidity when the pores are partially clogged with the lead sulphate; the resistance of the active material and the electrolyte increases as the discharge progresses; and, finally, it is not practical to discharge the battery to zero voltage.

As the battery discharges, the voltage at the terminals falls gradually from its open-circuit value, or slightly below, until the end of the discharge is approached, when it begins to fall much more rapidly. This point indicates that the exhaustion of the cell is near. If a curve is plotted, showing the voltage throughout the period of the discharge, the rapid fall begins at what is commonly known as the knee of the curve. The discharge may be continued slightly beyond this point, but only a small percentage of the total capacity can be obtained after the knee of the curve is passed. The amount of the actual capacity of the battery which remains after reaching the knee of the curve depends on the rate at which the battery is being discharged, the percentage being greater the higher the current. Standard practice has fixed some of the final voltages for discharges at various rates. For stationary batteries of the lead type at the 8-hour rate this is 1.75 volts per cell. From this value the final voltages decrease as the discharge current increases, due allowance being made for the voltage drop in the cells and connectors because of their ohmic resistance. As an illustration of the variation of voltage with the rate of the discharge, the figures in Table XXXVIII for cells of the vehicle type are given for various multiples of the normal 6-hour rate of discharge.

TABLE XXXVIII

Final Voltages for Cells of thf Lead-Acid Type

(The table applies primarily to vehicle cells.)

Multiples of Normal Rate, 6 Hours	Volts per Cell
½	1.78
1	1.76
2	1.72
3	1.68
5	1.59
10	1.38

TABLE XXXIX

Final Voltages For Edison Cells

(The voltages are for various types and sizes of cells discharging at multiples of the normal rate, which for types A, B, C, and D is 5 hours and for types G and J 3⅓ hours.)

Multiples of Normal Rate	Volts per Cell *
½	1.05
1	1.00
2	0 91
3	0.82
4	0.73
5	0.64

* The final voltage for Edison cells is often specified as 1.0 volt per cell, irrespective of the rate; see Fig. 67.

It is not economical to discharge the battery beyond the proper final voltage.

2. FACTORS DETERMINING CAPACITY

The principal factors which affect the capacity of storage cells are as follows: the amount of material within the cell, the thickness of the plates, the rate of the discharge, the temperature, the concentration of the electrolyte, the porosity of the plates, the design of the plates, and the previous history of the plates. These factors will be taken up, one by one, in the succeeding pages.

a. The Amount of Material within the Cell

Application of Faraday's Law. According to Faraday's law, 96,500 coulombs transform one equivalent of lead. Since the atomic weight of lead is 207.2 and the valence 2, the equivalent weight of lead is 103.6 grams. From this we may readily calculate the number of grams of lead, on the negative plate, that are transformed into lead sulphate during the passage of one ampere-hour. As 96,500 coulombs are equivalent to 26.80 ampere-hours, we have 3.866 grams of lead corresponding to 1 ampere-hour. Similarly, there are 4.463 grams of the peroxide, or active material of the positive plate, taking part in the reaction per ampere-hour. Two molecules of sulphuric acid in the electrolyte are transformed for each molecule of lead or lead peroxide, in accordance with the equation:

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

The molecular weight of sulphuric acid is 98.076, and since the valence is 2, there are 98.076 grams of acid reacting for each equivalent of the lead. This amounts to 3.660 grams per ampere-hour. The net change in the weight of the electrolyte during charge or discharge differs from 3.660 grams per ampere-hour because of the formation of two molecules of water during discharge for each two molecules of the acid which take part in the reaction. When the battery is on charge the reverse takes place; that is, two molecules of water disappear for each two molecules of acid which are formed. The net change on discharge is, therefore,

$$-\ 2H_2SO_4 + 2H_2O \rightarrow -\ 2SO_3$$

This equation shows that the actual change in weight is 160.12 grams for every two gram-molecules taking part in the reaction. This loss in weight of the electrolyte is balanced by a corresponding gain in weight of the plates.

The mass of the electrolyte reacting at the positive plates during discharge is slightly greater than at the negative plates. This may be seen from the formula for the chemical reactions taking place at the positive and the negative plates, as follows:

At + $$PbO_2 + H_2 + H_2SO_4 = PbSO_4 + 2H_2O$$

At − $$Pb + SO_4 = PbSO_4$$

The actual consumption of sulphuric acid at the two plates differs more than the formula indicates, because it is necessary to take into account also the concentration changes caused by the migration of the hydrogen (H^+) and the sulphate (SO_4^{--}) ions.

During discharge sulphate ions are consumed at both the positive and the negative plates. Sulphate ions migrate toward the negative plates and away from the positive plates. Hydrogen ions, on the other hand, migrate away from the negative plate toward the positive plate, where part of them are consumed in the formation of water. The net change taking place is therefore a greater loss of acid at the positive plate than at the negative. If this be considered together with the amount of water formed at the positive plate, it is found that the positive requires about 1.6 times the amount of acid that the negative plate requires during the discharge period. This fact is the principal reason for placing the corrugated side of the separators next to the positive plate in order to allow more space for acid. An interesting illustration of the necessity for the corrugations in the separator is furnished by tests which were made on small storage cells for signal purposes, in which the manufacturer had used thin wood separators without corrugations of any kind. It was found impossible either to charge or discharge the cell by more than a very small amount of its estimated capacity. It is sometimes noticed, when separators are renewed in old batteries of the starting and lighting type, that the capacity of the battery is considerably increased. This is undoubtedly due in part to the additional acid space provided next to the positive plates by new separators, since the ribs of the old separators are generally worn down almost to the web of the separator by the time that they require renewal.

Limitations to the Use of the Materials. The foregoing figures showing the relation of lead, lead peroxide, and sulphuric acid consumed per ampere-hour are based entirely upon theoretical considerations. The practical amounts of the active materials required are considerably greater than those calculated from theory. There are several reasons for the limited use of the materials in actual service. The lead sulphate which is formed during the process of discharge is a non-conductor and increases the resistance of the active material of the plates. When the active material contains 50 per cent of sulphate, the resistance has risen to a very high value. Another reason is the stoppage of the pores of the plates by the lead sulphate, which hinders the diffusion of the electrolyte. A third reason is the increasing resistance of the electrolyte itself. It was shown in Chapter III that the minimum resistivity of the electrolyte occurs at a specific gravity of approximately 1.225. As the specific gravity decreases below this point the resistivity increases, slowly at first, and then more rapidly as the concentration falls below 1.100. A fourth reason, which involves the design of the plate itself, is the limited contact between the active material of the plate and its support. In the case of Planté plates, the support is the lead in the central portion of the plate itself. The support for pasted plates is the lead-antimony grid. The active material which is in immediate contact with the supporting material, and also in contact with the electrolyte, is in the most favorable position to take part in the reactions.

The ratio of the amount of active material taking part in the reactions to the total amount of active material present in the plates is called the coefficient of use. This coefficient differs markedly with the thickness and porosity of the plate, the rate of discharge and the temperature. A cell of good quality will have normally a coefficient of 0.25 or more. Lower values are to be attributed to deficient amount of electrolyte, lack of porosity of the plates, or improperly designed separators. Figure 56, from an article by Skinner,[1] shows the distribution of discharged material in plates $\frac{7}{32}$ and $\frac{9}{64}$ inch thick. The heavy shading indicates a high percentage of discharged material; the light shading, little or no discharged material. From this figure it will be seen that the reactions of discharge penetrate into the plate only a portion of the way. For this reason, cells which contain thin plates are found to have greater capacity than cells of similar size containing thicker plates. This is particularly true at high discharge rates. Thin plates do not have a greater capacity *per plate* than thick plates. As a matter of fact, the capacity per plate is somewhat less, but owing to the larger number of plates that can be used in a cell of given size, the capacity of the cell as a whole may be considerably greater. For example, when two cells of equal size containing plates which are $\frac{14}{64}$ inch in thickness and $\frac{9}{64}$ inch in thickness are compared, it is found that the capacity of the thinner plate is 91 per cent of the capacity of the thicker plate, although the former has only 64 per cent of the thickness of the other. In a given jar, therefore, there can be installed 56 per cent more of the thinner plates, assuming a corresponding reduction in the thickness of the separators. The relative capacity of the two cells, neglecting the effect of separators, can be calculated by multiplying 156 per cent by 91 per cent. This gives 142 per cent as the capacity for the cell containing thin plates, as compared with the capacity of the same cell with the thicker plates taken as 100 per cent. The increase in capacity is, therefore, 42 per cent, which agrees very closely with laboratory measurements on such cells.

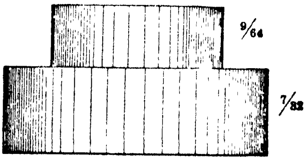

Fig. 56. Distribution of discharged material determined by analysis and amount indicated by the shading.

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[1] Electric Vehicle Assoc., February 25, 1913.

Maximum Output Obtainable. The maximum output obtainable from storage cells can be computed. It is desirable to do this in order to determine how nearly the cells in common use approach the maximum possible output. It will be necessary to assume, for this estimate, thin plates of high porosity discharging at a low rate over a long period of time. The grid of a pasted plate amounts to 35 to 50 per cent of the weight of the finished plate, 50 per cent being a figure more commonly found than 35 per cent. It was found on page 198 that 3.866 grams of lead and 4.463 grams of lead peroxide are required per ampere-hour. This is a total of 8.329 grams of active material as the theoretical requirement for each ampere-hour. We shall assume that the coefficient of use, as defined above, is 50 per cent. This is rather more than can ordinarily be obtained, even with soft plates, when discharging at the 5-hour rate. Dividing 8.329 grams by 0.50 gives 16.65 grams of active material as the best possible equivalent per ampere-hour. Assuming that the grid is only 35 per cent of the finished weight of the plate, the active materials will constitute 65 per cent and, dividing 16.65 by 0.65, we obtain 25.62 grams per ampere-hour as the weight of the plates. It is necessary now to ascertain the relation between the weight of the plates and the weight of the complete cell. This varies considerably among the cells made by different manufacturers, but in the following table are given the weight of each of the different parts of the cell in grams and the per cent of the total weight.

TABLE XL

RELATIVE WEIGHTS IN GRAMS AND PERCENTAGES OF VARIOUS PARTS OF THE COMPLETE CELL

(Figures are for cells of the same size containing 15, 17, and 21 plates. The data for the 15- and 17-plate cells are the mean of three different makes; and for the 21-plate cells the mean of two different makes.)

Plates	Total Weight	Positives	Negatives	Yokes	Electrolyte	Wood Separators	Rubber Separators	Jar	Cover, Vent, and Sealing Compound
Thick.......15	21,237	7660	6657	982	4021	420	153	1150	194
	Per cent	36.1	31.3	4.6	18.9	2.0	0.7	5.4	0.9
Medium....17	21,528	7738	6203	1133	4561	403	269	1281	320
	Per cent	35.9	28.8	5.3	21.4	1.9	1.2	5.9	1.5
Thin........21	20,913	7077	5970	1240	4710	354	221	1187	154
	Per cent	33.9	28.5	5.9	22.5	1.7	1.0	5.7	0.7

In the table it is shown that the positive and negative plates constitute from 62 to 67 per cent of the total weight of the cell. Resuming the example, the weight of the cell per ampere-hour is therefore 25.62 divided by 0.624, or 41.1 grams per ampere-hour, as the result computed for the 21-plate cells. This corresponds to a maximum value of 24.2 ampere-hours per kilogram or 11.0 ampere-hours per pound of the cell. If we may assume that the average voltage during the discharge of the cell is 1.95 volts, the energy capacity becomes 47.2 watt-hours per kilogram or 21.4 watt-hours per pound.

Having calculated the maximum output obtainable, we shall now compare it with the actual output of several different types of storage cells.

TABLE XLI

THEORETICAL AND ACTUAL CAPACITY OF STORAGE BATTERIES

(Starting and lighting batteries (7-plate cells) discharged to 1.70 volts per cell at 5-hour rate and 1.50 volts at 20-minute rate, assuming the grid to be 50 per cent of the weight of the positive plates.)

Kind of Plate	Weight of Positive Active Material, Grams	Complete Theoretical Capacity, Ampere-hours	Actual Capacity 5-hour Rate, Ampere-hours	Coefficient of Use, Per Cent	Actual Capacity 20-minute Rate, Ampere-hours	Coefficient of Use, Per Cent
Soft	504	113	49	43	28	25
Medium	552	123	40	33	23	19
Hard	528	118	35	30	17	14
Very hard	603	135	27	20	12	9

Batteries containing soft, medium, hard, and very hard plates have been chosen for this table. Column 2 shows the weight of the positive active material, since it is the positive plate which limits the capacity of the cell.

The effect of hardness of the plates on the utilization of the active materials is better illustrated by these batteries of 20 years ago than by batteries of the present day which differ much less in hardness of plates. The batteries containing medium plates, Table XLI, correspond to 13-plate batteries of 96 ampere-hours, discharging at the 20-hour rate. The measured capacities are equivalent to 2.5 ampere-hours per pound per cell for the very hard plates and 4.5 ampere-hours per pound per cell for the soft plates, at the 5-hour rate of discharge.

Special thin plate batteries of this type, designed for airplane service, have in some cases given as high as 6 ampere-hours per pound per cell at the same rate.

The output of storage cells of the motive-power type per unit of weight and space is given for the 5-hour rate of discharge in Table XLII. For this table, cells containing 15, 17, and 21 plates per cell have been chosen. The cells are, however, of the same external dimensions. The last figure given for the watt-hour capacity per cubic foot of the 21-plate cells indicates about 2 hp per cubic foot of the space occupied by the battery.

TABLE XLII

Output of Storage Cells of the Motive-Power Type per Unit of Weight and Space, 5-hour Rate of Discharge

(The cells were all nominally of the same external dimensions. The ampere-hours and watt-hours per unit of weight are based on the weight of a single cell. The watt-hours per unit of volume are calculated from observations on a battery of twelve cells. The plates were 21.9 cm. by 14.6 cm. (8$\frac{5}{8}$ by 5$\frac{3}{4}$ inches).)

Number of Plates per Cell	Thickness of Positive Plates		Ampere-hours per		Watt-hours per			
	Cm.	Inches	Kilogram	Pound	Kilogram	Pound	Dm.^{3}	Cubic Foot
15	0.60	15/64	10.9	4.9	21.2	9.6	45	1263
17	0.52	13/64	11.7	5.3	22.6	10.3	48	1350
21	0.44	11/64	13.1	5.9	25.4	11.5	51	1440

As a third example, a certain stationary battery will be considered. This contains plates which are 10½ by 10½ inches. The projected area of the plate is therefore 110 square inches. The ratio of the developed surface of the plate to the projected area is 7 to 1 and, allowing for the two sides of the plate, the actual surface of the plate is computed to be 1540 square inches. If the cell contains six positive plates the total area will be 9240 square inches, or 59,600 square centimeters. The capacity of this cell at the 8-hour rate is found to be 480 ampere-hours, or 1 ampere-hour to 19.2 square inches (124 cm.^{2}) of plate surface. The complete cell weighs 232 pounds, and the output is, therefore, 2.07 ampere-hours per pound per cell. Assuming the average voltage on discharge to be 1.97, the watt-hour capacity is 945 and the watt-hours per pound 4.1, or 9 watt-hours per kilogram.

b. Thickness of the Active Material

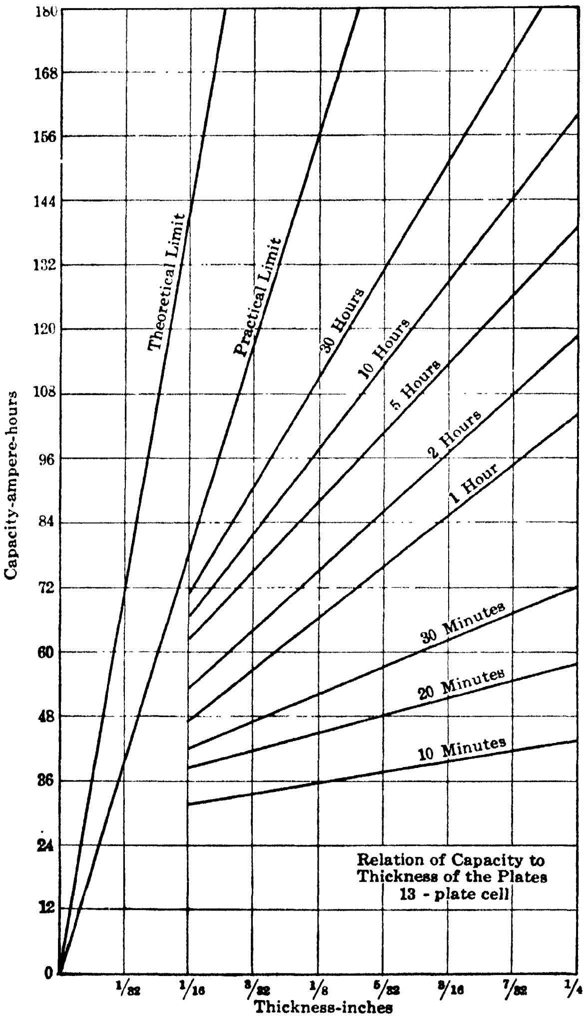

FIG. 57. Dependence of capacity on thickness of the plates.

The capacity of a storage cell increases with the thickness of the active material of the plates at moderate rates of discharge, assuming that the plates have sufficient porosity for the electrolyte to reach the inner recesses. The effect of thickness cannot be considered apart from the rate of the discharge, because the faster the discharge the more nearly is the total output of the cell confined to the layers of active material that are in immediate contact with the free electrolyte. At excessively high rates of discharge, the output of the cell becomes practically a surface phenomenon. This is because there is insufficient time for the electrolyte to diffuse into the pores of the plates, and the sulphate forming at the surface clogs the pores. At low rates of discharge, on the other hand, almost any depth of the active material may become effective. For example, Fig. 57 shows the relation of capacity to the plate thickness for a certain make of starting and lighting battery containing plates varying from $\frac{1}{16}$ inch to $\frac{1}{4}$ inch in thickness. These results are calculated for a battery containing 13 plates to the cell. The very great difference between discharges made at high rates and at low rates for plates of different thickness may be illustrated as follows: At the 10-minute rate of discharge, the $\frac{1}{4}$-inch plate gives only 38 per cent more capacity than the plate $\frac{1}{16}$ inch in thickness, but at the 30-hour rate it gives 170 per cent more.

The negative plates are more sensitive to changes in thickness than the positive plates. This means that, if the capacities of the positive and negative plates are equal at any high rate of discharge, the negative will exceed the capacity of the positive at any lower rate of discharge.

c. Area of the Plates

In the preceding paragraphs a discussion of the amount of material in the cell and the thickness of the plates in relation to the capacity has been given. For any specified amount of material and thickness of the plate, the area of the plates is necessarily determined. The area is, therefore, not an independent factor in determining the capacity, but, since it is most easily measured, it is desirable to discuss the output in its relation to the surface of the plates. The area of the plate requires careful definition, since it may be taken to mean the area as calculated from dimensions of width and height, or the entire developed surface in the case of Planté plates, which is seven to ten times the area calculated from the dimensions. The area of pasted plates is calculated from the width and height and doubled to allow for both sides of the plates.

The output obtained from a given area of plate varies with the type of plate and the rate of the discharge. For Planté plates an output of 1 ampere-hour for each 100 to 125 square centimeters (15 to 20 square inches) of developed surface is about the average. The output for pasted plates of the motive-power type is given in Table XLIII, showing that the capacity per unit of area is somewhat less for the thin plates than for the thicker plates. In the aggregate, however, the capacity for the thin-plate cells is greater, because the increased surface of the plates more than offsets the decreased capacity per unit of area. The values given in the table are for motive-power cells discharging at the 5-hour rate.

Jones[2] gives an equation relating area and thickness of plates to capacity, standardized by the British Post Office.

$$\text{Amp.-hours} = 1.03\, A \sqrt[5]{T^2}$$

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[2] *Post Office Elec. Eng. J.*, 21, p. 227, 1928.

TABLE XLIII

OUTPUT PER UNIT OF PLATE AREA FOR MOTIVE-POWER TYPE CELLS OF NOMINALLY SAME SIZE

Plates per Cell	Area Positive Group, Sq. Cm.	Capacity 5-Hour Rate, Amp.-hour	Ampere-hours per	
			Sq. Cm.	Sq. In.
15	4480	228	0.051	0.329
17	5120	244	0.048	0.309
21	6400	260	0.041	0.264

where A is area of plate in square inches and T is thickness in inches. The capacity is measured to specified final voltages. Although the equation does not hold for all types of batteries, it is said to apply to both positive and negative plates made by various manufacturers and designed for use in stationary cells.

In order to study the relation of plate area to the rate of discharge, reference is made to Fig. 57 in the preceding section, which is calculated for a cell of thirteen plates. We shall take as an example a cell containing thirteen plates, $\frac{3}{16}$ inch in thickness, and compare with it another cell of similar size having double the number of plates, which are $\frac{3}{32}$ inch in thickness. It is obvious that the volume of the plates in each case is the same, but that the area of the plates in the latter case is double that in the former. At the 30-hour rate, the cell containing the $\frac{3}{32}$-inch plates has an aggregate capacity of 182 ampere-hours. The cell containing the $\frac{3}{16}$ inch plates has a capacity of 152 ampere-hours. Halving the thickness of the plates, and thereby doubling the area, has increased the capacity 20 per cent at this low rate of discharge. At the 10-minute rate of discharge, the cell containing $\frac{3}{32}$-inch plates has a capacity of 67 ampere-hours and the other cell with $\frac{3}{16}$-inch plates has a capacity of 40 ampere-hours. At this high rate of discharge, halving the thickness and doubling the area has increased the capacity of the cell 68 per cent. This example illustrates the importance of plate area, particularly in the case of batteries which are designed for discharge at high rates.

An effort to get greater area of plates is found particularly in the case of airplane batteries, for which plates as thin as 0.050 inch are often used. Thin plates possess two advantages for heavy service. The first is increased capacity for unit of space and weight. The second advantage is decreased resistance, which permits the cell to deliver very large currents with a small waste of energy within the cell itself.

d. Rate of Discharge

It is a familiar fact that storage cells will not give as great capacities when discharging at high rates as when discharging at lower rates. The causes of the decreased capacity at the high rates are the following: the sulphation on the surface of the plates, which closes the pores; the limited time available for diffusion of the electrolyte; and the loss of voltage because of internal resistance of the cells.

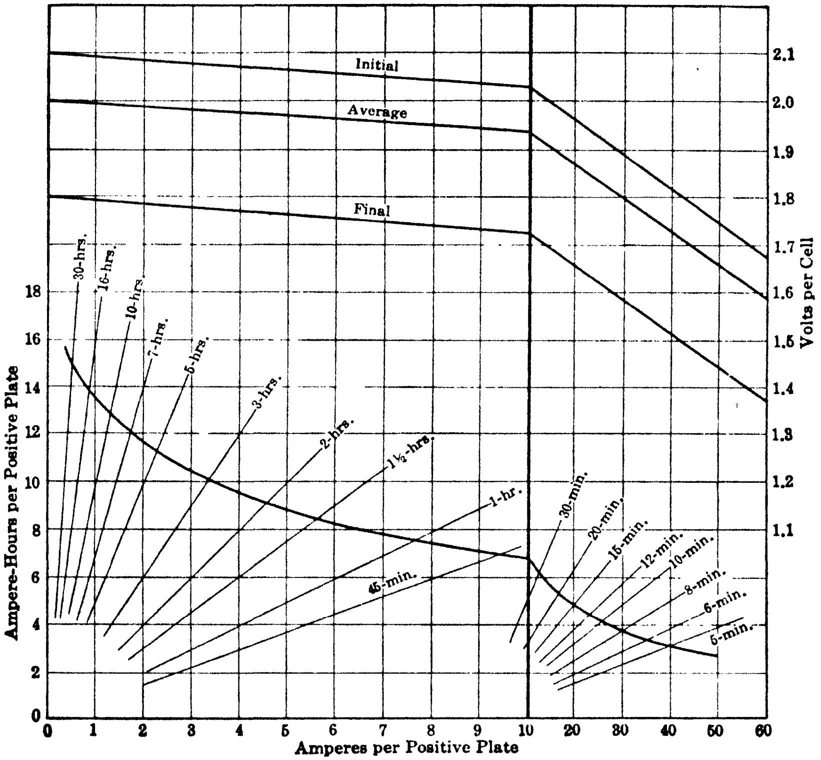

FIG. 58. Discharge characteristics of a plate of the starting and lighting type.

Variation of Capacity with Time and Rate. Figure 58 shows the discharge characteristics of one type of storage cell designed for starting and lighting service. The capacity is expressed as ampere-hours per positive plate, as a function of the current discharged per positive plate. That is to say, if a cell contains six positive plates, the ampere-hour capacity indicated for any given rate or time of discharge is to be multiplied by six. The capacities are shown for all rates of discharge, from the 5-minute rate to the 30-hour rate, but it should be noted that the scale of the abscissa is arbitrarily changed at 10 amperes per positive plate, in order to make it possible to show the complete characteristics of cells of this type within the limits of a single illustration. The diagonal lines intersecting the curve of capacities give the time of discharge. This figure applies to batteries containing any number of plates of the type to which this characteristic curve applies. The figure shows the capacity for any rate of current and for any time of discharge. It shows the time of discharge for any given current or delivered capacity, and the current for any given time or delivered capacity. It also shows the voltages, initial, average, and final, for any current rate or for any period of time. The watts or watt-hours for any current or time of discharge may readily be computed.

Successive Discharges. The capacity of storage cells is seen from Fig. 58 to increase as the rate of discharge becomes lower. The physical significance of this effect lies chiefly in the diffusion phenomena. After a battery has been discharged to its final voltage at any given rate, it may be further discharged at any lower rate. That is to say, the total capacity of the battery is equal to the summation of terms in accordance with the following equation:

$$C = \Sigma I_1 t_1 + I_2 t_2 + I_3 t_3 \ . \ . \ . \ I_n t_n$$

where I_1, I_2, I_3, etc., are successively lower values of the current, and the t's represent the time during which the battery was discharging at the rate indicated by I with corresponding subscripts. Deception has in many cases been practiced upon automobile owners in order to sell special electrolytes for which extraordinary claims are made, by making use of the fact expressed in the equation above, the deception consisting in the failure to state that the same result may be obtained with the ordinary electrolyte as with the special product whose merits are exploited. A storage cell for demonstration purposes is discharged to the point where it fails to crank the engine, and then is allowed to rest for a period of a few minutes. During this time the more concentrated electrolyte in the cell is diffusing into the pores of the plates, and it is possible to discharge the battery again, the current, however, being somewhat lower on the average than in the preceding experiment. This may be repeated a number of times, and so it may appear, in the absence of exact measurements, that the battery has acquired an unlimited capacity because of the electrolyte which it contains.

Equations to Relate Current and Time. A number of attempts have been made to develop equations which should relate the current to the time of discharge, in order that the capacity of batteries may be computed for any rate or time of discharge. The most widely used of these equations is Peukert's equation,[3]

$$I^n t = C \tag{1}$$

In this equation, n and C are constants which may be evaluated by tests made on any cell or battery at two different rates of discharge. It will be assumed that the different rates are I_1 and I_2, the times of these discharges corresponding to t_1 and t_2. The values for n and C may therefore be calculated as follows:

$$\left.\begin{aligned} I_1{}^n t_1 &= C \\ I_2{}^n t_2 &= C \end{aligned}\right\} \tag{2}$$

$$\left.\begin{aligned} n \log I_1 &= \log C - \log t_1 \\ n \log I_2 &= \log C - \log t_2 \end{aligned}\right\} \tag{3}$$

$$n = \frac{\log t_2 - \log t_1}{\log I_1 - \log I_2} \quad . \tag{4}$$

The numerical value for n being found for any particular type, the other constant C may be determined by solving either of the equations (2).

Peukert's equation was derived and originally applied to batteries made in European factories. It will be interesting, therefore, to apply Peukert's equation to an American-made battery of the starting and lighting type, since this battery is used over a wider range of discharge currents than any other. The data on which the following example is based are taken from Fig. 58.

Example 1. A battery of 15 plates of the type illustrated, containing 7 positive plates to the cell, is tested at the 2-hour and the 5-hour rates and the following data obtained. Required the values of n and C of Peukert's equation.

$$\begin{aligned} I_1 &= 4.6 \times 7 = 32.2 & t_1 &= 2 \\ I_2 &= 2.3 \times 7 = 16.1 & t_2 &= 5 \\ \log 5 &= 0.699 & \log 32.2 &= 1.508 \\ \log 2 &= \underline{0.301} & \log 16.1 &= \underline{1.207} \\ & 0.398 & & 0.301 \end{aligned}$$

$$n = \frac{0.398}{0.301} = 1.32$$

Solving for C $\qquad C = (32.2)^{1.32} \times 2 = 195.6.$

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[3] *Elektrotech. Zeit.*, 18, p. 287, 1897.

Example 2. Using the values of n and C obtained in the preceding example, compute the length of time t of discharge for a 15-plate battery at 4, 20, and 100 amperes and compare the results obtained with the experimental data given in Fig. 58.

$$t = \frac{195.6}{(4)^{1.32}} = 31.4 \text{ hours; by the curve 33 hours.}$$

$$t = \frac{195.6}{(20)^{1.32}} = 3.75 \text{ hours; by the curve 3.74 hours.}$$

$$t = \frac{195.6}{(100)^{1.32}} = 0.45 \text{ hour; by the curve 0.41 hour.}$$

Other equations which have been suggested, to relate the capacity of the storage cells to the current at which they are discharged, are those of Schroeder[4] and Liebenow.[5] Schroeder's equation is

$$K\sqrt[3]{I^2} = m$$

K = capacity of the cell expressed in ampere-hours;
I = current rate of the discharge, and
m = constant.

This equation possesses an advantage in that it has only one constant, and it is therefore necessary to make only one discharge of any battery in order to compute the value of m and use the equation. However, the results calculated by this equation differ considerably from the experimental values obtained on cells of American manufacture. Liebenow's equation is

$$K = \frac{m}{1 + aI}$$

This equation contains two constants, m and a, which may be evaluated from the results of two discharges on a storage cell at differing rates. In Fig. 59 is shown a comparison of the values computed by the equations of Peukert, Liebenow, and Schroeder, with the values as actually observed and taken from Fig. 58. The values for the current and time of discharge in Fig. 59 are given on a logarithmic scale, in order to permit of a wide range of current values. Curve II represents the values actually observed. It will be seen that Curve I, representing the results computed from the formula of Peukert, lies very close to the observed values. This affords a striking confirmation of the validity of Peukert's formula. The capacities calculated from the formulas of

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[4] *Elektrotech. Zeit.*, 12, p. 587, 1891.

[5] *Zeit. f. Elektrochem.*, 3, p. 71, 1896.

Liebenow and Schroeder differ from the observed capacities by considerably more.

e. Temperature

The temperature plays an important part in determining the capacity which can be delivered by a storage cell under any specified conditions of rate and final voltage. Because batteries are commonly used when atmospheric temperatures are low, interest centers on improving their output under such conditions. Low temperatures cause a decrease in the capacity of storage batteries because resistance and viscosity of the electrolyte are increased, and separators are adversely affected.

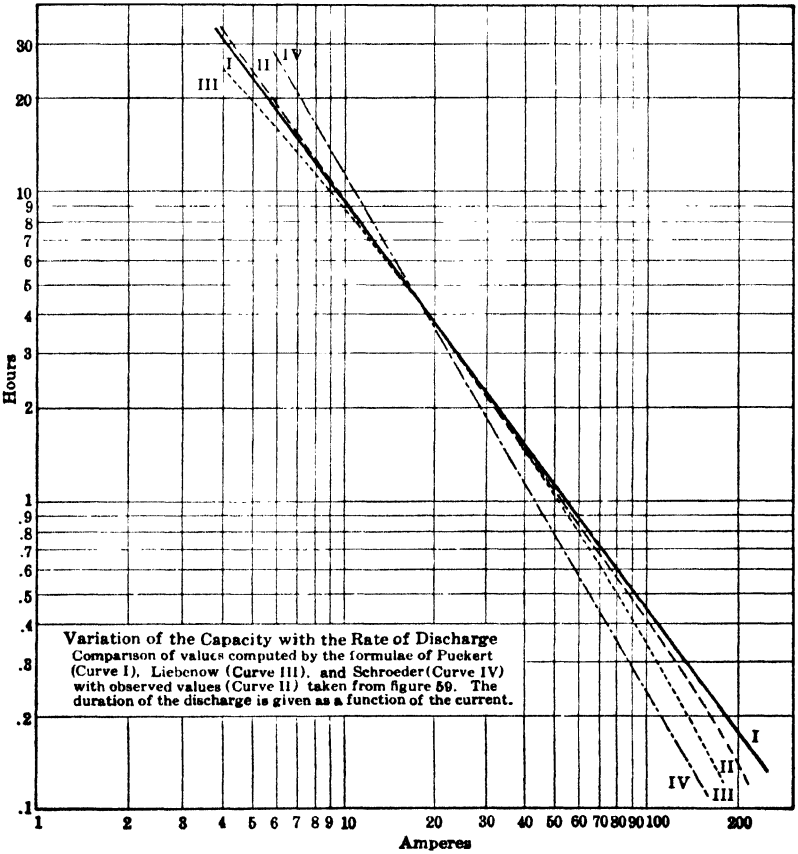

FIG. 59. Comparison of observed capacities with those calculated from various formulas.

Figure 60 shows graphically the effect of temperature on resistivity of the electrolyte. The concentration is limited to about 1.280 sp. gr. when the battery is charged, if the negative plates are to function properly. When the battery is discharged the specific gravity cannot be allowed to fall below the limits set by the freezing-point curve. The resistivity increases very rapidly at temperatures below 0° C. (32° F.) as shown by the curves.

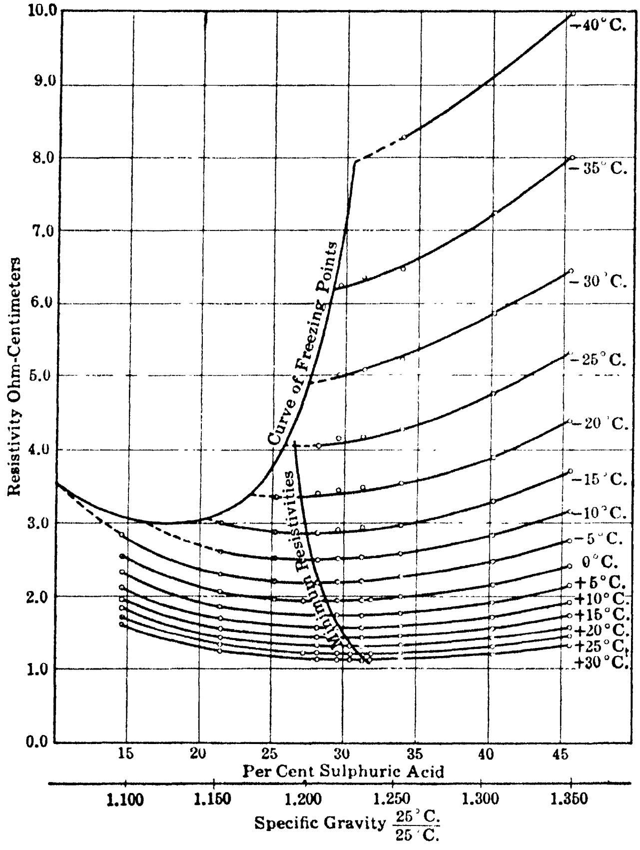

FIG. 60. Effect of temperature on the resistivity of sulphuric acid solutions.

Low temperatures increase the viscosity of the electrolyte, impairing its circulation in the pores of the plates. The increase in viscosity becomes very rapid at temperatures below 0° C. (32° F.) as shown in **Fig. 61**. At −50° C. (−58° F.) the viscosity is nearly thirty times as great as at ordinary temperatures. This illustration shows rather better than the preceding figure, the limitations imposed by the two arms of the freezing-point curve. The range of concentrations within which the electrolyte remains a liquid becomes increasingly narrow as temperature is decreased. The extreme low temperatures shown in these figures are not below possible atmospheric temperatures.

Temperature Coefficient of Capacity. Many experiments have been made to determine the temperature coefficient of capacity of storage cells. One per cent per degree Centigrade (0.56 per cent per degree Fahrenheit) for cells containing Planté plates is a value which has been given in several previous books. Liebenow[6] states that he found the capacity to be a linear function of the temperature, and the increase for 1° rise in temperature to be 1 per cent of the capacity at 15° C.

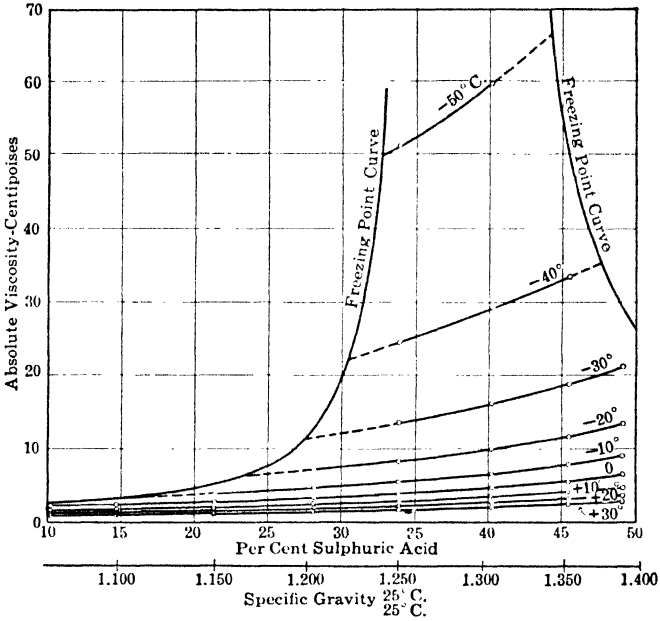

FIG. 61. Effect of temperature on the viscosity of sulphuric acid solutions and the limitations imposed by freezing points.

Within recent years the capacity of batteries at low temperatures has been considerably improved by the use of organic expanders in the negative plates, and the curves relating capacity to temperature do not fall as rapidly in the region of low temperatures as was formerly

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[6] *Dependence of Capacity on Current Strength,* Inaug. Dissert., Göttingen, p. 6, 1905,

the case. Figure 62 shows a group of curves based on comprehensive tests made by Chubb and Harner.[7] The relative capacity is expressed in ampere-hours, but, as they have chosen a standard battery having a capacity of 100 ampere-hours at the 20-hour rate and 80° F., the relative capacities may be read as percentages of that condition. The curves show the relation of capacity to current as well as temperature. These data were obtained on batteries of the starting and lighting type

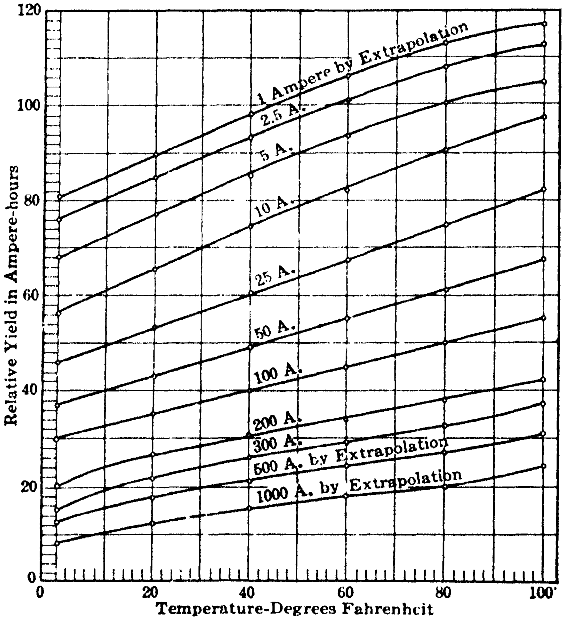

FIG. 62. Relation of capacity to temperature and rate of discharge. Positive plates limit the capacity at all rates and temperatures.

which are normally rated at the 20-hour rate, but they indicate, qualitatively at least, what may be expected of other types.

Variation of the Coefficient with the Rate. Since temperature affects the rate of diffusion and the resistivity of the electrolyte, it may readily be expected that the temperature coefficient of capacity will vary with the rate of discharge. Using the data in Fig. 62, at 5 amperes, the capacity is 100 ampere-hours at 80° F. and 68 ampere-hours at 0° F. The available capacity at 0° F. is, therefore 68 per cent of the capacity at 80° F. At a discharge rate of 100 amperes, the capacities

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[7] Yields at Varying Rates and Temperatures, Bulletin of Eagle Picher Lead Co

at 80° and 0° F. are 50 and 30 ampere-hours, respectively, and the available capacity at the lower temperature is 60 per cent of that at the higher temperature. Stated in another way, the percentage of available capacity at lower temperatures decreases as the rate of discharge increases. Woodbridge [8] compared the 6-hour and 1-hour rates for truck batteries at various temperatures between 120° F. and 20° F. Assuming the capacity at 80° F. for these respective rates to be 100 per cent in each case, he finds the capacity at 30° F. to be 80 per cent at the 6-hour rate and 70 per cent at the 1-hour rate.

f. Concentration of the Electrolyte

Change in Capacity with Concentration. The concentration of the acid in the pores of the plates is a vital factor in determining the voltage and capacity of a cell. Unless a sufficient amount of sulphuric acid can be maintained in the pores during discharge, the voltage at the terminals of the cell will decrease rapidly and the cell will become exhausted. The concentration affects the capacity, first, because it determines the potential of the plates; second, because it affects the resistance of the electrolyte to the passage of the electric current; third, because it affects the viscosity of the electrolyte and thereby the rate of diffusion; fourth, because differences in the concentration of the electrolyte in the pores of the plates and outside also affect the rate of diffusion.

Liebenow's Experiment. Liebenow [9] carried out a celebrated experiment which has often been quoted to show the influence of concentration on the capacity of the plates. He welded a negative plate of the pasted type to form a window in the side of a lead vessel which he then placed in a larger vessel. By varying the height of the electrolyte in the two vessels, it was possible to exert a hydrostatic pressure to force the electrolyte through the plate, which served as a window of the inner compartment, in either direction, or, if the electrolyte were at the same level in the two vessels, to eliminate the hydrostatic pressure. Liebenow suspended a positive plate inside of the inner vessel and determined the capacity of this arrangement when the electrolyte had the same level in the two vessels. The capacity was found to be about 14 ampere-hours. After this the level of the electrolyte in the inner compartment was maintained higher than in the outer vessel, so that the acid was continually passing through the plate. He again determined the capacity and found it to be approximately 42 ampere-hours,

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[8] *Handbook for Electrical Engineers*, Pender and Del Mar, 7, p. 15.

[9] *Zeit. f. Elektrochem.*, 4, p. 63, 1897.

or three times as great. This experiment shows that, if the concentration of the electrolyte in the pores of the plate can be maintained during the discharge period, the cell will have a much greater capacity. In other words, the capacity of the cell in the ordinary case is limited by the supply of electrolyte. Only in extreme cases, when the discharge takes place at very low rates and the coefficient of utilization of the active material is very high, can the capacity be said to be limited by the amount of active material available.

Maximum Capacity. Experiments to determine the concentration of electrolyte for which the capacity of any given storage cell is a maximum have been made by numerous observers. Their conclusions have varied from concentrations of 1.100 to 1.270 sp. gr. The wide divergence of their results is probably accounted for by the varying conditions of their experiments.

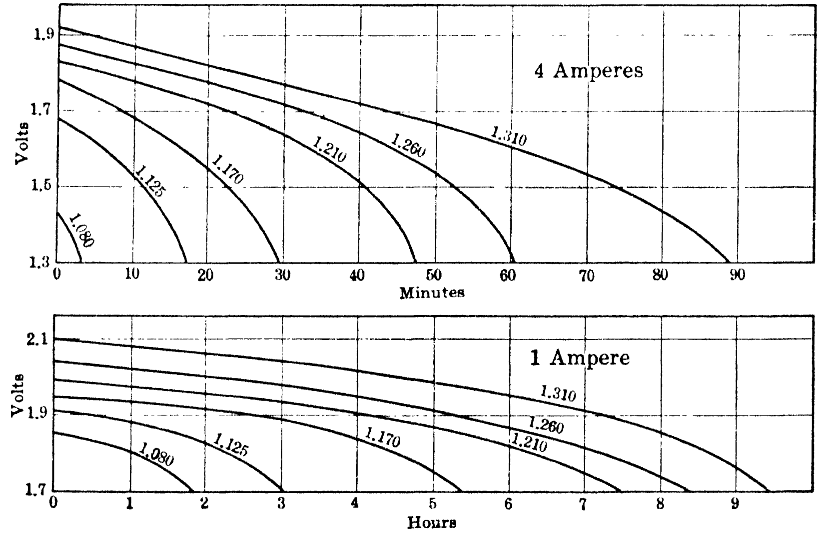

FIG. 63. Effect of concentration of the electrolyte on the capacity of cells discharging at 1 ampere and at 4 amperes.

The capacity of the cells increases as the specific gravity increases, within the range now employed. This is particularly true at high rates of discharge when the capacity of the cells is limited by the positive plates. Figure 63 shows a series of experiments made on small cells of the couple type having pasted plates and containing electrolyte of specific gravities ranging from 1.080 to 1.310 at the beginning of the discharge. The figure shows the characteristic curves for discharges at 4 amperes and 1 ampere. The plates were 3 inches wide by 4 inches high. This figure shows that when the rate of discharge was decreased from 4 amperes to 1 ampere, the time of discharge for the cell containing the highest specific gravity was increased 6.4 times, but the cell containing the lowest specific gravity gave 35 times the length of discharge at the lower current rate.

The final specific gravity is an important factor, since the final specific gravity determines the rate of diffusion at the end of the discharge. In present-day practice, cells are operated over a great range of specific gravities, and because of the limited space it is necessary that the initial specific gravity should be high in order that the final specific gravity may not be too low.

Comparison of Effects of Concentration and Temperature on Positive and Negative Plates. Although a high concentration of the electrolyte is favorable for the positive plates, it may be detrimental to the negative plates. The capacity of the negative plates in an electrolyte of 1.315 sp. gr. is less than in an electrolyte of 1.140 sp. gr., particularly at high rates of discharge and low temperatures. The negative plates may thus become the limiting factor. Cases are on record showing that it has been necessary to reduce the concentration of electrolyte in airplane batteries, for example, in order that they might meet the capacity requirements specified for them. The reduced concentration may reduce slightly the capacity at normal rates and temperatures when the positives limit the capacity, but this is more than offset by the gain in capacity under more severe conditions that result in limitations imposed by the negatives.

In order to study the effects of temperature and concentration on the positives and negatives separately, Vinal and Snyder[10] made use of small cells in which the capacity could be limited arbitrarily by the plates of either polarity. Figures 64 and 65 show the results for positive and negative plates discharging at a rate that approximated the 5-hour rate at normal temperatures. The concentrations stand in reverse order in the two figures. Furthermore, the temperature coefficient of the negative plates as measured by the slope of the curves is greater than that of the positives. Both facts help to explain the behavior of airplane batteries mentioned above It must not be concluded, however, that a specific gravity as low as 1.140 is always the most favorable for the negative plates. The same cells discharging at a higher rate (two amperes) gave the best results when 1.240 sp. gr. acid was used. The possibility of freezing when the specific gravity is too low should

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[10] *Trans. Am. Electrochem. Soc.*, 53, p. 233, 1928.

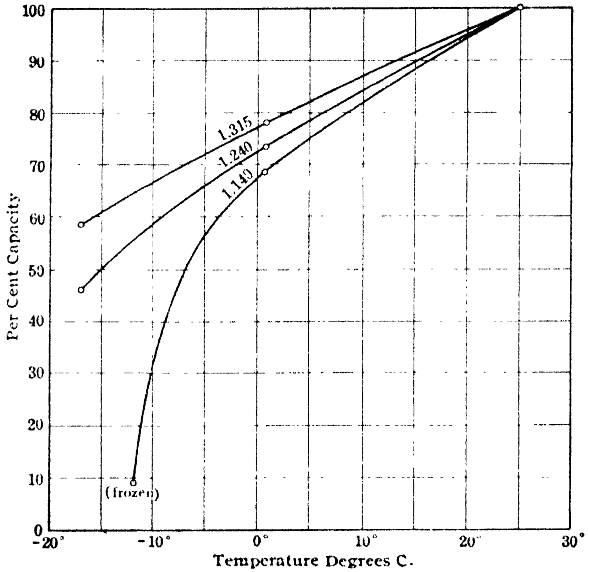

FIG. 64. Effect of temperature on the capacity of positive plates.

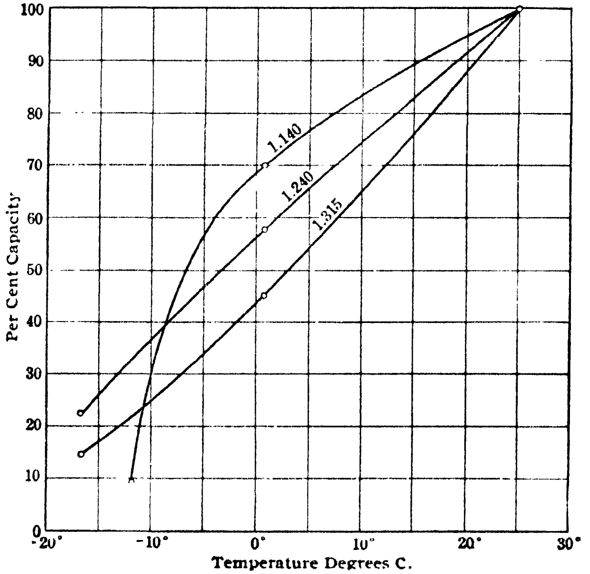

FIG. 65. Effect of temperature on the capacity of negative plates.

not be overlooked. In any case the choice of the strength of the solution involves a compromise, depending on the conditions of service.

g. Porosity of the Plates

The importance of porosity of the plates in facilitating the access of electrolyte to the active material has been treated in connection with other factors previously discussed. The porosity of the finished plate varies with the material from which it was made and with its state of charge. The aggregate porosity of the plate is a matter of 50 per cent of the entire volume of the plate, but the individual pores are probably little more than molecular in size.

While the term porosity is generally understood to indicate the possession of absorption qualities similar to those of a sponge, it is desirable to establish a definition for porosity. The porosity is equal to 1 minus the ratio of the apparent density of the active material to the real density. From this definition the percentage of porosity of the plates may be obtained in any case by multiplying by the factor 100.

Variation of Porosity with State of Charge. The porosity of the plate varies with the state of charge. Lead sulphate, which is formed as a product of the discharge of the cells, is less dense than either lead or peroxide of lead. It therefore occupies more space than the active materials, yet the apparent volume of the plate does not change. The reason for this is that the expansion is taken care of by the pores of the plates. If the discharge is greatly prolonged, however, beyond the customary end points, the amount of sulphate formed may become so great that the pores of the plate are no longer adequate to supply room for it. Then the active material bulges or is pushed out altogether from the plate. The difference in porosity of the active material in the charged and discharged condition was demonstrated by experiments made by Duncan and Wiegand.[11] They determined the amount of acid diffusing from the pores of plates in the charged and discharged conditions and found that the amount of acid diffusing from a given plate was twice as great when charged as when discharged.

Measurement of Porosity. The relative porosity of storage-battery plates can be determined by the amount of water that can be absorbed by the pores when they are initially in the dry condition. Such a measurement, however, is seldom accurate, and it is preferable to determine the actual porosity by calculation as follows:

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[11] *Trans. Am. Inst. Elec. Engineers*, 6, p. 217, 1889.

Example. Determine the porosity of a positive plate of an airplane battery. The three dimensions are as follows:

Length	12.46 cm.
Width	14.28 cm.
Thickness	0 1275 cm.

(In order to obtain a sufficiently accurate determination of the thickness, it is necessary to use a micrometer caliper and to take the mean of a number of readings at different parts of the plate.)

The volume of this plate is 22.632 cc. To this must be added the volume of the lug, 1.03 cc. The total volume of the plate is 23.662 cc. The volume of the grid equals the weight of the grid divided by its density. Its density is determined by Table III, given in Chapter II, after a chemical analysis has been made to find the percentage of antimony which it contains. In this example the volume of the grid equals 81.215 divided by 10.85 = 7.485 cc. Deducting the volume of the grid from the volume of the plate, we obtain the space available for the active material, 23.662 − 7.485 = 16.177 cc. The weight of the fully charged plate washed and dried was 143.3 grams. Deducting the weight of the grid, 81.22, the weight of the active material is 62.08 grams. The actual volume of the active material is equal to the weight divided by the density = 62.08 divided by 8.8 = 7.06 cc. The pores of the plate are equal to the space available for the active material minus the actual volume of the material = 16.18 − 7.06 = 9.12 cc. The porosity equals the ratio of the pore space to the total space available for active material = 56.5 per cent. *Answer.*

A determination of the porosity of the same plate by the absorption method, the water being drained off for about one minute, gave the porosity as 50.5 per cent. The porosity as determined by water is consistently less than the calculated value because of the rapid evaporation of the water on the surface of the plates and the capillary action of the pores. Determining the porosity of the negative plates requires a special procedure, because the negative plates in the battery oxidize spontaneously when exposed to the air, accompanied by a marked rise in temperature. Fully charged negative plates have been successfully dried without oxidation in atmospheres of inert or reducing gases and in vacuum.

When a storage battery discharges, the lead sulphate tends to form at the mouth of the pores. If the discharge is made at a very high rate, the formation of sulphate becomes almost entirely a surface phenomenon and the plate is incrusted with the sulphate, which hinders the free access of electrolyte to the active material. This clogging of the pores naturally limits the available capacity of the cell. When discharges are made at low rates there is less tendency for the sulphate to form on the surface exclusively, and there is opportunity, therefore, for the electrolyte to diffuse into the pores during the discharge. Very porous plates are less sensitive to changes in the current strength.

Diffusion Phenomena. The diffusion which takes place during both the charging and discharging periods is an important factor in the operation of the cell. According to the kinetic theory of diffusion, the molecules and ions in the electrolyte are in continual motion. The proof of this theory is found by examination of colloidal solutions in which the Brownian movement of the colloidal particles can be clearly seen. The motion of the particles to and fro is resisted by the viscosity of the solution.

Fick's law states that the rate of diffusion varies as the difference in the concentration and as the area of the pores, and inversely as the length of the path to be traveled. We may, therefore, write the equation for the amount of acid diffusing in a given time as follows:

$$Q = D \Delta C \frac{a}{l}$$

Q = quantity of acid diffusing in a given time;
D = diffusion coefficient;
ΔC = difference in concentration between the electrolyte within the pores and that outside;
a = aggregate cross section of the pores, and
l = distance through which the acid must diffuse.

In order to obtain a definite idea concerning the process of diffusion, it is necessary to make application of gas laws to the electrolyte, since the phenomena of the diffusion of gases have received more extended study. Sutherland[12] has given a formula for D as follows:

$$D = \left(\frac{RT}{N}\right)\left(\frac{1}{3\pi\eta d}\right)$$

R = gas constant;
T = absolute temperature;
N = Avogadro constant;
η = viscosity of the solution, and
d = diameter of the diffusing particles.

The most significant terms in this equation are those for the temperature and the viscosity. The equation states that the rate of diffusion depends on the absolute temperature and inversely on the viscosity.

The viscosities for solutions of sulphuric acid of the specific gravities which are used in batteries are given in Table XVII in Chapter III. This table shows that the viscosity of solutions having a specific gravity

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[12] *Phil. Mag.*, 9, p. 781, 1905.

1.300 is practically double that for solutions of 1.100. The viscosity decreases as the temperature increases. At 45° the viscosity is only half of its value at 15° C.

The displacement of acid as a result of the diffusion process into the pores when the battery is discharging and out from the pores when the battery is charging is a controlling factor. Einstein has deduced a formula for displacement, which is as follows:

$$X = \sqrt{2Dt}$$

In this equation

X = distance through which the displacement takes place;
D = diffusion coefficient as given above, and
t = time.

Combining this equation with the preceding one and substituting known values for R, T, and N, we may eliminate D and obtain an expression given in a paper by Wells and Gerke[13] as follows:

$$t = \frac{X^2 d}{4.7 \times 10^{-11}}$$

From this equation it appears that the time required for the acid to travel a given distance increases as the square of the distance. The process is therefore slow when the diffusion must take place through any considerable thickness of the active material. Although this equation has been derived from laws governing the diffusion of gases and applied to the movement of colloidal particles, it nevertheless gives an insight, in a qualitative way at least, into the diffusion process in liquids. It explains why so thin a layer of the active material actually takes part in the reactions and why the capacity is increased as the rate of discharge is decreased. If the ions and molecules were not very small, diffusion of the electrolyte would be an extremely slow process.

Other phenomena related to diffusion deserve mention, although they affect the operation of the cell to a very small extent. Electrical endosmosis undoubtedly takes place through the porous separators during both charge and discharge. It does not occur within the porous sections of the plates, however, because the active material of the plates is an electrical conductor, and therefore the potential differences are small in spite of the difference of concentration of the electrolyte in the pores of the plates and outside. There is an electromotive force at the

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[13] *J. Am. Chem. Soc.*, 41, p. 312, 1919.

liquid junction between the two concentrations. This is caused by the unequal speed of the ions. The hydrogen ions move the most rapidly, carrying with them positive charges. Since the electrolyte in the pores of both positive and negative plates becomes depleted on discharging, the liquid-junction potentials are in opposite directions at the two plates and nearly equal in magnitude. Hence their combined effect is negligible. For a discussion of liquid-junction potentials, reference is made to Clark.[14]

h. Previous History of the Plates

Variations of Capacity during Life. When the plates in a storage battery are new, there is an increase in the capacity during the first few cycles of charge and discharge, up to a maximum value beyond which the capacity becomes relatively constant and then gradually falls off. Thin plates reach their maximum capacity after a smaller number of cycles than thick plates, but beyond this point their decrease in capacity is more rapid. Thin plates of one manufacturer may be superior to equally thick or even thicker plates made by another manufacturer. After the capacity of the plates has fallen to 80 per cent of their initial capacity, they are considered worthless. During the later cycles in the life history of the plates, the decrease in capacity of the negative plates is caused primarily by a decrease in the porosity of the material or shrinkage of the plate itself. The loss of capacity of the positive plates is caused by loosening of the active material. In addition to these effects, however, there is a third effect arising from the wearing of the separators. As the separators become thinner and thinner, particularly the ribbed portions, the space available for the electrolyte next to the positive plate becomes inadequate, and the capacity of the cell may be limited by insufficient acid for the action of the positive plate.

Effect of Previous Discharges. The capacity of the plates is affected by the discharges immediately preceding. For this reason it is desirable to run a few preliminary cycles at the same rate of discharge as is to be used in a formal test. This hysteresis effect was observed by Jumau [15] and has been confirmed at the Bureau of Standards. Jumau found that the capacity delivered at any given rate depends on the previous discharge. The capacity is lower if the discharge has been preceded by a discharge at a higher rate, and it is higher if preceded by a discharge at a lower rate. This effect, although small, is never-

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[14] *Determination of Hydrogen Ions*, p. 264, 1928.

[15] *L'écl. électr.*, 16, p. 413, 1898.

TABLE XLIV

Hysteresis Effect

(Average measurements on four thin-plate batteries showing the variation of capacity with changes in the rate of discharge).

Rate of Discharge	Ampere-Hour Capacities	
	Batteries 1 and 2	Batteries 3 and 4
5-hour rate	31.5	65 9
20-minute rate	17.8	41.6
Subsequent discharges at this rate	15.0	31 7
5-minute rate	6.9	14.7
Subsequent discharges at this rate	6.1	13.0
20-minute rate	13.7	32 2
Subsequent discharges at this rate	....	....
5-hour rate	30 8	63.9
Subsequent discharges at the 5-hour rate	31.6	64.6

theless of importance in making tests. Table XLIV gives measurements on thin-plate airplane batteries illustrating this effect. There is also a sluggishness which is caused by inactivity for any considerable period of time. This may be overcome by charging and discharging the cells for a few cycles.

Effect of Purity of the Materials. A third effect influencing the capacity is the purity of the materials of which the plates are made. If small traces of copper and iron are present in the paste, they will gradually pass into solution and affect the capacity as a result of local action. The amount of impurities found in solution of a new cell may be considerably less than if the test for purity is deferred for a longer time.

Period of Standing. It is, of course, obvious that the charging must be adequate if the battery is to deliver its capacity satisfactorily, particularly if a long period of time is to elapse between the charge and the discharge. The rate at which the battery is charged is of little moment in its effect upon the capacity, provided the total amount of charge is sufficient.

3. CAPACITY OF EDISON BATTERIES

a. Rating

Edison batteries of types A, B, C, D, M, N, and F are normally rated at the 5-hour rate of discharge. Types G, J, and L batteries are rated for $3\frac{1}{3}$ hours. The capacities for standard types and sizes of plates have been given in Table X at the end of Chapter II.

b. Amount of Material within the Cell

As in the case of the lead-acid batteries, the capacity of the Edison batteries is dependent on the amount of active material within the individual cells. The amount of nickelous hydroxide which is used in filling the tubes is about four times the amount theoretically required. Assuming the oxide of nickel, NiO_2, to be the highest reaction product and the nickel oxide, NiO, to be the lowest, the reaction may be expressed by the equation:

$$NiO + O = NiO_2$$

Since the electrochemical equivalent of oxygen is 0.2984 gram per ampere-hour, it may readily be calculated that 1.3932 grams of NiO are required for the reaction. The NiO would require 124.12 per cent of its weight as the nickel hydrate and, therefore, the amount of the nickel hydrate theoretically required is 1.729 grams per ampere-hour. Actually the amount necessary is much greater than this.

Representing the reaction at the negative plate by the equation

$$Fe + O = FeO$$

the theoretical amount of iron required per ampere-hour is calculated to be 1.042 grams. The actual amount used is about 5.5 times this.

The electrolyte of the nickel-iron type of battery does not change materially in chemical composition or density (considered as a whole) during charge and discharge. As will be shown later, the discharge of these batteries is terminated because of the exhaustion of the available active material of the positive plate, and not because of lack of electrolyte in the pores, as in the case of the lead-acid type of battery. The capacity of the cell is independent of the amount of electrolyte that it contains, provided the plates are covered.

c. Thickness of the Plates

The A type of plate for Edison cells contains thirty tubes which are $\frac{1}{4}$ inch in diameter. The G type of plate having the same length and width contains forty tubes which are $\frac{3}{16}$ inch in diameter. The ratio of capacity of the G plate to the A plate is 25 ampere-hours to 37½ ampere-hours. From this it is evident that the capacity of the thinner plate is considerably less. Comparing equivalent sizes of cells, however, the type A6 and its equivalent G9 of the same external dimensions both have the capacity 225 ampere-hours. The object of thin plates in the Edison battery is, therefore, not to increase the capacity, as was the case with lead batteries, but to reduce the internal resistance for certain types required for heavy duty.

d. Effect of the Rate of Discharge

The relation of capacity to the rate of discharge of Edison cells is quite different from that of the lead-acid batteries. Nearly full capacity of an Edison battery may be obtained, irrespective of the rate of the discharge, but the voltage will be lower if the current is higher than the normal rate. This effect is shown by the curves of Fig. 66 which apply to a cell of the A type. It will be observed that the capacity delivered at 180 amperes is approximately the same as the capacity at 15 amperes, but the voltage at the terminals oi the cell is very much lower. Two reasons may be assigned for this peculiar effect. The active material of the positive plate, which limits the discharge of an Edison cell, contracts during discharge. The pores of the plate are thus expanding during the discharging process and allow free access of the electrolyte to the material. There is nothing analogous in the operation of the Edison plate to the formation of sulphate which clogs the pores of the lead batteries. Although Edison batteries can deliver nearly full

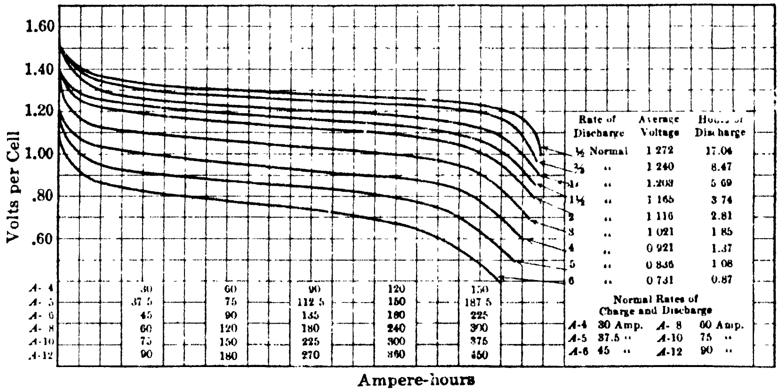

Fig. 66. Discharge curves of Edison type A cells at various rates subsequent to normal charge.

ampere-hour capacity even at high rates of discharge, there are practical limitations which make this effect of less importance than would otherwise appear. In operating the motor on a truck, for example, it is necessary that the voltage at the terminals of the battery should be maintained above a certain minimum value if the truck is to maintain its speed.

If arbitrary final voltages are assigned, it will be found that the capacity of the Edison batteries to those voltages decreases as the rate of discharge increases, in much the same way as was found with the lead batteries. See Fig. 67. The watt-hours delivered at high rates of discharge decrease as the rate of discharge increases because of the fall in the average voltage.

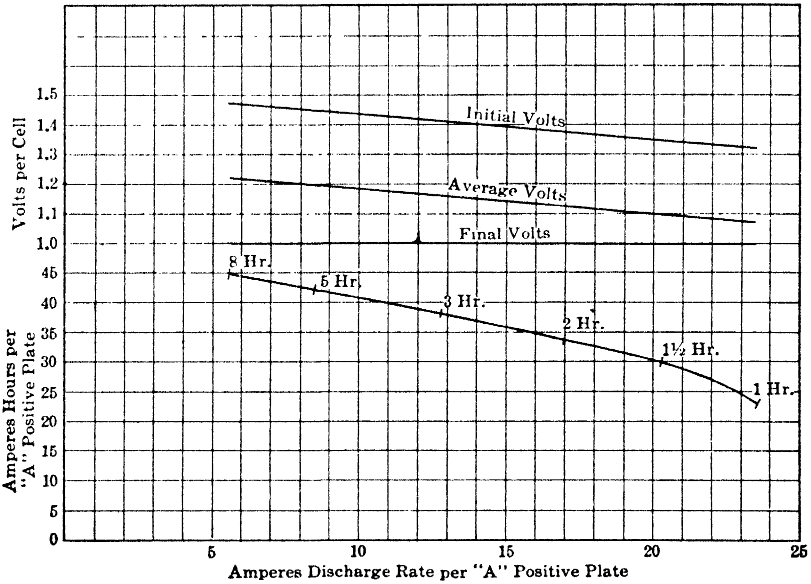

FIG. 67. Discharge characteristics of Edison nickel-iron-alkaline cells, type A, in fully active condition at rates ranging from the 8-hour to the 1-hour rate, all to a final voltage of 1.00 volt per cell, temperature 80 to 85° F.

e. Effect of Temperature

The capacity of Edison batteries is decreased as the temperature is decreased. The relation does not, however, follow a nearly linear law as in the case of lead batteries. The Edison batteries have a critical temperature which varies with the rate of the discharge. Below this critical temperature the output is small; above it, practically the full capacity of the battery may be obtained. The diminished capacity of the cells at low temperatures appears to be due to the temporary passivity of the iron electrode. Comparatively little information is available on this subject, but a paper by Holland[16] gives data for cells of the type A6 discharging at currents ranging from 15 to 75 amperes. The normal rate of discharge for this size of cell is 45 amperes. At the normal rate the critical temperature of the electrolyte is in the neighborhood of 2° C. (36° F.). For rates of discharge in excess of this, the critical temperature is higher, and for smaller rates it is lower. This does not mean that Edison batteries cannot be used at atmospheric temperatures below the critical temperature. The ohmic resistance in cells of this type is sufficient that the heat which is liberated within the cell, equal to the product I^2R, warms the cell appreciably and keeps it above the critical temperature under ordinary conditions of operation. The cell will be operative although used at ambient temperatures much below the critical value, provided the temperature of the electrolyte within the cell does not fall below the critical value.

Ventilation of battery compartments is desirable and in many installations necessary for control of the temperature of the battery as well as to provide for the escape of gases. Edison cells are spaced in their trays so that air can rise between the cells if openings are provided in both top and bottom of the compartment. The amount of ventilation which is necessary will vary with the size of the battery, its average rate of discharge, and the ambient temperature. Truck and tractor batteries which are used principally indoors and batteries of mine locomotives should be provided with maximum ventilation. They operate in nearly even temperatures the year round. Street trucks and electric locomotives which are used outdoors regardless of low atmospheric temperatures should be provided with means to keep the electrolyte temperature within a satisfactory range. The ventilation must be sufficient to prevent excessive temperatures when the outside temperatures are high. It may be necessary to vary the amount of ventilation from one time of the year to another. As a result of tests on Edison batteries, Allen[17] recommended providing a ventilation area, both in top and bottom of the battery compartment, of 3 square inches for each A4 equivalent of battery capacity. As an example, if 21 cells of Edison A6 are used, the ventilation area in top and bottom would be $\frac{6}{4} \times 21 \times 3 = 94.5$ square inches.

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[16] *Central Station,* 11, p. 135, 1911.

[17] *Ventilation of Battery Compartments in Motive Power Service,* Edison Storage Battery Division, Thomas A. Edison, Inc., 1935.

High temperatures, higher than the normal operating limits, may result in permanent loss of capacity if soluble iron compounds are formed. Beside the loss of material at the negative plate, the iron in solution may react with the nickel oxides of the positive plates and impair their capacity.

f. Concentration of the Electrolyte

The concentration of the electrolyte in the Edison cell is of comparatively little importance. The concentration does not change during the charging and discharging of the cell but falls gradually over a long period of time. This decrease undoubtedly affects the rate of diffusion as well as increasing the resistivity. It is therefore considered advisable to renew the electrolyte when it has decreased to certain values as indicated in Chapter III (p. 147).

g. Previous History of the Plates

The previous history of the plates affects the capacity of Edison batteries in much the same way as is found in the case of lead batteries. Sluggishness occurs when the battery is allowed to stand idle for a considerable period of time, or if the battery is operated for a long period of time at rates considerably below normal. This sluggishness is caused by the slow oxidation of the iron in the pockets of the negative plates, which may result in temporary passivity of the iron electrode. The temporary loss in capacity which results from this effect may require several cycles of charge and discharge to overcome. A battery of the Edison type which has stood idle for two months should receive the following treatment in order to restore it to the former capacity. Discharge it at normal rate through a suitable resistance to zero voltage. Then short-circuit it in groups of not more than 5 cells for at least 2 hours. Charge again at the normal rate for not less than 15 hours (type G cells, 10 hours) and discharge at the normal rate again to one volt per cell. Follow this by a charge at the normal rate for not less than the usual time, following which the battery is ready for service. Under normal conditions the capacity of the battery will increase during the first 125 cycles to about 115 per cent of rated capacity and then decrease slowly until the electrolyte is changed, when the capacity should immediately be increased. The useful life is ended when capacity falls below 80 per cent of the rated capacity.

If Edison cells are to be idle for some time, it is advisable that they be discharged to zero voltage and short-circuited in groups of not more than five cells before being placed in storage.

4. PLATE CAPACITIES

In addition to determining the capacity of storage cells, it is sometimes necessary to determine the capacity of the positive and negative plates separately, as a means of locating faults in the operation of the cells. The capacity of the cells of both the acid and alkaline types is normally limited by the capacity of the positive plates. When the capacity of one or more cells in a battery is found to be below normal, and the cause cannot be attributed to internal short circuits or to faulty insulation, the cause of the trouble may often be found in the condition of the active materials. One or the other of the plate groups may be only partially charged, although the battery as a whole is supposed to be fully charged. Inequalities may occur as a result of change in the size of the plates, the loss of active material, or the action of certain impurities. In some lead batteries of poor manufacture, the active material may separate from the grid with the inevitable result that a layer of sulphate forms between the grid and the active material. This layer of sulphate is non-conducting and the active material is prevented from receiving the charging current. The nickel-iron batteries also occasionally show inequalities in the plate capacities which may be due to periods of inactivity or to the materials.

The capacity of the positive and negative plates may be determined separately by the use of a constant auxiliary electrode immersed in the electrolyte of the cell. It is necessary that this electrode should maintain a constant potential with respect to the solution, so that the changes taking place in the positive and negative plates may be measured by the potential differences against this electrode.

a. Auxiliary Electrodes

A number of different electrodes have been proposed, but the one most generally used for the lead-acid batteries has been the cadmium electrode. The hydrogen and the mercurous sulphate electrodes are the most accurate for laboratory purposes, but they are not well adapted to ordinary testing. The cadmium electrode is convenient and, if properly used, sufficiently exact for ordinary purposes.

The Hydrogen Electrode. This gas electrode consists of hydrogen gas absorbed in a layer of platinum black, which may be deposited on one of the noble metals, such as gold or platinum. When the electrode is immersed in a solution containing hydrogen ions, a difference of potential exists between the solution and the electrode. This difference depends on the concentration of the hydrogen ions in the solution. To maintain this potential difference constant at a standard value, the electrode is partly dipped in a solution having a known concentration of the hydrogen ions, such as a normal or a tenth-normal solution, and a stream of purified hydrogen is passed over its upper surface continuously. We cannot measure directly the difference of potential that exists between the electrode and the solution, but we can easily measure the difference in potential between the hydrogen electrode and another electrode with which it is in electrolytic contact. As the basis for an arbitrary scale, the potential of the electrode in a solution that is normal with respect to the hydrogen ions, is sometimes assumed to be zero. With such an electrode as a standard, it is possible to measure the progressive changes that take place in the potential of the plates of an acid storage battery. For the details of the hydrogen electrode and its use, reference should be made to Chapters X to XII of Clark's "Determination of Hydrogen Ions" (1928).

This electrode is adapted to use with the lead-acid batteries, because the solution which is used with it may be sulphuric acid which cannot contaminate the battery electrolyte in any way. The instrument is delicate and requires a potentiometer for measuring the voltage and a supply of hydrogen gas. It is, therefore, not readily portable.

The Mercurous Sulphate Electrode. This electrode is also suitable for use with the lead-acid storage batteries. The cell consists of pure mercury covered with a layer of pure mercurous sulphate and a solution of 1.250 sp. gr. sulphuric acid. This electrode, like the former, is intended for laboratory use only. The constancy of this electrode may be judged from the fact that it is similar to the positive limb of a standard cell.

The Calomel Electrode. In appearance and structure, this electrode is very similar to the mercurous sulphate electrode, but as the solution which it contains is potassium chloride it is adapted for use with the nickel-iron storage batteries. It consists of a layer of pure mercury covered with mercurous chloride, commonly called "calomel," and the solution of potassium chloride of a definite concentration. In using either of these electrodes, the end of the glass tube of the electrode is dipped into the electrolyte of the battery.

The Cadmium Electrode. Cadmium is a metal resembling zinc. It is usually obtained in sticks about $\frac{5}{16}$ inch in diameter, which is a convenient shape for the electrode. Pieces from one to several inches in length are used. The electrodes are prepared for service by keeping them immersed in sulphuric acid solution of about the strength used in the batteries. It is necessary that new electrodes should be in the acid for several days before being used to measure plate potentials.

The sulphuric acid corrodes the surface of the electrode, and an equilibrium state is eventually reached.

The cadmium must be insulated so that it cannot come in contact with the plates of the cell, but at the same time the electrolyte of the cell must have free access to the cadmium. A perforated rubber separator from a storage cell is suitable for making the necessary cover for the electrode. A flexible wire for connection is attached to the cadmium. Readings are taken when the current of the battery is flowing, usually on discharge, but sometimes on charge also. The readings are meaningless if the cell is on open circuit. It is sometimes difficult to obtain accurate cadmium readings on Exide-Ironclad cells because of the interference of the rubber strips on the tops of the plates.

The cadmium electrode is reproducible to about 0.02 volt if precautions are taken. It will remain constant during several hours to within 0.01 volt, but may vary from day to day by 0.02 volt. Amalgamation of the electrode, which is often recommended, does not improve its reliability.[18] In case the electrode surface becomes dry, it must be soaked in the acid for at least one-half hour before being used again. The electrode should be immersed as far as possible in the electrolyte in order that as much as possible of the cadmium surface may be used, to avoid polarization.

The greatest error in the use of the cadmium electrode, as found by Holler and Braham, is due to polarization. The ordinary voltmeter of low voltage range has from 100 to 300 ohms resistance. When such an instrument is used it permits sufficient current to flow to polarize the cadmium electrode. The error thus introduced may amount to 0.1 volt, which would lead to false conclusions about the condition of the negative plates. The polarization of the electrode is proportional to the potential being measured. It is, therefore, many times greater in measuring the potential of the positive plates than the negative plates, because the potential difference of the electrode and the positive plates is about 2 volts, while the difference between the electrode and the negative plates is only one-tenth as great. The error may be avoided entirely by measuring the voltage on a potentiometer or a high-resistance voltmeter. Such voltmeters may be obtained with a resistance of 3000 ohms and a special scale of 0.25—0—2.65 volts. In the absence of such means for measuring the voltage, the best procedure is to measure the potential of the negative plates, and from this and the cell voltage calculate the potential of the positive plates. This is easily done, since the potential of the positive

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[18] "The Cadmium Electrode for Storage Battery Testing," by H. D. Holler and J. M. Braham, *Technologic Paper* 146, Bureau of Standards, 1919.

plates is the algebraic difference of the cell voltage and the potential of the negative plates. Metallic impurities in the electrolyte, if they are electropositive to cadmium, may lead to false indications of the cadmium electrode. Copper, which is often found in small amounts in storage-battery electrolyte, is an example of this class of impurities. The copper will deposit on the cadmium when it is put into the electrolyte and alter its potential. Reliable readings of the plate potentials can only be obtained with care, and it is essential that the conditions of the experiment be understood to avoid drawing false conclusions in some cases. Typical curves, showing the relation of the cadmium electrode to the potential of the plates, are given in the next section. Zinc is sometimes used in place of cadmium. It is not recommended for lead-acid batteries but may be used in the alkaline type.

b. Plate Potentials during Discharge and Charge

Lead-Acid Cells. The voltage of the cell is dependent on the potentials of the positive and negative plates with respect to the solution. Since these potentials may vary independently, there are a number of possible combinations of plate potentials that will give any particular cell voltage. For example, if a group of three cells is measured with a cadmium electrode when each cell has reached its cut-off voltage of 1.8 volts, the following values may be found:

Cell 1,	Positive plate,	2.10	Cell voltage.........	1.80
	Negative plate,	0.30		
Cell 2,	Positive plate,	2.00	Cell voltage.........	1.80
	Negative plate,	0.20		
Cell 3,	Positive plate,	1.95	Cell voltage.........	1.80
	Negative plate,	0.15		

These results require interpretation in the light of the cell's rated capacity and normal performance. The values of the potentials vary with the rate of the discharge, the concentration of the electrolyte, and to a less extent with other factors also. It must be assumed that the voltage drop within the cell, which is equal to the product of the current and the resistance, IR, is negligible. If I is not too large this will be the case, since R is small.

Considering the example given above, the plate potentials of Cell 1 show that the negative plate has reached the limit of its capacity before the positive plate is fully discharged, or in other words, the discharge has been terminated by the negative plate, which is not normal. The positive plate ordinarily limits the capacity of the cell;

therefore, in considering the values for Cell 3, it is necessary to know whether the cell gave its rated capacity before reaching the final voltage 1.80. If it did not, the potential readings indicate the positive plates to be deficient in capacity. Although the plate potentials near the end of the discharge are the most important, it is desirable to take the readings throughout the discharge at frequent intervals and from them to plot curves. The values for Cell 2 are about normal for a cell in good condition.

Figure 68 shows in a graphical way the relation of plate potentials of a cell of the lead-acid type designed for service on an electric vehicle, discharging at its normal rate of 45 amperes. The curves show that the capacity of the negatives exceeds that of the positives. They also show that very satisfactory agreement may be obtained between measurements of the plate potentials obtained by the hydrogen electrode, the mercurous sulphate electrode, and the cadmium electrode. In order to superpose the determinations of these three electrodes, it has been necessary to displace the zero reference line for each by an amount equal to the difference in potential of the several electrodes. When this is done, the observed values fall on the same curves with a high degree of accuracy.

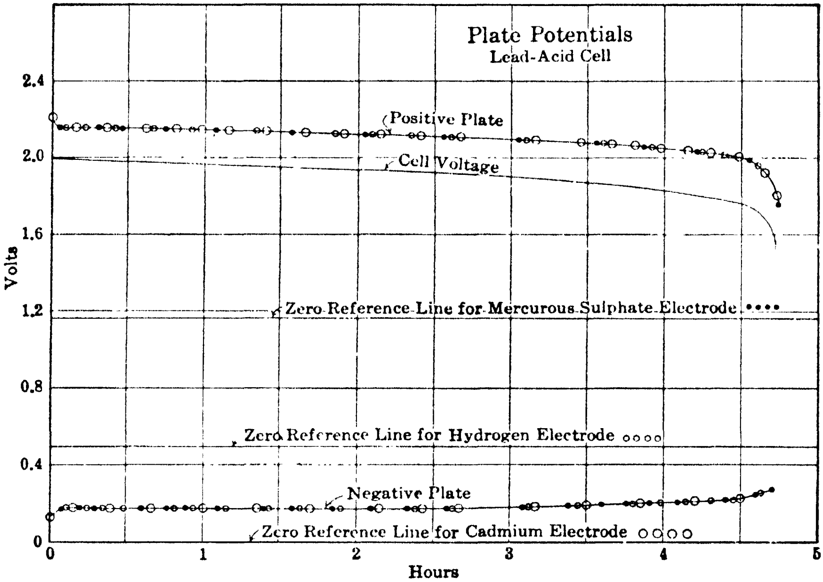


FIG. 68. Comparison of three auxiliary electrodes for measuring potentials of the plates.

When lead cells are charged, the relations of the plate potentials are somewhat different. In particular, the potential of the negative plate should reverse toward the end of charge, the lead sponge becoming negative with respect to the cadmium by about 0.15 volt. When this occurs the voltage of the cell becomes greater than the potential of the positive plate. At the end of charge, the plate potentials are about as follows:

Positive plate,	2.45	Cell voltage.	2.60
Negative plate,	−0.15		

In old cells it is sometimes difficult to make the potential of the negative plate reverse, because of antimony, which accounts for the lower charging voltages of old cells.

Edison Cells. The capacities of the positive and negative plates of the nickel-iron batteries may be determined by the use of auxiliary electrodes, in much the same manner as has been described for the lead-acid batteries. If there is an actual falling off in capacity, it is desirable to determine the weak electrode as a first step in seeking the cause of the trouble. Suitable electrodes are the calomel electrode, for use in the laboratory, or a section of a positive tube taken from an alkaline battery. Connection to this electrode should be made by the same kind of metal as used for the support of the active material, or else the tube should be made long enough to project out of the liquid. The electrode must be insulated so that it cannot touch the plates. For this purpose a perforated rubber sheet is suitable.

Since it was shown, in the section on the theory of the alkaline batteries, that the positives suffer a spontaneous decomposition of the nickel peroxide to a lower state of oxidation after the charge is completed, it is necessary to discharge partially the intermediate electrode (tube) after charging it, in order to bring it to a stable state. In addition to this precaution, it is also desirable to season the electrode by allowing it to stand in the battery electrolyte for a day or two before use.

The decrease in voltage of the Edison cell during discharge is caused almost entirely by the fall of potential of the positive plate, if the cell is in normal condition. The potential of the iron plate falls slightly at the beginning of discharge to a value which remains practically constant throughout the remainder of the discharge. If the active material of the negative plate is sluggish, however, the negative plate may limit the capacity of the battery, as can easily be determined by single potential measurements.

CHAPTER VI

OPERATION

1. METHODS OF CHARGING

Direct current alone can be used for charging If alternating current only is available, it must be converted into direct current. This can be done by means of: (1) synchronous converter, (2) motor-generator, or (3) rectifier.

There are two systems of charging in general use: (1) constant current, and (2) constant potential or constant voltage. This latter method is usually modified slightly by the addition of a fixed resistance of small value in series with the battery in order to limit the starting, or inrush current. Such a system is called a semi-, or modified, constant-potential system.

The positive terminal of the charging source is to be connected to the positive terminal of the battery so that the charging current flows through the battery in the direction opposite to that of the discharge current.

a. Constant Current

In the constant-current system, as the name implies, the current is held constant by means of a rheostat in series with the battery or by controlling the voltage of the source.

The current is maintained at the normal rate by adjusting the rheostat, cutting out or decreasing the resistance as the charge progresses. This increases the voltage impressed on the battery. The value of the current flowing through the battery is dependent upon the difference between its voltage and that impressed on it.

Let the impressed voltage $= E$;
the current flowing at any chosen instant $= I$;
the counter-electromotive force of battery $= E_c$;
the resistance of the battery $= R$.

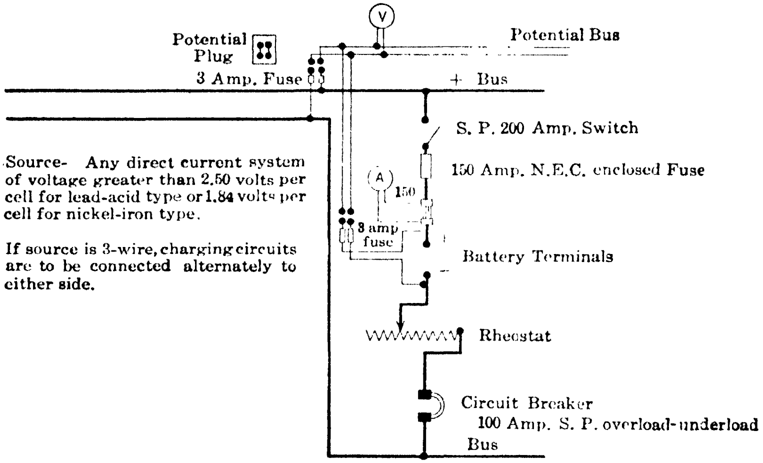
Then:

$$E = E_c + IR$$

whence

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

Therefore, when the voltage of the battery and the charging system are the same, no current will flow; when the voltage of the battery is lower than that of the charging system, current will flow into the battery and charge it; and when the voltage of the battery is higher than that of the charging system, current will flow out of the battery and discharge it. As the voltage of the battery increases gradually with the progress of the charge, it is apparent that the voltage impressed across its terminals must be increased in order to maintain a constant value for the charging current. For batteries of the lead-acid type, the specified current is maintained until all cells are gassing freely and then reduced to a much lower value designated as the finishing rate, at which the charge is continued to the end. The value of the finishing rate is approximately 40 per cent of the starting rate. The ampere-hours required to produce free gassing of a lead battery at the normal starting rate of charge will be approximately 90 per cent of the ampere-hours previously discharged. This applies to batteries which have been fully discharged. Gassing may be expected earlier if the previous discharge was incomplete. When free gassing occurs the current should be cut down to the finishing rate and the charge continued until the battery begins to gas freely again.



Source- Any direct current system of voltage greater than 2.50 volts per cell for lead-acid type or 1.84 volts per cell for nickel-iron type.

If source is 3-wire, charging circuits are to be connected alternately to either side.

FIG. 69. Battery-charging circuit, constant-current method. A, ammeter; V, voltmeter.

Figure 69 is a diagram of connections for a typical constant-current charging circuit.

In order to obtain most efficient results with batteries of the lead-acid type, the voltage of the charging circuit should be approximately

2.5 volts per cell at normal temperatures with current flowing at one-half the value of the finishing rate. When the voltage of the circuit exceeds this value, the maximum resistance of the rheostat must be sufficient to permit of a reduction in voltage to this value. It is desirable that the ampere capacity be sufficient to permit a current value of four or five times the normal, to permit of boosting (see p. 249), provided that the wiring of the charging circuit can safely carry that current. In a new installation, this condition can be provided for readily. In modifying an existing installation, the current capacity of the rheostat need not exceed the safe current-carrying capacity of the circuit.

The value in ohms of the resistance equals

$$\frac{E - (B \times C)}{D}$$

in which E = voltage of system;
B = number of cells in battery;
C = volts per cell, a constant, 2.5 for all types and sizes of lead-acid cells;
D = 50 per cent of finishing rate in amperes for lead batteries.

Example. Assume a 17-plate battery of 24 cells having a normal charging rate of 45 amperes and a finishing rate of 18 amperes; charging circuit 110 volts.

Resistance in ohms equals

$$\frac{110 - (24 \times 2.5)}{9} = 5.6$$

The current capacity equals

$$5 \times 45 = 225 \text{ amperes.}$$

Such a rheostat, unless properly designed, would be large and expensive. The excessive capacity may be reduced by designing the variable portion so that at each step the current-carrying capacity is just within the safe limit. A simpler arrangement, which would provide for the boosting current and also permit of sufficiently good regulation for charging under ordinary conditions, could be made as follows: Ten fixed resistances, each connected as required between the bus and the battery by a single-pole switch, are arranged so that the first three switches would connect in 6 ohms each; the next three, 3 ohms each; and the seventh to the tenth switches, 1.5 ohms each. This rheostat would provide, under the conditions given in the example, a maximum current of 210 amperes, and a minimum current of 8.3 amperes. The maximum kilowatt capacity when all resistances are in parallel would be 10.6 kilowatts, and the minimum capacity 0.4 kilowatt for the smallest charging current.

Edison batteries are charged at the full normal rate, without reduction to a finishing rate. The maximum resistance is required, therefore, at the beginning of charge when the counter-electromotive force of the battery is a minimum, about 1.55 volts per cell. In using the above equation, C is taken as 1.55 and D as the normal charging rate.

b. Final Charging Voltage

The voltage of a storage battery rises during the charging period, reaching a maximum value when charge is complete. What this value will be, depends on (1) the charging current, (2) the temperature, (3) the internal resistance of the cell, and (4) the presence or absence of certain impurities in the electrolyte. Constancy of maximum voltage is a better criterion, therefore, than any particular value when one wishes to determine that charging is complete. There are other means of telling when charge is complete, such as: (1) the specific gravity of the acid electrolyte, (2) the extent and uniformity of the gassing, (3) plate potentials, and (4) measured input in ampere-hours. Figure 70, from a paper by Woodbridge,[1] shows the variation of final voltage of the acid cells with temperature and rate of charge. These curves apply to a particular type of cell, but they illustrate the principles involved and show the necessity of temperature compensation if voltage relays

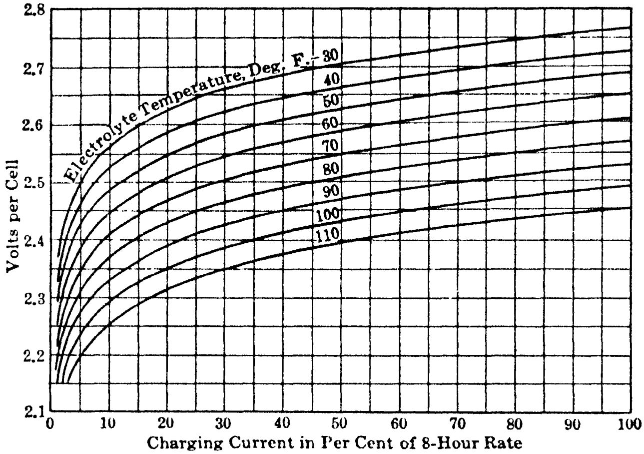


FIG. 70. Final charging voltage at various rates and temperatures, lead-acid batteries.

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[1] *Trans. Am. Inst. Elec. Eng.*, 54, p. 516, 1935.

are employed to terminate the charge of a battery of any considerable number of cells.

The effect of temperature on the charging voltage of alkaline storage batteries (Edison type) is given in Table XLV.

TABLE XLV

EFFECT OF TEMPERATURE ON CHARGING VOLTAGE OF EDISON BATTERIES AT NORMAL RATE OF CHARGE

Temperature		Average Voltage, in Volts	Maximum (Final) Voltage, in Volts
°C.	°F.		
2	35	1.88	1.94
13	55	1.81	1.92
24	75	1.76	1.88
35	95	1.70	1.85
46	115	1 67	1 77

c. Ampere-Hour Law

Because the lead-acid storage battery in a normal discharged state can absorb electrical energy very rapidly without overheating or excessive gassing, it is possible to begin charging at a high rate of current, usually much in excess of the so-called normal or starting rate of charge. In fact, the term "starting rate" for lead-acid batteries is rapidly disappearing from use, but finishing rates are a matter of importance. The practical limitations to the rate at which a battery can be charged are (1) temperature rise to excessive values and (2) excessive gassing. These are matters of judgment and a more definite answer is needed if we are to learn what is the shortest time in which a lead-acid battery can be charged. Woodbridge[2] says: "As a result of numerous tests, it has been found that if the charging rate in amperes is kept below a value equal to the number of ampere-hours then out of the battery the conditions as to gassing and temperature will be met." That is, if 200 ampere-hours have been discharged, the charging rate may begin at anything less than 200 amperes, but obviously this must be progressively reduced so that the charging current in amperes is always less than the number of ampere-hours which the battery lacks to complete 100 per cent charge. This is known as the ampere-hour law.

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[2] *Trans. Am. Inst. Elec. Eng.*, 54, p. 519, 1935.

The older method of constant-current charging in two steps, beginning with a "starting rate" and ending with a "finishing rate" complied substantially with requirements of the ampere-hour law but failed to make use of possibilities for most rapid charging. If charging is done at successively lower rates according to the ampere-hour law, the process is sometimes referred to as "step method of charging." Practical limitations will dictate how many steps there shall be, but theoretically for an infinite number of steps, the charging current follows an exponential law expressed by the equation, $I = A\epsilon^{-t}$, where I is the current in amperes, t the time in hours and A the number of ampere-hours out of the battery when charging begins, that is, when $t = 0$. Figure 71 from Woodbridge's paper shows that charging a battery in accordance with this law restores 90 per cent of the ampere-hours previously withdrawn in 2 hours and 20 minutes. Practical tests reported by him show that the minimum time for a complete charge, including 15 per cent overcharge, is about 4 hours.

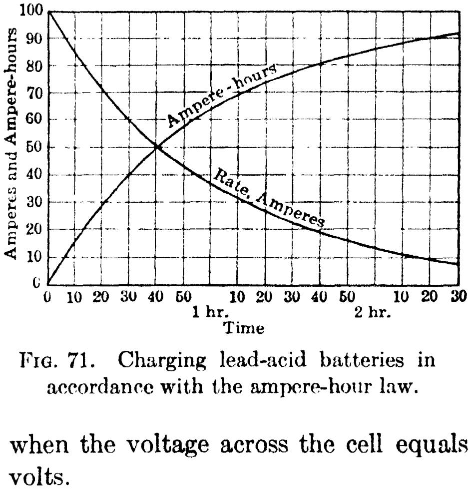

FIG. 71. Charging lead-acid batteries in accordance with the ampere-hour law.

Another method of controlling step charging is to reduce the current at intervals when the voltage across the cell equals a predetermined value as 2.35 volts.

For batteries of the nickel-iron type, charging at constant current is carried on at the normal rate for the full period of time required, normally 7 hours for batteries having plates of the A type or 4¾ hours for plates of the G type, or until the voltage becomes constant, at a value usually between 1.8 and 1.9 volts per cell, the exact value depending on the temperature. As the specific gravity of the electrolyte of batteries of this type remains constant during charge and discharge, the only indications of complete charge are the condition of voltage as stated above and the length of time taken for the charge. If the battery shows a temperature exceeding 46° C. (115° F.), it should be cut off immediately and allowed to cool.

d. Constant Potential

In the constant-potential or constant-voltage method, the voltage is maintained at a constant fixed value per cell. The value of the initial, or starting, current of a completely discharged battery when first put on charge is much in excess of the so-called normal rate. During the charge, as the voltage of the battery gradually rises, the current falls off to a value much below that of the normal rate, and at the end of the charge is below that of the finishing rate of the constant-current system. The average value of the current is about equal to that of the normal rate.

For batteries of the lead-acid type, the maximum voltage for unmodified constant-potential charging should not exceed 2.35 volts per cell, and the minimum should not be less than 2.25 volts per cell. The average should be approximately 2.3 volts per cell at the terminals of the battery.

With the average voltage thus established at approximately 2.3 volts per cell, a battery in any state of discharge may be put on charge and it will automatically receive the proper charge without reaching the free gassing point or excessive temperature. Caution is necessary, however, as slight variations in the line voltage produce large variations in the charging current. The "modified" constant-potential method of charging, described below, is a safer method.

e. Modified Constant Potential

It usually happens that the charging unit or generator is of relatively small capacity, compared with the very large rate of the charging current at the beginning of an unmodified constant-potential charge. In such a case it is necessary to limit the initial or starting current, and to accomplish this a fixed resistance of small value is placed in series with the battery. This is known as a semi-constant-potential or a modified constant-potential system.

In practice, when using the modified constant-potential method, the voltage at the bus may be kept constant at any value from 2.5 volts to 3.0 volts per cell, although 2.60 seems to be the most generally suitable value for lead-acid cells and 2.00 volts per cell for the nickel-iron type.

Figure 72 is a diagram of connections for such a system with a three-wire supply. For a two-wire supply the connections are the same as shown on this diagram for circuit B, or between the two outside wires.

Figure 73 [3] is a series of curves from which the value of fixed resistance and the initial current of a modified constant-potential charging system may be obtained.

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[3] Reference should be made to *Standard Specifications of Automatic Battery Charging Motor-generators and Panels,* adopted by The Industrial Truck Statistical Association, March 7, 1939.

These curves relate primarily to Ironclad cells, having a capacity of 100 ampere-hours at the 6-hour rate. Curve A shows maximum values of bus voltage per cell for types MVM, KXK, ML and ME. Similarly, Curve B applies to types TLM, MEH and FLM.

The horizontal scale of Fig. 73 shows the "bus volts per cell"; that is, the total available voltage at the bus divided by the number of cells in the battery. The vertical scale for the lower set of curves shows values of the modifying resistances to be used per cell for specified bus voltages. As the cell to which these curves apply has an assumed capacity of 100 ampere-hours, the proper values for cells of other capacities are inversely proportional to their capacities. When the proper external resistance per cell has been calculated, it must be multiplied by the number of cells in the battery. The vertical scale for the upper set of curves gives values of the initial charging current, and, when applied to batteries of other capacity, the current will be in proportion to cell capacity.

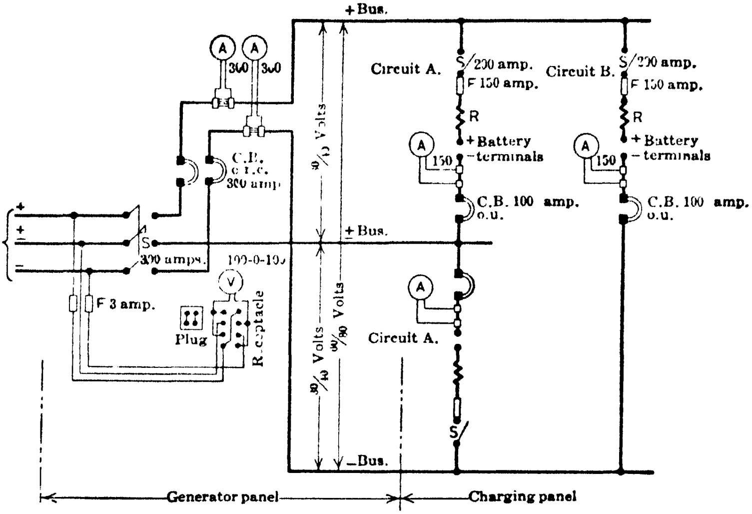

FIG. 72. Battery-charging circuit, modified constant-potential method. A, ammeter; V, voltmeter.

Values of initial current shown in Fig. 73 are subject to changes in the bus voltage for which a tolerance of ±3 per cent is usually specified. The initial current will be higher than indicated by the curves when the bus voltage is above normal and to allow for this the rating of panel wiring and equipment should be based on current corresponding to a bus voltage of 103 per cent of normal. This is covered in the specifications referred to above.

In using the curves, some variation in the time for a complete charge must be expected because of variations in temperature, type and age of the battery, and time it has stood idle since the last discharge. When applied to other types of cells, the values are only approximate.

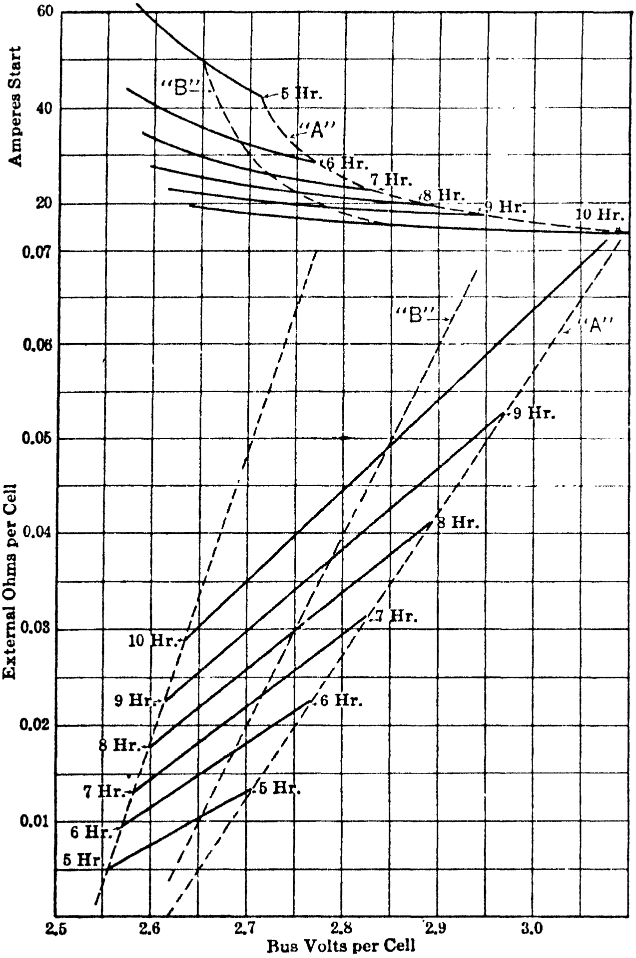

FIG. 73. Modified constant-potential charging data.

When it is desired to make the charging system automatic, an ampere-hour meter or voltage relay affords the most reliable means for terminating the charge. In this connection a contactor must be provided to open and close the battery circuit and thus avoid arcing at the contact of the ampere-hour meter. The meter is to be provided with a zero contact, a resetting device, and a fixed red hand set at the discharge limit. It should be adjusted to run slower on charge than on discharge. The meter can be connected in the battery circuit during discharge as well as during charge. For motive-power services, the newer installations usually provide the ampere-hour meter on the charging panel and the extent of the previous discharge must be determined by specific gravity readings on lead batteries or by the charge test fork for nickel-iron cells.

For lead batteries, the higher the bus voltage the greater will be the loss in the resistance, with a decrease in efficiency and an increase in the length of time required for the charge. On the other hand, if the bus voltage is but little higher than that of the battery, the charging current will become more or less unstable and subject to considerable variation with changes in temperature of the battery and slight changes in the bus voltage.

When the time available for charging is limited, or when efficiency is of considerable importance, a bus voltage of approximately 2.6 volts per cell is found to be generally satisfactory. If the supply voltage is in excess of a value for which the charge can be completed in a specified time, counter cells may be used to reduce the voltage at the terminals of the battery to the proper value.

As the bus voltage and resistance are increased for the same number of cells in the battery, the charging current becomes more nearly constant throughout the charge, thus approaching the constant-current method.

A more modern method of decreasing the time necessary for completing the charge for lead cells when the bus voltage is too high to permit this to be accomplished in the time available is to resort to "two-step constant-potential charging." The first step, using a low fixed resistance, permits high charging rates during the early part of the charge when the battery can absorb energy very rapidly, and a higher resistance for the second step reduces the charging current to safe rates during the latter part of the charge. There is no need for the charging rate at the end to be lower than the finishing rate. The change from the first to second step is accomplished automatically by an ampere-hour meter with auxiliary contact or by a voltage relay.

When an ampere-hour meter is used, the position of the auxiliary contact is the determining factor in choosing the proper value of the external fixed resistance, because the current must be so chosen that it will not exceed both the finishing rate and the requirements of the ampere-hour law at any time prior to the change to the lower rate. The low rate of charge, on the other hand, is determined by the finishing rate for the particular battery, regardless of the ampere-hour meter. The auxiliary contact on the meter will be at a certain number of ampere-hours on the scale. If this is 80 and the capacity of the battery is 320 ampere-hours, the ratio is 25 per cent. With this percentage

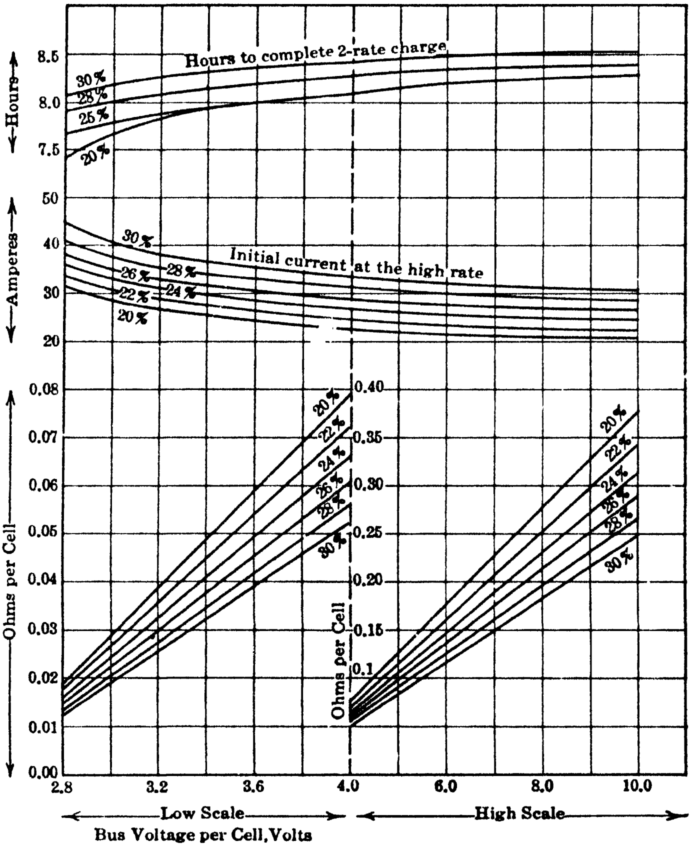

FIG. 74. Two-step constant-potential charging data, ampere-hour meter control.

and the bus voltage in mind the value of the fixed resistance is selected from the lower set of curves of Fig. 74. These apply to a battery of 100 ampere-hour capacity and are to be interpreted in the same way as for curves in Fig. 73. The middle set of curves gives the initial current at the high rate, and the top set of curves gives the time required to complete charge.

Equipment necessary to change the rate of charge includes a contactor which shunts out part of the resistance in series with the battery during the high-rate portion of the charge. The auxiliary contact on the meter is connected to the closing coil of the contactor and for all positions of the meter's pointer below this auxiliary contact the contactor is closed. After charge is completed, the circuit may be opened or a trickle charge provided.

When a voltage relay is used its coil is connected across the battery terminals and is adjusted to operate the relay at the point where the battery voltage begins to rise rather rapidly and gassing increases. The battery is nearly, but not fully, charged at this point. Charge is completed at a lower rate, or transferred to a trickle-charge circuit.

For batteries of the nickel-iron type, the impressed voltage should not be less than 1.70 volts per cell. As in the case of the lead-acid type, the voltage at the charging panel must be slightly higher than this value. In practice this can be 1.84 volts or more, with best conditions usually about 2.00 volts per cell. When batteries of this type are to be charged from a modified constant-potential system, the resistance *R* is found in Table XLVI.

f. Equalizing Charge

Once a week, a lead battery in daily use for operating a truck or tractor should be given an overcharge known as an "equalizing charge." For this purpose the charge is to be continued from the normal end at a rate not higher than the finishing rate, and lower if practicable, until all cells are gassing freely and uniformly, and until three consecutive readings of the specific gravity and voltage taken at half-hour intervals show no increase. If the battery shows a temperature exceeding 43° C. (110° F.) it should be cut off immediately and allowed to cool. Batteries not in daily use require an equalizing charge less frequently.

Once every 3 or 4 months, the voltage and gravity readings of each cell should be recorded. These will serve as an indication of trouble within the cells, such as sulphation or leakage, if there is a progressive change of the gravity readings.

The gravity of the individual cells should be adjusted to the proper value when the battery is first put in service or when it has been necessary to add electrolyte to any cell to replace electrolyte which has been spilled or otherwise lost. This should be done at the end of the equalizing charge. If the gravity of the cell is too high, a portion of the electrolyte may be withdrawn with the hydrometer syringe and replaced by distilled water. Similarly, the gravity may be increased by replacing the portion drawn off by electrolyte of not over 1.400 sp. gr. Before

TABLE XLVI

MODIFIED CONSTANT-POTENTIAL CHARGING OF EDISON BATTERIES

(The fixed resistance to be placed in series with the battery is the product of the number of cells in the battery and the ohms per cell which are required for the type and the available bus voltage.)

Bus volts		1.84	1.90	2.00	2.10	2.20	2.30
Initial rate, % of normal		165	155	140	128	124	120
Final rate, % of normal		65	70	78	84	86	88
Type of Cell	Charge, Normal Rate (amps.)	Fixed Resistances, Ohms per Cell, for Modified Constant-Potential Charge					
B1, L20	3.75	0.04000	0.05600	0.08270	0.10933	0.13600	0 16267
B2, L40	7.50	.02000	.02800	.04133	.05467	.06800	.08133
B4	15.00	.01000	.01400	.02067	02733	.03400	04067
B6, A3	22.50	.00667	.00933	.01378	.01822	.02267	02711
A4, G4	30.00	.00500	.00700	01033	.01367	.01700	02033
A5, G5	37.50	.00400	.00560	.00827	.01093	.01360	.01627
A6, C4, G6	45.00	.00333	.00467	.00689	.00911	.01133	.01356
A7, G7	52.50	.00286	.00400	.00590	.00781	00971	.01162
C5	56.25	.00267	.00373	.00551	.00729	.00907	.01084
A8	60 00	.00250	.00350	.00517	.00683	.00850	.01017
C6, G9	67.50	.00222	.00311	.00459	.00607	.00756	.00904
A10	75.00	.00200	.00280	00413	.00547	.00680	.00813
C7	78.75	.00190	.00267	.00394	.00521	.00648	.00775
G11	82.50	.00182	.00255	.00376	.00497	.00618	.00739
A12, C8, D6	90.00	.00167	.00233	.00344	.00456	00567	.00678
A14, G14	105.00	.00143	.00200	.00295	.00390	.00486	.00581
C10	112.50	.00133	.00187	00276	.00364	.00453	.00542
A16, D8	120.00	.00125	.00175	.00258	.00342	.00425	.00508
C12, G18	135.00	00111	.00156	.00230	.00304	.00378	.00452
A20, D10	150.00	.00100	.00140	.00206	.00273	.00340	.00406
G22	165.00	.00091	.00127	.00188	.00248	.00309	.00370
A24, D12	180.00	.00083	.00116	.00172	.00228	.00283	.00339

the adjustment is considered complete, the equalizing charge should be continued to mix the electrolyte of the cell. The final value is shown by several consecutive constant readings at 15-minute intervals. The gravity should be adjusted to within 5 points, corrected for temperature, of the proper value.

Equalizing charges are not required for Edison batteries, if they are given the proper amount of excess charge over previous discharge on each cycle. When the specific gravity of the electrolyte for these has fallen to the limits set in Chapter III the electrolyte should be renewed.

g. Boosting

Under certain conditions, the ampere-hour capacity of the battery may be insufficient for the day's work. In such a case, charging at a high rate of current for a short time may be resorted to. Such a charge is known as "boosting" and is usually given the battery during the noon hour. Figure 75 shows the value of current, with time, to be used for boosting batteries of lead-acid type.

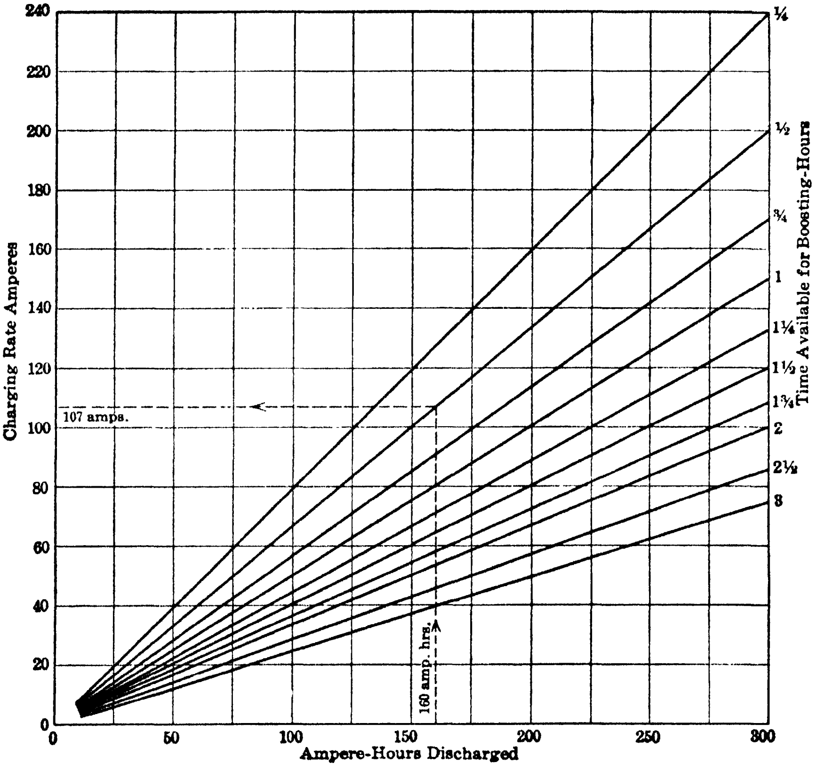

Fig. 75. Maximum rates for boosting lead-acid cells of any capacity.

Example: If 160 ampere-hours have been discharged and one-half hour is available for boosting, follow the dash lines in the direction of the arrows. The proper value of the current to use is found to be 107 amperes.

Edison batteries of the nickel-iron type may be boosted, provided the temperature of the inside cells does not exceed 46° C. (115° F.). The rates of charge recommended by the manufacturer are:

5 minutes at 5 times normal rate.
15 minutes at 4 times normal rate.
30 minutes at 3 times normal rate.
60 minutes at 2 times normal rate.

Frothing at the filler opening is an indication that the boosting has been carried too far.

With the constant-current system, the rheostat is adjusted in order to maintain the current at the constant value. When charging is to be done by the modified constant-potential method in a given number of hours, reference should be made to Fig. 73 or Table XLVI.

h. Trickle Charge

A trickle charge, as the name implies, is a continuous charge at a low rate approximately equal to the internal losses of the battery and suitable to maintain the battery in a fully charged condition. Low-rate charges are satisfactory for lead batteries provided the total amount of charge received by the battery is sufficient to cover the local action. This method of charging is better adapted to plates of the pasted type. Several applications have been made of trickle charging. One of them is to put lead batteries in so-called "wet" storage. At regular intervals, the filling plugs should be removed and water added to the cells if necessary. At the beginning of the charge the specific gravity of each cell should be read and recorded, and this operation should be repeated at intervals. The charging current may then be reduced to the lowest limit which will keep the specific gravity constant.

The term trickle charge is also applied to very low rates of charge which are sufficient not only to compensate for the internal losses of the battery but to restore intermittent discharges of small amount.

Trickle charging may also be applied to batteries of the Edison type. The recommended rate, depending on the nature of the application, may vary from 0.125 to 0.25 ampere per positive plate of the A type and proportionately more or less for larger or smaller plates.

The actual value of the trickle charge rate employed in any particular case depends on the discharge rates to which the battery is subject. Higher trickle charge rates are employed when discharges are at the normal 5-hour rate or above and the lower limit specified is applicable to batteries discharging at relatively low rates. If properly done, the capacity of a battery for discharge may be increased by such a procedure.

In addition to the trickle charge rates specified above, charging current must be provided to compensate for intermittent discharges which occur under service conditions. An excess of 10 per cent over the average discharge should be added for this purpose. Allen's[4] empirical formula for calculating the proper trickle charge rate for any type of Edison battery, based on the higher limit mentioned previously, is as follows:

$$I = \frac{(C \times 0.16) + (D \times 1.10)}{24 - H}$$

In this equation I is the current in amperes, C the rated ampere-hour capacity of the battery, D the average number of ampere-hours discharged per day, and H the aggregate time in hours of discharge. It should be noted however that H must be small in comparison with 24, the number of hours in a day. Otherwise, the charging rates which would be calculated by the formula can no longer be regarded as trickle charging rates.

i. The Conditions for Floating

A battery is said to float upon a charging line when the voltage of the charging line is slightly greater than the open-circuit voltage of the battery (see Table XXXVI), and opposite in polarity. For the ordinary type of lead cell, the voltage at which the cell will float is about $2\frac{1}{10}$ volts, but there is a range of approximately 0.1 volt from 2.05 to 2.15 volts, between which the charging or discharging current from the battery is extremely small. When a floating battery is connected to a line of which the voltage is approximately equal to the open-circuit voltage of the battery, the battery will charge or discharge according as the fluctuations of voltage of the line rise above or fall below the battery voltage.

A battery which is properly floated upon a power line will automatically take care of the power required for a fluctuating load, and the battery will be maintained in the fully charged condition. Railway signal batteries illustrate one form of the floating battery. The voltage provided by the rectifiers is approximately 2.15 volts per cell. By maintaining the voltage at this figure, the battery is on charge at a very low rate, but when required to furnish power for the operation of signals or track switches the battery discharges through a circuit in parallel with the charging circuit.

Storage batteries are commonly installed in power stations and substations to insure an uninterrupted supply of current for the operation of control and protective equipment as well as for emergency lighting. Such batteries often consist of 60 cells. The charging of the batteries

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[4] *Electrical Engineers' Handbook*, Pender and Del Mar, IV, p. 7-31, 1936.

is accomplished by floating them on a suitable source of direct current, such as a small motor-generator set whose generator is of the shunt type with a decided drooping characteristic. This generator normally carries the steady load and keeps the battery charged, but when a heavy demand occurs practically the entire load is taken by the battery. The maintenance of the proper floating voltage is an important factor in determining the life of the battery. The recommended average for this service is 2.15 volts with maximum and minimum limits of 2.20 and 2.10 volts, respectively, for batteries containing electrolyte of 1.215 sp. gr. If the battery should become discharged, recharging may be accomplished by raising the generator voltage to 140 volts, or 2.33 volts per cell. Such batteries have very little work to do. They are fully charged, ready for instant service, have a long life and are maintained economically. If the specific gravity of the electrolyte is in the range 1.250 to 1.280, the average floating voltage should be 0.05 volt higher.

While nickel-iron batteries have a somewhat larger differential in voltage between charge and discharge, they are applied to floating services such as signal operations, alarm systems and circuit-breaker control.

2. CHARGING AND DISCHARGING LEAD BATTERIES

a. Discharge

Voltage Characteristics. When a storage battery of the lead type begins to discharge, there is an initial drop in voltage, which may be attributed in part to the ohmic resistance of the battery and in part to the sudden decrease in concentration of the acid in the pores of the plates, which reduces the potential of the plates. This abrupt drop in voltage is often followed by an almost equally abrupt rise in voltage. Such an effect may be seen at the beginning of the discharge curve in Fig. 76. No designation in English has been applied to this peculiar phenomenon, but in French it is referred to as the *coup de fouet* (stroke of a whip). This effect which has been ascribed to various causes, is not always present. After the sudden decrease in concentration of the acid when discharge begins, the diffusion process is started and the stronger acid from outside the plates, diffusing into the pores of the plates, tends to restore the voltage.

In addition to this effect, there may also be a gradual rise in voltage during the early stages of discharge, particularly if the battery has stood for some days since being charged. This is attributed in part to the decreased resistance of electrolyte as the temperature is raised and also to the decrease in concentration within the range 1.300 down to 1.225, for which the resistivity is a minimum. During the greater part of the discharge, the voltage falls slowly from a value approximately equal to the open-circuit voltage to about 1.8 volts. The decrease in voltage is caused by a decrease in the plate potentials, as the rate of diffusion of the electrolyte fails to keep pace with the consumption of acid within the pores of the plates; to a less extent it may be attributed also to the increasing resistivity of the electrolyte as the concentration falls below a specific gravity of 1.225. When near the end of the discharge, the curve shows a more abrupt drop; this point is known as the knee of the curve. It signifies that the complete exhaustion of the cell is approaching. The knee of the curve is less distinct in discharges at high rates than at low rates.

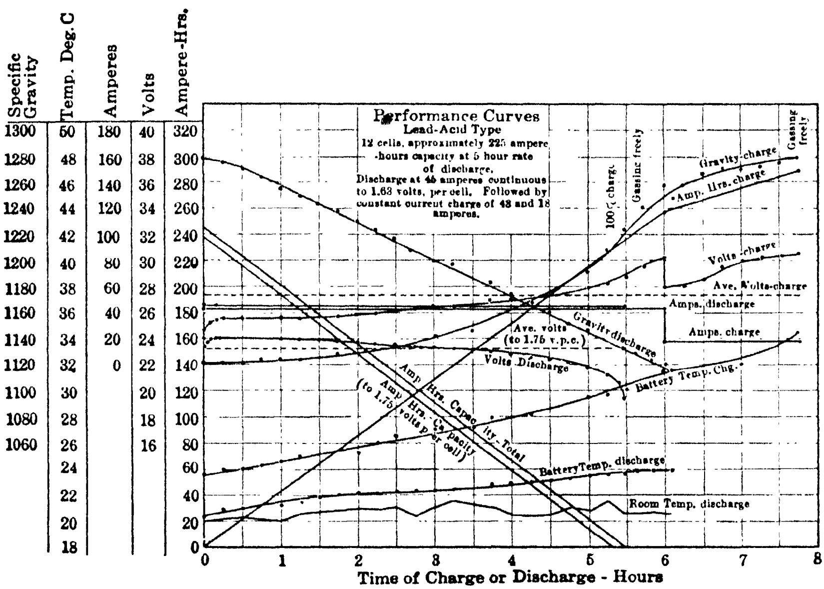

Fig. 76. Curves of discharge of a lead-acid battery, followed by charge by the constant current method. Cells were of the motive-power type.

The average voltage during the period of the discharge is the factor which is of importance in determining the amount of energy delivered by the battery. The average voltage is determined from the time integral of the voltage curve from the beginning to the end of discharge. The average voltage varies with the rate at which the discharge takes place, with the type and construction of the cells, and also with the final voltage. Under normal conditions for motive-power batteries of the lead-acid type, the average voltages are approximately as follows:

Multiple of Normal Rate	Volts per Cell
½	1.94 to 2.00
1	1.92 to 1.98
2	1.87 to 1.94
3	1.83 to 1.90
5	1.75 to 1.83
10	1.53 to 1.64

Wide separation of the plates, abundance of electrolyte, and relatively low rates of discharge afford discharge curves with the most nearly flat characteristic.

Temperature. The temperature of batteries of the lead-acid type rises slowly during discharge, but the effect is less than is observed when the same batteries are on charge at the same current. The reason for this has been pointed out in Chapter IV, where it was shown that there are two heat effects, one caused by the ohmic resistance and varying as the square of the current, and the other a reversible heat effect varying directly as the current. These two heat effects are opposed during discharge. The one resulting from the ohmic resistance of the cell generally overbalances the second heat effect, so that the temperature of the battery rises. Since the irreversible heat effect varies as the square of the current, the temperature rise will be considerably greater when the rate of discharge is increased.

Specific Gravity. The specific gravity of the electrolyte falls almost linearly during discharge, provided the discharge current is constant. The specific gravity of the electrolyte, therefore, affords a valuable means of checking the state of charge of the battery. If readings are taken for a time after the discharge has been stopped, it will be observed that there is a continued fall in specific gravity until the concentration of the dilute electrolyte in the pores of the plates has been equalized with the more concentrated acid outside.

b. Charge by Constant-Current Method

Voltage Characteristics. When a storage battery is first put on charge, a sharp rise in the terminal voltage of the cell is noticed. This is probably to be ascribed to the sudden increase in concentration of the electrolyte as sulphuric acid is liberated in the pores of both the positive and negative plates. The diffusion processes begin and check the rise in voltage. Equilibrium is reached when the rate of diffusion of the concentrated acid from within the pores keeps pace with its formation. There is sometimes a slight drop in voltage after the first few minutes, which gives to the curve a shape somewhat similar to the *coup de fouet*, noticed in connection with the voltage characteristics on discharge, but in the reverse direction. The cause for this drop is not known with certainty but has been ascribed to the breaking down of a continuous film of sulphate with consequent decrease in the internal resistance of the cell.

Following this point, the curve representing the terminal voltage of the cell continues to rise gradually to the point which is designated as 100 per cent charge in Fig. 76. By 100 per cent charge is meant a charge equal in ampere-hours to the preceding discharge. In Fig. 76 the 100 per cent point is found at 5¾ hours. The increase in the potential at the cell terminals during this period is ascribed to the increasing concentration of the acid within the cell. It cannot be accounted for on the ground of internal resistance, since it is well known that the internal resistance of a cell decreases during the charging period.

At the time the 100 per cent charging point is reached, or slightly before, a more abrupt rise in the voltage is noted. This is due only in part to the increasing concentration of the acid within the pores. At this time, most of the sulphate which is readily available for the action of the current has been broken down and the concentration of lead ions in the electrolyte has diminished. A consideration of the Nernst equation, relating the potentials of the plates to the ionic concentrations in the electrolyte, shows that as the number of divalent lead ions is diminished the voltage of the battery is increased. Therefore, when the lead sulphate on the plates becomes exhausted and the lead sulphate ions in the electrolyte are diminished, the plate potential will rise to a point at which decomposition of water will take place. This is made evident by the formation of gas, including both oxygen and hydrogen, which escapes freely from the cell during the latter part of the charge. The gassing becomes free, as Fig. 76 indicates, at the end of about six hours. If the charging rate is reduced at this time, the voltage of the battery is lowered and the gassing is decreased.

It is common practice in charging a storage battery by the constant-current method, to decrease the charging current to what is called the finishing rate near the end of the charge. The object of this is to avoid the hard gassing which would otherwise take place. The best rule is to reduce the starting rate to the finishing rate when the battery begins to gas freely. At this time the battery lacks about 20 per cent of being fully charged, depending on the temperature, rate of charge and other conditions. In Fig. 76 the reduction was made about half an hour after this point was reached.

The voltage at the terminals of the cell begins to rise again after dropping with the reduction in charging rate as shown in Fig. 76. It finally reaches about 2.5 to 2.6 volts per cell, at which time the battery is again gassing freely.

Gassing. The point at which gassing of a storage battery begins while on charge is determined by the voltage, but the quantity of gas depends on the portion of current which is not absorbed by the battery. The gases liberated are oxygen, evolved at the positive plates during charge, and hydrogen, evolved at the negative plates. It is not uncommon, however, for one plate to begin gassing before the other, and therefore the gas liberated from a storage cell, in the early stages at least, does not always correspond to the proportions of oxygen and hydrogen which form water. The gassing begins when the voltage at the terminals of the battery has reached about 2.3 volts per cell. The following table, obtained from a test, shows that during the early stages the gas is almost equal parts of oxygen and hydrogen; but as the charge approaches the end, when the voltage has risen to 2.5 per cell, the gas has a composition of two parts hydrogen to one of oxygen.

TABLE XLVII

DATA ON GASSING

(Per cent by volume.)

Cell Voltage, Volts	Gassing	Composition	
		Hydrogen, Per Cent	Oxygen, Per Cent
2.20	None	..	..
2.30	Slight	52	47
2.40	Normal	60	38
2.50	Hard	67	33

Since oxygen and hydrogen unite with explosive violence to form water, it is necessary that certain precautions be taken to avoid accident. Open flames of any kind in a storage-battery room are not permissible, and suitable ventilation should be provided to prevent an accumulation of hydrogen. Four per cent of hydrogen in the atmosphere is dangerous, and the concentration should be kept much below this figure. In the latter part of this chapter is an illustration, Fig. 113, which shows the result of an explosion of the gas in a storage cell.

Other gases are not to be expected under normal conditions, but may be liberated if certain impurities are present. Haring and Compton[5] detected small amounts of stibine in gases liberated during overcharge. Carbon dioxide may be liberated, if organic matter is being oxidized. Chlorine in relatively large amounts may be liberated, if sea water enters the battery. This comes from the positive plates which are discharged by the action of the sodium chloride with the formation of lead sulphate and sodium sulphate.

Storage cells of the lead-acid type do not gas during discharge or when standing idle under ordinary conditions. There is, however, often a slight liberation of hydrogen from the negative plates because of local action which takes place when the cell is idle. It should always be presumed, therefore, that hydrogen is present within the space over the electrolyte, and precautions, necessary to avoid explosions as when the cell is on charge, should be observed at all times. It is particularly dangerous to use a lighted match over the vent of a cell to see how high the liquid stands.

Specific Gravity. The changes in specific gravity of the electrolyte during the charging period are shown by a curve in Fig. 76. The most noticeable fact concerning this curve is the very slow rise during the first two hours. After this time the curve rises more rapidly, following in an approximate way the curve representing the ampere-hours of input. Toward the end of the charging period, the curve of specific gravity rises much more slowly, practically following the decrease in charging rate. One may ask why the specific gravity shows such a slow rise during the first few hours, although the fall in specific gravity when the same cell is on discharge is well marked during that period. The reason is that the concentrated acid, as it is liberated from the pores of the plates, falls to the bottom of the cell. The rapid rise when the cell begins to gas freely is caused by the bubbles of gas stirring up the electrolyte. In the case of the discharge, the more dilute electrolyte rises to the top. In a cell made as compactly as the motive-power type, for which performance curves are shown in Fig. 76, it is not possible for the acid to circulate throughout the cell as rapidly as would be the case in a cell of the stationary type with wider separation between the plates.

Temperature. Referring again to Fig. 76, the temperature of the battery is seen to rise continuously throughout the period of charging, and it should be noted that the increase in temperature during the charging period is considerably greater than during the discharge of the same cell at the same rate of current. This is explained by the fact that heat generated because of the internal resistance of the cell and

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[5] *Trans. Electrochem. Soc.*, 68, p. 283, 1935.

the reversible heat effect, which was discussed in Chapter IV are both in the same direction. The reversible heat effect in this case is exothermic, whereas on discharge it is endothermic.

c. Charge by Modified Constant-Potential Method

Tapering Current. In addition to charging batteries by the constant-current method, which has been described in the preceding section, it is possible to charge them by the modified constant-potential, or tapering-current, method. Characteristic curves are shown in Fig. 77.

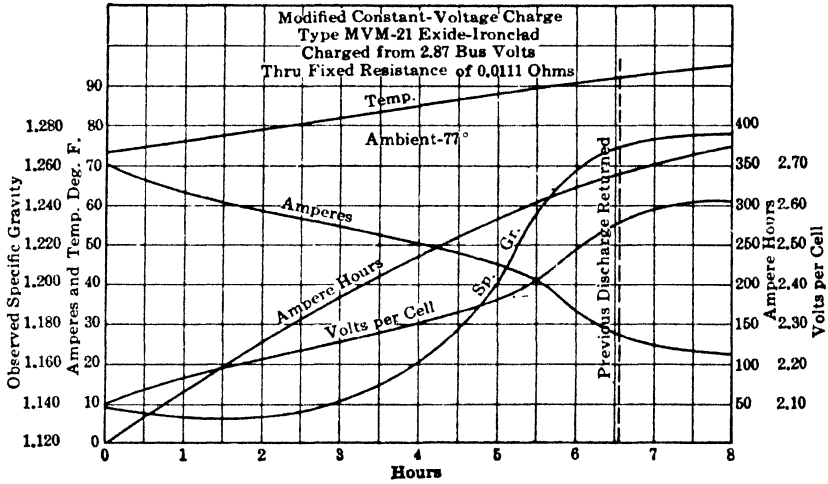

FIG. 77. Modified constant-potential charge of a lead-acid battery.

d. Comparison of the Constant-Current and Constant-Potential Methods of Charging

In Fig. 78, which is taken from an article by Woodbridge,[6] a comparison of the rate of charging by the constant-current and constant-potential methods and its relation to the state of charge and the gas liberated is shown. It has been stated above that charging takes place more rapidly by the constant-potential method during the early stages of the charge, and Fig. 78 applies particularly to a comparison of the two methods when the charge is nearly complete. A storage battery of 300 ampere-hour capacity, fully charged, was discharged to the extent of 60 ampere-hours and then put on charge by the con-

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[6] *Railway Electrical Engineer*, 9, p. 6, 1918.

stant-current and constant-potential methods successively. The curves show that the rate of charging by the constant-potential method is slightly greater than by the constant-current method, but that the curve representing the state of charge by the constant-current method lies slightly above the state of charge by the constant-potential method, since the latter approaches full charge asymptotically. When the curve representing the state of charge by the constant-current method begins to deviate from the ampere-hours actually put in by this method, it will be noted that a marked rise in the curve representing the ampere-hours wasted in gassing begins, and that this curve becomes parallel to the curve of ampere-hours input. The physical significance of the parallelism of these curves is that all of the ampere-hours supplied to the battery are eventually used in the decomposition of water. The curve representing the ampere-hours wasted in gassing by the constant-potential method shows that only a negligible part of the quantity of electricity passing through the cell is expended in this way. These curves also indicate that the constant-potential method of charging provides the maximum current input which the battery can absorb without the waste of energy in producing gas.

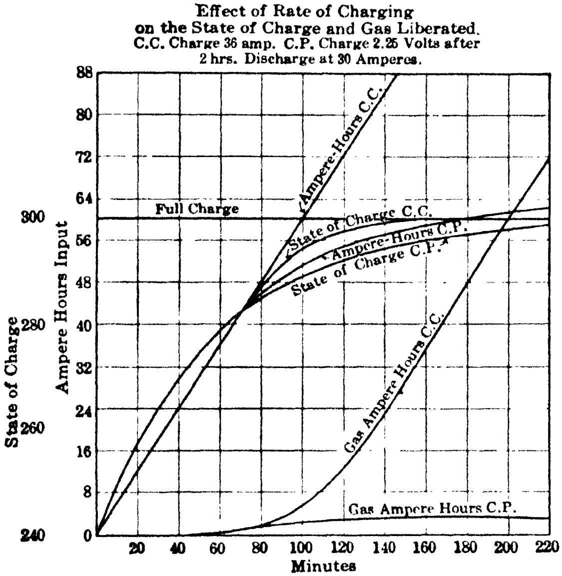

FIG. 78. Comparison of the constant-current and constant-potential methods of charging lead-acid batteries.

3. CHARGING AND DISCHARGING EDISON BATTERIES

The characteristic curves for charging and discharging an Edison storage battery are given in Figs. 79 and 80. The discharge curve resembles that for the lead battery, but the fall in voltage is somewhat more steep. The voltage curve on charge rises rapidly at the beginning and then more slowly until 5 hours have elapsed, following which the terminal voltage of the cell becomes constant at about 1.80 volts per cell. No specific gravity readings are recorded, since the electrolyte in these cells does not change in concentration during either the charging or discharging period. The temperature of the batteries rises markedly during both the charge and the discharge. In order to maintain Edison batteries in a state of maximum activity, the charging rate should be maintained at an average of the normal rate and should not be less than half the normal rate, but this does not preclude the use of trickle charging if proper application as to size and type of cell and recommended rates of trickle charge are followed. Edison batteries gas throughout the entire period of charge.

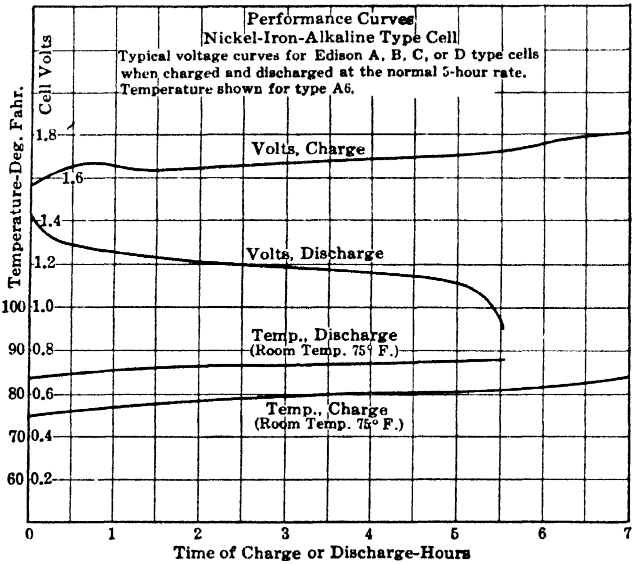

FIG. 79. Curves of charge and discharge of an Edison cell, constant current at the normal rate.

These cells may be charged by the constant-potential or tapering-charge method. It is necessary to maintain a sufficient cathodic polarization during charging to liberate hydrogen, in order that the iron may be properly activated.

Table XLVIII gives the average voltages for discharge of various types of cell and Table XLIX gives terminal voltages for varying amounts of discharge at various rates of discharge. The values given in these tables are voltages at cell terminals with no allowance for connectors.

It has been found that the life of alkaline batteries is prolonged by operating them at moderate temperatures. Charging them at high temperatures is more detrimental than discharging them when hot, but the latter may result in harmful reactions in extreme cases. At 50° C. (122° F.) slight gas evolution occurs from cells on open circuit as a result of local action. The gas is mostly hydrogen which is produced by the attack of the electrolyte on the iron of the negative plate. Charging the batteries when they are hot results in diminished capacity on the succeeding discharge. The largest immediate output is obtained by charging at a temperature of about 25° C. (77° F.) and discharging at 50° C. (122° F.), but it is wise to limit the upper temperature to about the same figure as for lead batteries, at most 46° C. (115° F.)

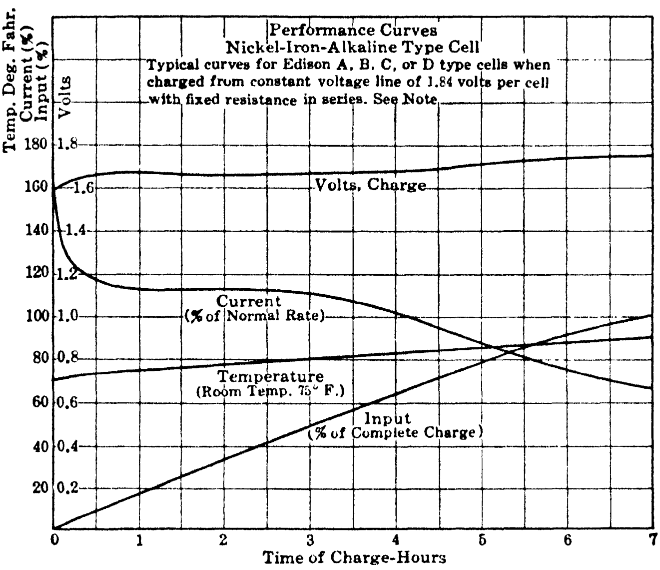

FIG. 80. Modified constant-potential charging curves of an Edison cell.

The knee of the discharge curve in Fig. 79 marks the end of the useful discharge of the battery. Beyond this a second stage of dis-

TABLE XLVIII

Average Voltage, Edison Cells

(Computed for discharges of various types and sizes of cells in fully active condition at normal temperature to end voltages equivalent to 1.0 volt per cell at the normal rate. Normal rate for types A, B, C, and D is 5 hours, for types G and L, 3⅓ hours. Based on cells giving 110 per cent of their rated capacity.)

Multiples of Normal Rate	Average Voltage
½	1.27
1 (normal)	1.23
2	1.13
3	1.04
4	0.94
5	0.85

TABLE XLIX

Edison Cell Voltages, Discharge

(The voltages are for various types and sizes of cells in fully active condition discharging at multiples of the normal rate following normal charges and at normal temperatures. Normal rate for types A, B, C, and D is 5 hours, for types G and L, 3⅓ hours. Based on cells giving 110 per cent of their rated capacity.)

Per Cent of Rated Capacity Taken Out	Cell Voltages for Discharges Expressed in Terms of the Normal Rate					
	0.5	1 (Normal)	2	3	4	5
0*	1.51	1.47	1.39	1.31	1.23	1.14
0†	1.46	1.42	1.33	1.25	1.16	1.08
5	1.38	1.34	1.25	1.16	1.07	0.98
10	1.35	1.31	1.22	1.13	1.04	0.95
20	1.32	1.27	1.18	1.09	1.00	0.91
40	1.28	1.23	1.14	1.05	0.96	0.87
60	1.26	1.21	1.12	1.03	0.93	0.83
80	1.24	1.19	1.09	0.99	0.89	0.78
90	1.23	1.17	1.06	0.96	0.86	0.74
100	1.20	1.13	1.01	0.90	0.78	0.64
110	1.11	1.01	0.86	0.73	0.60	....

* Immediately following charge.

† After standing 6 hours.

charge may be observed in certain types of alkaline batteries (not including Edison batteries). Positive plates, except those containing graphite, do not contribute to this secondary discharge. Since the positive plate is normally the limiting factor, this second stage discharge is not of practical importance and it should be avoided.

The operation of alkaline batteries can be controlled by voltage measurements on a pilot cell when discharging through a predetermined resistance. Comparisons of the readings are made with a table to determine the approximate state of charge of the battery. The instrument used is the "charge test fork."

TABLE L

Edison Cell Voltages, Charge

(The voltages are for cells charging at the normal rate.)

Percentage of Rated Capacity Remaining	Cell Voltage		
	35° F. (2° C.)	75° F. (24° C.)	115° F. (46° C.)
0	1.64	1.57	1.48
50	1.88	1.73	1.64
100	1.94	1.88	1.77

The error in estimating the state of charge by such measurements is no greater than the error in determining the state of charge of lead batteries by specific-gravity readings. Table L gives the approximate steady voltages per cell that may be expected when the battery has been on charge for a few minutes at the rate which is normal for the particular type of battery. The data in this table are reasonably consistent with the curves in Fig. 79 if interpolation is made for the temperature. Ampere-hour meters connected in circuit with the batteries are the most satisfactory means of terminating the charge. Lacking such instruments, however, recourse may be had to voltage measurements when the batteries are charging at specified rates and temperatures.

Charging and discharging curves of another type of alkaline battery (not the Edison type) are shown in Fig. 81. These were obtained on a cell of European manufacture, having positive plates of nickel peroxide and negative plates of cadmium. This type of cell has been more fully described at the close of Chapter II. The most significant feature of these curves is the rise in the charging voltage which occurs near the end of charge. In this respect the curve is like that of lead-acid cells.

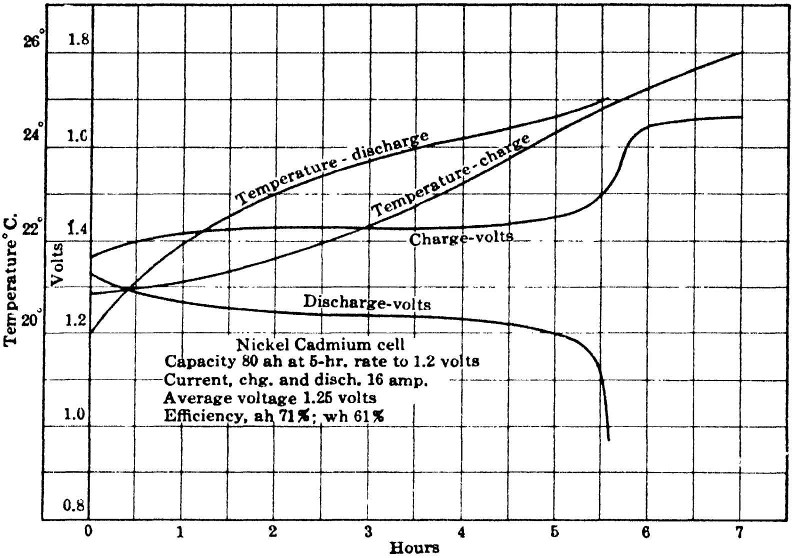

FIG. 81. Characteristics of a nickel-cadmium cell.

4. CHARGING EQUIPMENT

Except in the case in which direct-current bus bars of suitable voltage are provided for battery charging, the charging equipment will ordinarily include a motor-generator set, synchronous converter, or rectifier, to provide direct current at the proper voltage. Standard specifications for automatic battery-charging motor-generators and panels are available.[7]

a. Selecting Equipment

It is not within the scope of this book to give any description of motor-generator sets, but rather to give such information as may be required to plan the equipment which may be necessary in any particular case.

Battery Data. The batteries which are to be charged must be classified according to the number of batteries of each kind, the number of cells in each battery, the type of the battery, whether of the lead-acid

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[7] Industrial Truck and Statistical Assoc., 1939.

or of the alkaline type, the capacity of the cells, and the purpose for which they are used. It is also necessary to know the maximum number of batteries which will be charged at one time, in order that the maximum capacity of the charging equipment may be calculated.

Charging. The rate of charging will ordinarily be determined by the type and size of the batteries which are used. If it is necessary to give the cells boosting charges, this fact should also be taken into account in computing the maximum capacity required of the charging equipment.

The method of charging, whether constant-current or constant-potential, must be chosen in advance, since generators of somewhat different characteristics are required for these methods. Generators for constant-current charging are ordinarily of the shunt-wound type with hand regulation capable of reducing the terminal voltage of the machine to one-half its normal value.

The trend in industry indicates that provision should be made for automatic control of battery charging. The modified constant-potential method is generally applicable to both lead-acid and nickel-iron batteries and is preferred because of its simplicity and freedom from the necessity of manual control. For charging one battery a shunt-wound type of generator, designed to have particular voltage characteristics, is suitable, but, if more than one battery is to be charged at constant voltage, a flat-compounded generator is necessary. A voltage regulator is sometimes applied to the shunt field to provide uniform voltage regardless of temperature and load conditions. Each battery is connected to the charging source through a single fixed resistor. Batteries are removed from the line automatically as each finishes, and the generator is shut down automatically when the last battery is charged. In the event of power failure, the generator is disconnected from the batteries. This is quite necessary, but when the supply is restored the motor-generator is restarted and charging resumed.

For floating charge, the diverter pole generator, described by Smith,[8] has found increasing use, particularly in telephone offices and unattended substations. The generator maintains constant voltage from low loads to its full rated capacity, beyond which the voltage droops sharply. This transfers excessive current demands to the battery. Suitable voltage characteristics are obtained by placing the series windings on intermediate or diverter poles between the main poles and by the use of a magnetic bridge. By properly proportioning the shunt and series windings the flux in the armature can be made to

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[8] *J. Am. Inst. Elec. Eng.*, 48, p. 11, 1928.

vary with the load. The diverter poles and magnetic bridges also have an important function in stabilizing the machine in the event it should run as a motor during power interruption.

Grouping of the Batteries. The smallest batteries, particularly those for starting and lighting service, may be grouped in several different ways during charging. The most advantageous grouping will depend upon the capacity and the number of cells in each battery. Considering low-voltage batteries of 6, 8, and 12 volts, there is a choice of connecting them in parallel, in series, or in a combination of series and parallel. It is practical to charge these batteries in series up to bus-bar voltages of 115 volts, but higher voltages are not recommended for use in service stations, where the floors are often wet and the insulation not of the best.

Sectional Panels. Charging equipment can be obtained in the form of sectional panels, which are designed for any practical conditions or method of charging. The sectional panels include incoming line sections, generator control sections, and charging sections with resistors both variable and fixed, voltmeters and ammeters, overload and underload circuit breakers, ampere-hour meters, reverse-current cutouts and fuses. If a proper selection of control panels is made, a convenient charging switchboard may be easily arranged.

b. Rectifiers

A rectifier is essentially an electrical check valve which converts alternating current into unidirectional current by providing a low resistance path for the flow of current in one direction but interposing a high or infinite resistance when current would tend to flow in the other direction. Rectification may be accomplished by the use of mercury arcs, electrolytic valves, ionized gases, or synchronous switches, or by the flow of electrons across the junction of certain metals and semiconductors. The latter include oxides and sulphides formed on the surface of copper, and selenium which is spread on a surface of iron or nickel. Whatever the method, a pulsating direct current is produced which can be used for battery charging without the necessity of "smoothing" it. The process of battery charging is governed by Faraday's law and the electrochemical reactions which occur during an infinitesimal interval of time, dt, are, therefore, proportional to the quantity of electricity passing at that instant, that is, to Idt. For each half cycle the quantity of electricity flowing is equal to the average value of the current multiplied by the time that it flows. The current should be measured, therefore, with direct-current ammeters of the permanent-magnet moving-coil type. The magnitude of the current, as well as the time that the valve is open, are governed by relative values of impressed voltage, counter electromotive force and whatever capacitance, inductance, and resistance are present in the circuit.

If a single rectifying element is used, only one-half of the alternating wave is rectified, but two or more rectifying elements can usually be arranged to rectify both halves of the wave. This is called full-wave rectification. When half-wave rectification is provided the current cannot flow during one-half the cycle because it would have to pass in the high-resistance direction of the rectifier. Being stopped out, half the cycle is ineffective, but the efficiency is not materially reduced.

If the circuit is without appreciable inductance or capacitance, the rectified current is in phase with the impressed electromotive force and attains its maximum value once or twice each cycle, depending on whether half- or full-wave rectification is provided. This is illustrated in Fig. 82 by the tracing of an oscillogram shown for the simplest case of a circuit having no counter-electromotive force and negligible capacitance and inductance. The current begins to flow when the impressed voltage passes through zero value and each maximum of current is in phase with the maximum of voltage. If a battery is being charged, however, the electromotive force of the battery, which is relatively constant, opposes the periodic impressed electromotive force and current cannot flow until the impressed voltage has reached a value equal to the electromotive force of the battery, plus any other voltage losses. This is illustrated in Fig. 83. The valve opens at the point marked *A* and closes at the point marked *B*.

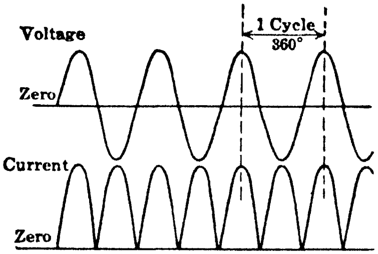

FIG. 82. Full-wave rectification in a circuit having no counter-electromotive force. Capacity and inductance are negligible; hence the current is in phase with the voltage.

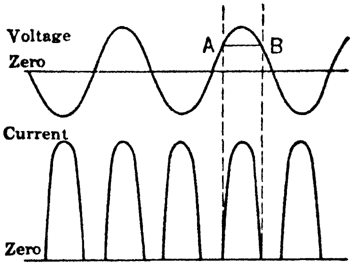

FIG. 83. Full-wave rectification in a circuit having a counter-electromotive force. The valve is open only from *A* to *B*, that is, when the impressed voltage exceeds the counter-electromotive force. If capacity and inductance are negligible, the current is in phase with the voltage.

If the value of the impressed voltage is not greater than the counter-electromotive forces opposing it, no charging current can flow. However, if the rectifier and battery have appreciable capacitance, an alternating current which leads the impressed electromotive force by 90° will flow through the battery, but this is entirely ineffective in charging it. Such a condition is shown in Fig. 84.

Capacity currents, and leakage currents too (if the rectifying film is imperfect), show negative loops in oscillograms of half-wave rectification. One may be distinguished from the other, however, by the fact that the capacity loop is leading the impressed voltage, while the leakage loop is always in phase with it.

In the foregoing discussion, it has been assumed that the circuit is essentially non-inductive. The battery has no appreciable inductance, but inductance may be added to the circuit for purposes of regulation or to extend the time that the valve is open. In Fig. 85, showing the effect of inductance, it may be seen that the current lags behind the impressed voltage. This oscillogram is for half-wave rectification. Current in the positive direction begins after the impressed voltage has attained a value predetermined by the counter-electromotive force. The current increases slowly at first, by no means as rapidly as the impressed voltage. It attains its maximum value 90° later than the voltage, or somewhat less if there is appreciable capacitance in the circuit. As the impressed voltage decreases, the current lags and the current may still be flowing in the positive direction when the impressed voltage has passed through zero and become negative. This is because

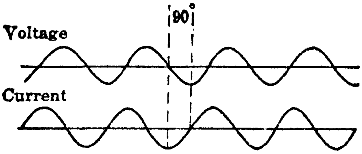

FIG. 84. Conditions when the impressed voltage is less than the counter-electromotive force. No rectification occurs, but a capacity current, leading the voltage by 90°, flows through the battery.

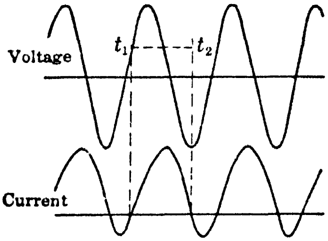

FIG. 85. Half-wave rectification in a circuit having counter-electromotive force and inductance. The valve is open from t_1 to t_2. The maximum of current lags behind the maximum of voltage. If an iron core is present, the hysteresis must be low to avoid loss.

of the induced electromotive force, which depends on the inductance, L, and the rate of change of current, $\frac{dI}{dt}\cdot$ The valve is open longer, therefore, when inductance is present, unless the conditions of the circuit are complicated by large hysteresis losses in iron cores. Actually the voltage across the valve, E_R, which determines when it opens and closes is the algebraic sum of the impressed voltage, $E_0 \sin \omega t$, the counter-electromotive force of the battery, E_B, the induced electromotive force, $L\frac{dI}{dt}$, and the IR drop. That is, the voltage across the valve is

$$E_R = E_0 \sin \omega t - E_B - L\frac{dI}{dt} - IR$$

Previous to the instant, t_1, that the valve opens,

$$I = 0 \text{ and } 0 < t < t_1$$

$$E_R = 0 \text{ and } \frac{dI}{dt} = 0$$

but the impressed voltage and the counter-electromotive force are equal and opposite, whence if a solution exists, $E_B < E_0$ and

$$\sin \omega t_1 = \frac{E_B}{E_0}$$

This determines in angular measure the time of opening the valve. To find the time of closing the valve is somewhat more difficult.

For this, $t_1 < t < t_2$ and in this interval $I > 0$

$$L\frac{dI}{dt} + RI = E_0 \sin \omega t - E_B$$

with the initial condition that

$$I = 0 \text{ when } t = t_1$$

so that

$$I(t) = \frac{E_0}{R^2 + \omega^2 L^2}\,[R \sin \omega\,(t - t_1) - \omega L \cos \omega(t - t_1) + \omega L e^{-\frac{R}{L}(t-t_1)}]$$

$$- \frac{E_B}{R}\,[1 - e^{-\frac{R}{L}(t-t_1)}] \quad \text{for } t_1 < t < t_2$$

where t_2 is to be determined as the next time in this interval that I vanishes, that is $I(t_2) = 0$

Write

$$\tau = t - t_1 \text{ and } \tan \alpha = \frac{\omega L}{R}$$

then

$$RI(t) = \frac{RE_0}{\sqrt{R^2 + \omega^2 L^2}} \sin (\omega\tau - \alpha) - E_B + \left[\frac{R\omega L E_0}{R^2 + \omega^2 L^2} + E_B\right] e^{-\frac{R\tau}{L}}$$

$$= E_0 \left[\cos \alpha \sin (\omega\tau - \alpha) - \frac{E_B}{E_0} + \left(\sin \alpha \cos \alpha + \frac{E_B}{E_0}\right) e^{-\frac{R\tau}{L}}\right]$$

For any particular case the values of E_B, E_0, L, and R are known so that it is not difficult to determine the value of τ which makes this expression for the current vanish. Using this and the value of t_1 determined previously,

$$t_2 = t_1 + \tau$$

Electrochemical Rectifiers. Aluminum, tantalum, and a few other metals possess the property of valve action when immersed in certain solutions. During the operation of the rectifier a film forms on the surface of these metals. This is permeable to hydrogen cations but not to anions, except those which act as "poisons" and destroy the film. The current can pass through the electrolyte to the valve electrode, but not from it, except at relatively high voltages when breakdown occurs. In addition to the valve electrode, each cell must contain another electrode to serve as an anode. This must be able to withstand the strong oxidizing conditions and must pass current in either direction. Lead, carbon, iron, chromium steel, and iron-silicon alloys have been used for this purpose.

The aluminum rectifier has been improved in recent years by adding about 0.1 per cent copper to the aluminum rod which serves as the cathode. Solutions of phosphates, borates, or tartrates may be used as electrolytes, but dibasic ammonium phosphate is perhaps the most used material. This may be improved by adding potassium phosphate, which increases the conductivity, and by the addition of small amounts of citric or malic acids, which retard the formation of a gelatinous precipitate of aluminum. The life of the rectifier is usually terminated by the exhaustion of the electrolyte. Cells containing about 1500 cc. of solution have a life of about 2500 hours at a current rate not exceeding one ampere.

Tantalum rectifiers consist of metallic tantalum as the cathode and lead or an alloy of lead as the anode in a solution of sulphuric acid, to which a small amount of ferrous sulphate is added. The specific gravity of the solution is about 1.250. Tantalum rectifiers can usually be used for larger currents than the aluminum rectifiers. With either type, it is usually best to use four cells in a bridge arrangement to provide full-wave rectification and to lessen potential stress across the film. The over-all energy efficiency is about 40 per cent. Aluminum rectifiers are used less now than formerly, having been replaced by copper oxide and gas-bulb types of rectifiers. Tantalum rectifiers, however, are used in railway signal service.

Copper Oxide Rectifiers. The copper-cuprous oxide rectifier which has developed from experiments made by Grondahl in 1920, depends for its operation on the asymmetrical resistance at the junction of copper and a layer of cuprous oxide formed on its surface. That is, current can flow more freely in one direction than in the other. From oxide to copper the resistance is low, but from copper to oxide the resistance is many times greater. Such an arrangement provides a valuable rectifying unit which has no moving parts or chemical reactions.

Copper of a high degree of purity is partially oxidized in air at a temperature of 1000° to 1040° C. The latter temperature is slightly above the melting point of the oxide, 1025° C. Red cuprous oxide, Cu_2O, is formed on the surface of the copper as an adherent layer. This in turn is usually covered by a layer of black cupric oxide, CuO, which has a high resistance and which must be removed by being dissolved in a mixture of acids at a later stage of the process. The heat treatment of the elements after oxidation has an important effect on the operating characteristics of the rectifier. Slow cooling produces elements of relatively high resistance which are adapted to use in high-voltage rectifiers, since the elements are able individually to withstand 10 to 30 volts in the reverse direction and since the matter of their forward resistance is relatively unimportant. On the other hand, elements which are quenched have a lower resistance but should not be subjected to more than 6 volts. These elements have a high ratio of resistances in the high and low directions. They are well adapted to use in rectifiers carrying considerable current.

The oxidized copper is prepared in a variety of sizes and shapes. Some of these are buttons only a few hundredths of an inch in diameter, others are disks or "washers" 1 to $1\frac{1}{2}$ inches in diameter and still others are rectangular plates 4 by 15 inches. Contact to the oxidized surface is made in various ways, such as sheets of lead over a coating of colloidal graphite applied to the oxide surface. The elements are assembled as shown in Fig. 86 from the paper of Grondahl and Geiger.[9] Ventilating fins are provided when necessary. These are interleaved with the elements.

Since rectification is distributed over the whole area of contact between the copper and the oxide, the current-carrying capacity may be increased by enlarging the area of contact (paralleling elements) and by forced ventilation. Without special ventilation a current density of 0.07 ampere per cm^2 is reasonable. The life of the rectifier is adversely affected by the high temperatures. Eighty degrees Centigrade is maximum, but for continuous operation, temperatures should not exceed 50° C. Higher voltages applied to these rectifiers are sustained by placing additional elements in series. There is the possibility of building rectifiers for a wide variety of operating conditions ranging from a few microamperes to many thousands of amperes and from microvolts to thousands of volts.

The boundary area between copper and oxide has a capacitance of about 0.006 microfarad per square centimeter. This is of some importance as the capacitive reactance must be large in comparison with the resistance component of the impedance in the low-resistance direction, otherwise rectification would be seriously impaired. At commercial frequencies the capacitive reactance is without detrimental effect on rectification and power factor.

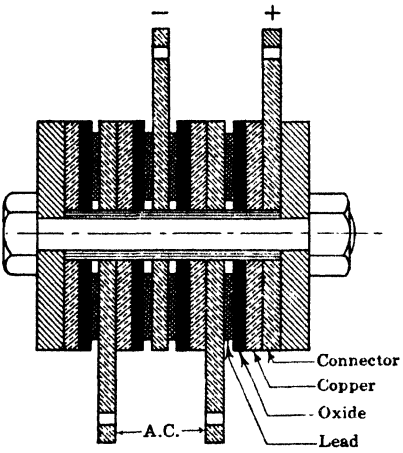

FIG. 86. Copper oxide rectifier.

No theory of operation has been proposed which is entirely satisfactory. Conduction of the current depends on the ease with which electrons can cross the boundary from copper to cuprous oxide. (This is opposite to the direction in which current is said to flow, because we are now speaking of electrons as carriers of current.) If this is true, the copper should furnish an inexhaustible supply of electrons and the life of the rectifier with only a thin film of oxide should be indefinitely long, provided the film is not punctured. Some ageing effects, which are accelerated by operation at too high temperatures, have been

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[9] *Trans. Am. Inst. Elec. Eng.*, 46, p. 358, 1927.

observed. These usually occur in relatively new rectifiers, but eventually the elements become stabilized. Ageing effects may alter slightly the ratio of resistances in the high and low directions of current flow, but this does not materially lessen the efficiency of the rectifier, which is from 50 to 80 per cent.

A wide variety of unit assemblies is available. These include single and double stacks with or without radiating fins. From these, rectifiers to meet any particular service condition of current or voltage can be built. Applications include the charging of batteries for automobiles, control systems, emergency lighting, signaling, industrial trucks, and P. B. X. boards.

Gas-Filled Bulb Rectifiers. A combination of a hot and a cold electrode in a vacuum may act as a rectifier, because the hot electrode throws off electrons when it is charged negatively, and these, traversing the space to the other electrode under the influence of an electrostatic field, constitute an electric current. Space charges, depending on the relative rates of emission of electrons and their conduction of current, may occur and cause some loss of efficiency. The high-vacuum type of bulb is adapted to high voltages, but for low voltages and relatively large currents bulbs filled with an inert gas, such as argon are better. The electrons streaming out from the hot electrode ionize the gas and permit considerable current to flow during the time that electrons are being emitted. On the other half cycle, neither electrode can emit electrons, and consequently no current can flow. Most of the current which passes through the bulb is carried by the ions from the gas. Rectifiers of this type are equipped with "Tungar" or "Rectigon" bulbs which were placed on the market about 1916. They are shown diagrammatically in Figs. 87 and 88. The cold anode of graphite is marked *a* and the hot cathode of spirally wound tungsten wire is marked

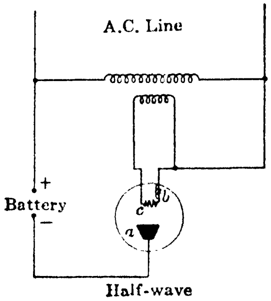

FIG. 87. Gas-filled bulb rectifier.

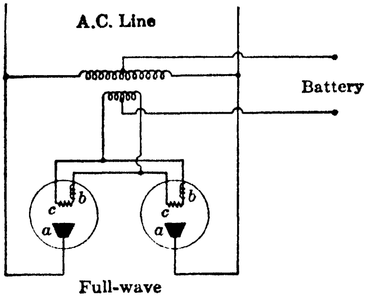

FIG. 88. Gas-filled bulb rectifiers.

c. A small ring of magnesium wire around the stem of the anode, marked *b*, is included within the bulb to react with any gas (except the inert gas) which may be present and liable to impair the life or efficiency of the bulb. By a flashing process after the bulb is sealed, this magnesium wire, called the "getter," is made to combine with the objectionable gases which may be present. The products of chemical combinations are deposited on the inner surface of the glass, giving it a mirror-like or sooty appearance. For this reason the bulbs are seldom clear, but this is no indication of bad condition. The gas pressure within the bulb may be from 0.01 millimeters to several centimeters. The connections for a bulb of this type to the alternating-current .circuit are also shown in these figures. By using two tubes it is possible to rectify both halves of the wave. Some rectifiers of this type contain auto-transformers connected as shown, but variations in the connections will depend upon whether the secondary circuit is grounded or not. The small winding shown is a low-voltage, heavy-current coil supplying current to heat the filament.

Rectifiers of this type can be operated in parallel, if provided with suitable reactance. Two bulbs alone will not operate in parallel, since the one with the lower arc drop takes the load. The power factor is about 50 per cent.

The bulbs are mounted with transformers which are designed for specified voltages. Certain precautions should be observed in operating these rectifiers, to prevent damage to the bulb. The bulb, once started, will continue to operate without the cathode excitation, since the cathode can be kept hot by the bombardment of the positive ions. This does not eliminate the energy loss involved in heating the cathode, as the voltage drop across the arc increases. The arc tends to concentrate on a few turns of the filament when its normal excitation is cut off, and the filament will burn through at this point. It is not desirable, therefore, to operate the filament without its normal current, as the life of the bulb will be greatly shortened. If the battery voltage is 40 volts or more, both alternating-current and direct-current circuits should be opened simultaneously by the rectifier switch, to prevent a possible surge of current through the bulb, which may happen when the alternating-current circuit alone is broken, particularly if this occurs at the instant of peak voltage. When such a surge occurs, a large current from the battery discharges through the bulb in the reverse direction, destroying it.

The efficiency of these bulb rectifiers may amount to 60 or 70 per cent when charging batteries of nearly the maximum voltages for which they are designed, but the efficiency decreases to less than 20 per cent when used for batteries of only a few cells. This is because the energy required to heat the filament and the energy loss in the arc itself, of which the voltage drop is about 6 volts, become a large part of the total energy received by the rectifier from the alternating-current circuit.

Eight or ten sizes of these bulbs are available, having direct current ratings of 0.25 to 15 amperes. The voltages range from 7.5 to 250 volts. Usually the bulbs with the smaller current ratings are applied to trickle-charging batteries. Complete charging units comprise: (1) rectifier bulbs (one for half-wave or two for full-wave rectification); (2) transformers (auto-transformers or two-winding, insulated transformers); (3) hand-operated selector switches for control of voltage and current to provide for charging any number of 3-cell batteries from one to 6, 12, or 24, according to the capacity and design of the charger; (4) a direct current ammeter of the permanent-magnet, moving-coil type; (5) switches, fuses, and leads for connection to the alternating-current supply and the direct-current load.

The choice of the proper charger depends on the average number of batteries to be charged and the time available. Thus, there are 6-battery chargers capable of charging 6 batteries at 6 amperes, and heavy duty, "one-day" chargers able to charge 6 batteries at 12 amperes, or 12 batteries at 6 amperes. In selecting any charger it is necessary to specify the alternating-current line voltage and the frequency, 60 cycles being the most commonly used. The over-all efficiency of the charger is better when the bulbs are operating at higher voltages because the *IR* drop within the bulb is of less importance.

Mercury-Arc Rectifiers. Mercury-arc rectifiers are particularly adapted to charging batteries of the vehicle type and others requiring larger currents than batteries of the starting and lighting type. The maximum capacity of the mercury-arc rectifier in glass is 50 amperes, limited in practice by the inability to blow satisfactory bulbs which will carry heavier currents. Mercury-arc rectifiers in tanks, capable of carrying as high as several thousand amperes at high voltages, have been constructed.

A glass bulb containing mercury vapor will permit the electric current to flow in only one direction, to the cathode, but these bulbs are arranged to rectify both halves of the wave by providing two anodes. The anodes marked *A* and *A′* in Fig. 89 consist of graphite, and the third electrode, marked *M*, of mercury.

In order to start a rectifier of this type, it is necessary to rock the bulb, which forms and then breaks a mercury bridge from the small starting anode, marked *S*, to the mercury cathode *M*. When the mercury bridge breaks, the cathode supplies ionized mercury vapor and this continues so long as the current is flowing toward the cathode. To prevent extinguishing the arc at the end of a half cycle, a large reactance is provided. The two anodes function in turn, the current flowing at any instant from the one which is opposed to the mercury cathode in polarity at that time.

For telephone and other "quiet" service, reactance is provided in the direct-current circuit. Such outfits also use two-winding instead of auto-transformers.

Mercury-arc rectifiers are not self-starting as are those of the gas-filled bulb type, but this feature can be added by using motor-drive or solenoid tilters, which are automatically cut out of circuit when the direct current starts to flow.

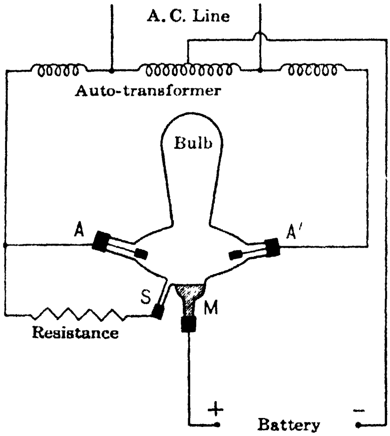

FIG. 89. Mercury-arc rectifier. A and A' are the anodes; S is the starting anode; M is the mercury cathode.

Mechanical Rectifiers. In the class of mechanical rectifiers may be included a wide variety of types, such as commutators driven by synchronous motors, vibrating reeds and switches, and the mercury-jet rectifiers of large current-carrying capacity. The vibrating reed rectifiers which were commonly used for charging small batteries have been largely superseded by other types.

Self-Regulating Rectifiers for Floating Batteries. Fully automatic control of battery charging by rectifiers is a recent development which has found application in the maintenance of floating batteries such as those used for circuit-breaker control, telephones, alarm and signal systems. Compared with cycle operation, floating the batteries increases their life and permits smaller sizes to be used. The new constant-potential chargers are designed for an output which varies with the load demand and the direct-current output is unaffected by considerable fluctuations in the alternating-current line voltage.

When the current demand is less than the rated output of the charger, all current is supplied to the direct-current circuit by the rectifier and simultaneously a trickle-charge current maintains the battery in a fully charged condition. When the load exceeds the rating of the charger, the excess is supplied by the battery until the load falls to its normal value, less than the rated current of the rectifier. Following this, the battery is quickly restored to a fully charged condition by a charging current, which for the time being, is in excess of the trickle-charge rate.

The control units which provide the automatic features of these rectifiers are saturable core reactors. These are essentially choke coils with two windings. An increase in the direct-current of one coil results in a proportionate decrease in impedance of the alternating-current coil. To prevent voltage fluctuations of the alternating-current line from interfering with the regulation of the direct-current load, an alternating-current stabilizer is added to the rectifier. This consists of a saturable transformer, reactor, and condenser. It holds the alternating-current input constant to ± 1 per cent, notwithstanding variations of ± 15 per cent in the line.

Figure 90 shows a Raytheon charger of this type with the outer case removed. The rectifying element, in the foreground, is the dry copper oxide disk type. Adjustment of the trickle charge rate can be made to meet existing conditions and provision is made also for equalizing charges when necessary. Properly installed, water is required for the battery at intervals of about 6 months. The charger has no moving parts and maintenance is reduced to a minimum. Continuous direct-current ratings are from 1 to 6 amperes for telephone batteries of 8 to 24 cells. The charger is protected against overload by a drooping characteristic beyond its rated capacity.

Another type of self-regulating charger for batteries operating at 120 volts or higher is known as the "Phano-charger." This is provided with saturable reactors and voltage regulating relays. The rectifying element consists of two phanotron rectifying tubes rated for 4.5, 12.5, and 25 amperes. The first two are for use on single-phase circuits and the last for three-phase circuits. The battery ordinarily receives a low-rate charge, but the rectifier will automatically furnish more current when the battery voltage is diminished as a result of previous discharge. Inherent overload protection is provided.

c. Ampere-Hour Meters

Since the ampere-hour is the unit commonly employed to measure the capacity of storage batteries, the ampere-hour meter is a convenient instrument for indicating the state of charge of a battery and for controlling the charge. Various types of ampere-hour meters have been developed, but the mercury-motor type is the most common form. This meter can be built as a rugged, dependable instrument which will keep in calibration and function satisfactorily even under severe conditions of service, such as may be encountered with mine locomotives, street trucks, or industrial tractors.

The mercury-motor type of meter consists of a copper disk immersed in mercury contained in a bakelite chamber. The current is taken in through a contact ear, passes across the disk and then out through a contact ear at the opposite side. Permanent magnets create a field cutting the disk, and rotation is produced on the well-known principle of Faraday's disk. Inasmuch as the field of the magnet is constant, the torque exerted on the moving armature is proportional to the current flowing. The magnets are so situated that the pole tips are directly above and below the disk on opposite sides of the main shaft.

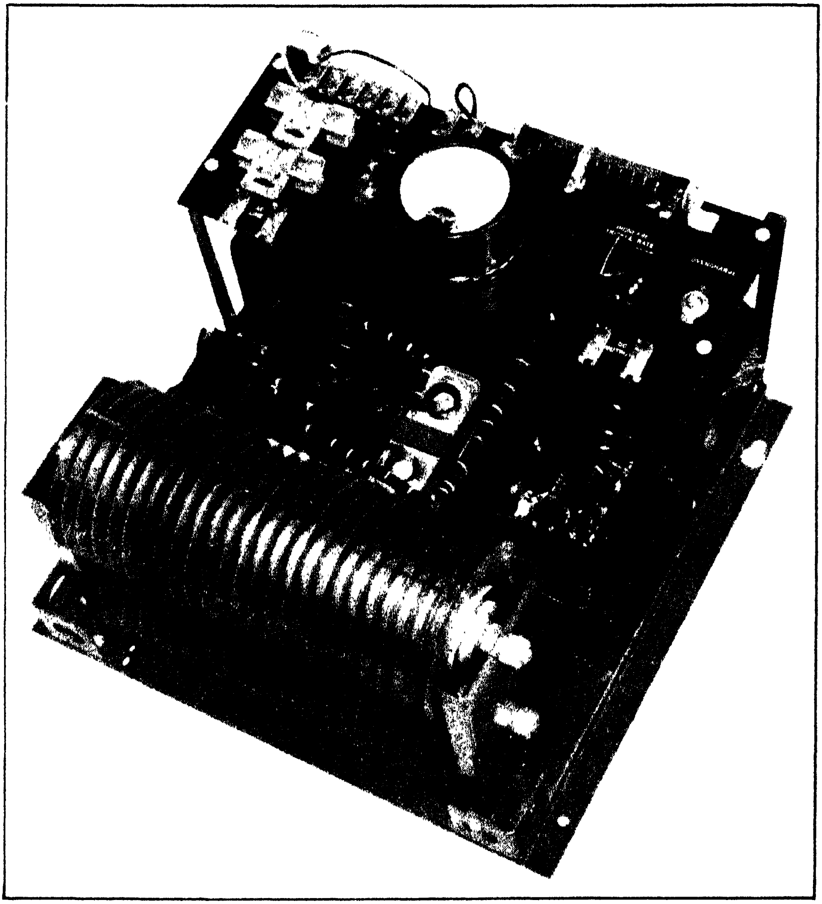

Fig. 90. Raytheon self-regulating rectifier, case removed.

When current is passed through the meter the disk rotates. This rotation induces eddy currents in the same disk, as it cuts the magnetic field and damping is thereby accomplished.

The ampere-hour efficiency of a storage battery is less than 100 per cent, and therefore a greater number of ampere-hours are required to charge it than were discharged previously. The efficiency depends on the construction of the battery, the rate at which it discharges, and the conditions of charging. It is possible to design the ampere-hour meter so that it will run slow during the charging period by a percentage that will be approximately equal to the difference between the efficiency of the battery under standard conditions and 100 per cent. The conditions of service must be carefully considered in determining the amount by which the meter should be retarded when running in the reverse direction.

d. Voltage Relays

Volt-sensitive relays afford another means for automatically controlling the rate of charge supplied to a battery. As charging progresses, the voltage at the terminals of lead-acid storage batteries rises slowly until gassing begins when a more abrupt rise of several tenths of a volt per cell occurs. At this point the battery is 90 per cent charged, or more, and charging should be completed at a lower rate. This abrupt rise in voltage is sufficient for operating a properly designed relay. However, the effect of variations in temperature of both battery and relay must be considered. For the same state of charge, the terminal voltage of the battery will be lower as the temperature is higher (see Fig. 91), but the operating voltage of an ordinary relay becomes higher as its temperature is increased. Such a relay is not well adapted to the purpose.

Inverse temperature compensation has been provided in the TVR relay so that its operating voltage is higher at lower temperatures by an amount which closely approximates the change in battery charging voltage for a corresponding difference in temperature. This is accomplished by using a bimetallic strip which varies the air gap between the magnet frame and the armature. The relay may be set to operate at a desired voltage such as 2.40 volts per cell when the battery is to be charged in 8 hours. The actual adjustment within a range of ±1 per cent is of no great importance as the battery voltage rises rapidly when gassing begins.

Figure 91 shows the volt-time characteristics of four similar batteries which, being fully charged initially, were discharged for one hour at the 8-hour rate and then recharged at one-third of this rate.

The abrupt rise in voltage occurred after about 3 hours, as would be expected. The figure shows also the operating limits for a TVR relay.

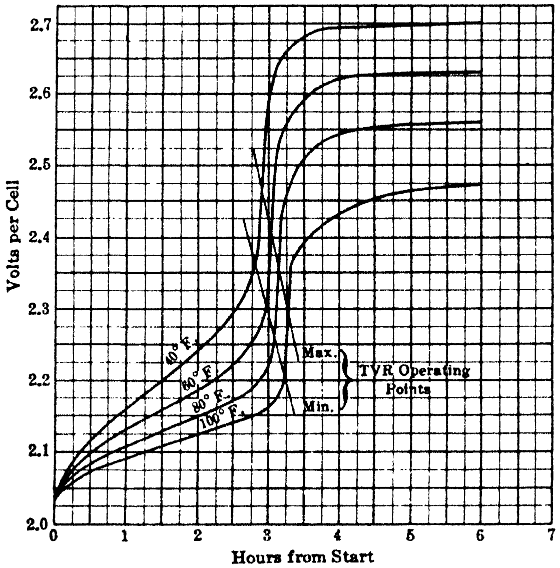

FIG. 91. Effect of temperature on charging characteristics of a lead-acid storage cell

When such a relay is applied to control a two-step charge, the circuit is like that shown in Fig. 92. The first step is at a high rate of charge and the second step may be a trickle charge. After the relay has "tripped," the relay must be reset to provide a higher rate of charge again. This is done by momentarily opening the circuit of the exciting coil manually, or by a supplementary relay in the load circuit, or by a clock mechanism. In any installation, the relay and battery should both be subjected to the same ambient temperature.

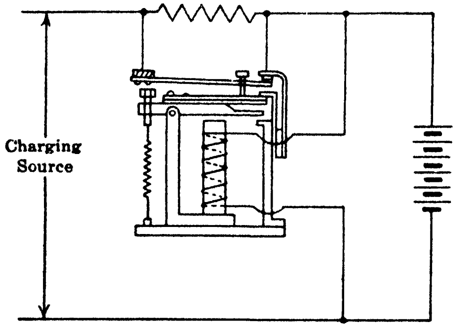

FIG. 92. Two-step charge control by a temperature compensated relay.

5. BATTERY REGULATION

In the preceding portion of this chapter, the voltage characteristics of the storage battery on charge and discharge have been discussed.

The terminal voltage of the cells decreases during discharge and increases during the charging period. It is necessary to compensate for these changes when the battery is used to maintain the potential of bus bars in power circuits. When the current flowing in the circuit is very small, this regulation is satisfactorily accomplished by the use of a regulating resistance. With cells of large capacity this would be a very wasteful and inconvenient method, and other methods must be employed. These may be classified as follows: end cells, counter cells, boosters, and methods of alternating-current regulation.

End-Cell Regulation. The falling voltage of a battery on discharge may be compensated for by adding additional cells from time to time. The name "end cells" comes naturally from the familiar arrangement of providing taps to each of a limited number of cells at the ends of a battery, so that any of these may be connected or disconnected at will without interrupting the flow of current from the battery to the bus bars. Figure 93 shows a simple diagram of such an arrangement for a three-wire circuit. If the battery is to be connected to the bus bars only during discharge or when floating on the line, a single end-cell switch at each end of the battery is all that is ordinarily required.

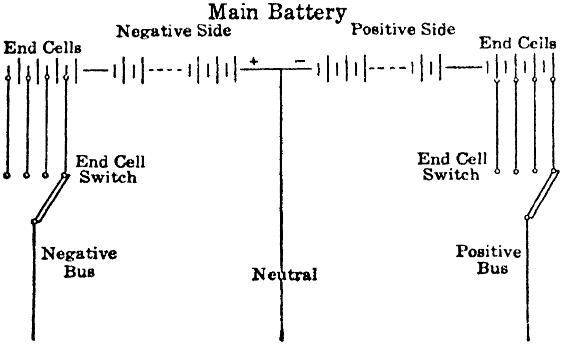

FIG. 93. Arrangement of end cells in a battery. For a two-wire circuit the end cell are at one end only.

The use of end-cells as a means of regulation is becoming more limited with changing conditions in central stations, where batteries are largely confined to emergency or "stand-by" service in which control of voltage on discharge is of minor importance. Telephone central offices, however, employ several end cells on 24-volt batteries and proportionately more on batteries of higher voltage.

The successful regulation of voltage by the use of end cells requires well-designed switches. These switches must not interrupt the connection between the battery and the bus bars, nor short-circuit any cell when the switch is being operated. The switch must be capable of carrying the maximum current of the battery. The switches must also be free from heating and sparking at the contacts.

The number of end cells which is required is calculated from the maximum voltage drop and the total number of cells in the main battery. In the simplest case, the initial discharge voltage may be assumed to be 2 volts per cell, decreasing as the cells discharge to 1.8 volts per cell, or 10 per cent. At least one end cell to each ten cells in the main battery is therefore required. If the battery is to be charged while on the line, additional end-cell connections will be necessary. The cells will increase to about 2.60 volts per cell, or 30 per cent, which, added to the 10 per cent required for discharge, makes a 40 per cent variation in voltage to be compensated for by the end cells. The actual number in any case can be calculated only when full data of the service are available. End cells are cut out on charge and in on discharge. In large stand-by batteries for central-station service it is not customary to provide enough end cells to maintain normal bus voltage during a heavy emergency discharge, and it frequently happens in such a case that all the cells are cut in immediately and the bus voltage allowed to drop where it will as the discharge continues.

End cells are usually of the same size as those in the main battery, although they are seldom used as much. The last cell cut in on discharge obviously delivers only a small portion of the ampere-hours delivered by the cells in the main battery. They are consequently charged in a shorter time and must be cut out of the circuit when the charge is complete.

Counter Cells. Counter cells of the lead-acid type are provided with grids in place of the regular plates. They have very little capacity, but develop a potential of 2.3 to 3.0 volts, depending on the current flowing, which opposes the potential of the main battery. The counter cells are placed at the ends of the battery, and the successive cells are cut out of the circuit as the voltage of the main battery falls, because their effect is subtractive instead of additive.

A new type of counter cell, consisting of nickel electrodes in an alkaline solution, has been found advantageous in telephone installations because of lower capacity and longer life than the lead cells. The counter-electromotive force of these cells is from 1.70 to 2.25 volts.

Alkaline counter-electromotive-force cells have largely replaced the lead type used formerly. The latter were subject to several operating difficulties, including a gradual increase in capacity, a high internal resistance after a period of idleness and the formation of a scaly sediment which sometimes caused short circuits. The ideal counter cell would have no appreciable capacity, low internal resistance, unattackable electrodes, and ample space for electrolyte so that water would be required infrequently.

The alkaline counter cells fulfill these requirements quite satisfactorily. Each cell (see Fig. 94) consists of a glass jar in which are contained pure nickel electrodes in a treated solution of sodium hydroxide or stainless steel electrodes in a similar solution. The solution is covered with a layer of oil. The electrode groups are identical and as the cells have no polarity can be used for either direction of current flow. Water is decomposed when current flows, oxygen being liberated at the anodic group and hydrogen at the cathodic group. Considerable water is required to replace that decomposed by the current, but several thousand ampere-hours can pass through the cells before they need watering. The layer of oil over the electrolyte prevents evaporation

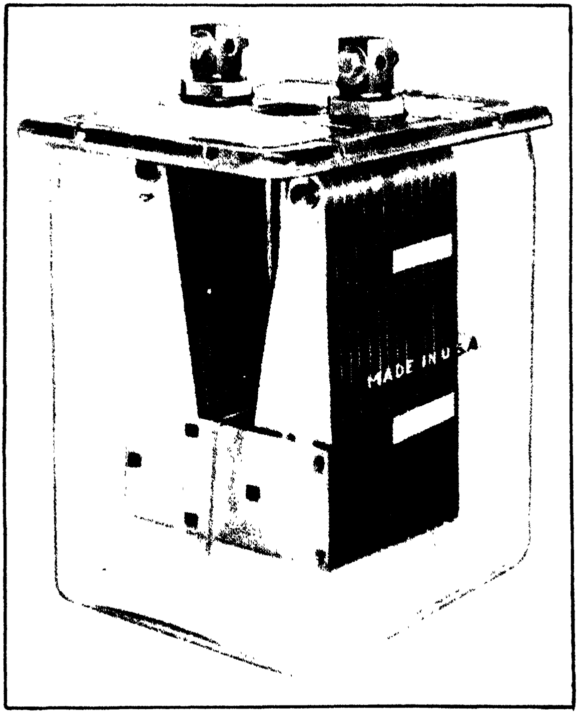

FIG. 94. Counter-electromotive-force cell, nickel-alkaline type NAK–30, continuous rating 60 amperes.

and protects the alkaline solution from the carbon dioxide in the air. The cells have covers similar to other storage cells.

The counter-electromotive force developed by the cells varies with the current. In terms of rated current for the various sizes of cells, the counter-electromotive force is as follows:

PER CENT OF RATED CURRENT	COUNTER-ELECTROMOTIVE FORCE, VOLTS
5	1.90
20	1.98
40	2 06
60	2.14
80	2.22
100	2.30

The electrolyte should be renewed at intervals of 2 to 4 years.

Boosters. A third means of regulation is by the use of boosters. In the Standardization Rules of the American Institute of Electrical Engineers, a booster is defined as a generator inserted in series in a circuit to change the voltage. The booster is usually motor-driven, and in such a case it is designated as a motor-booster. A wide variety of boosters are available for various purposes. These include (1) charging boosters used in connection with storage batteries, which discharge into a line and require the addition of a small voltage to the line voltage to complete the charge of the battery; (2) automatic regulating boosters for constant current or constant voltage, to take care of rapid fluctuations in the line; (3) separately excited differential boosters. Boosters are still used for charging purposes, but automatic battery control by means of boosters has practically disappeared with the disuse of regulating batteries.

Alternating-Current Regulation. Although the storage battery is a direct-current apparatus it has found some application in the past to the regulation of alternating-current systems. If the distribution system is alternating-current, but the load direct-current, the application of the battery may be at the point where the load is required and may consist of the usual arrangement of batteries. If, however, the load is alternating-current, conversion apparatus, such as motor generators or synchronous converters, is necessary in the battery circuit.

6. OPERATING CONDITIONS

a. Safety-Code Requirements

Rules relating to the installation of stationary batteries exceeding 50 volts are provided in the National Electrical Safety Code, Section 13.[10] These rules are as follows:

Rule 130. General

The provisions of this section are intended to apply to all stationary installations of storage batteries using acid or alkali as electrolyte, consisting of cells connected in series with a nominal voltage in excess of 50 volts and connected for service where so installed. [For exception see Rule 132(*b*).]

Nominal battery voltage shall be calculated on the basis of 2.0 volts per cell for lead acid type, and 1.2 volts per cell for alkali type. "End" or "Emergency" cells, held in reserve for connection into circuit only to maintain voltage during discharge, are not included in calculating nominal battery voltage.

Two types of cell construction are recognized in this section, viz:

(1) The sealed type in which the only passage for the escape of gases from the interior of the cell is provided by a vent of effective spray-trap design adapted to trap and return to the cell, particles of liquid entrained in the escaping gases.

(2) The non-seal type, in which gases escaping from the cell may carry entrained particles of liquid into the surrounding atmosphere.

Caution: Smoking, or the use of open flames, or of tools which may generate sparks, should be avoided except when cells are not actively gassing and when prior ventilation has been ample. Sparks from frictional or static electricity should be avoided as they may ignite the gas if discharged close to its source, as at the vent of a sealed-type cell during overcharging. The electrolyte of storage batteries and spray containing electrolyte are somewhat corrosive, particularly when concentrated by evaporation, and contact with body or clothes should be avoided.

Rule 131. Isolation

Storage batteries should be so located as to be not accessible to other than properly qualified persons.

Rule 132. Ventilation

(*a*) *Diffusion of Gases.* Provision shall be made for sufficient diffusion of the gases from the battery to prevent the accumulation of an explosive mixture.

(*b*) *Non-Sealed Type.* Batteries of the non-sealed type shall be located in separate rooms or enclosures so arranged as to prevent the escape into other rooms of objectionable quantities of electrolyte spray. This applies also to batteries of the non-sealed type not exceeding 50 volts nominal voltage if the capacity at the 8-hour discharge rate exceeds 5 kwhrs.

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[10] *National Electrical Safety Code*, 5th ed., Handbook Series of Bureau of Standards, No. 3, 1940.

Rule 133. Insulation

Cells of the non-sealed type shall be supported by suitable insulators such as glass, glazed porcelain, or oil type, or may be grouped and supported on glass or other suitable insulating trays.

Cells of the alkali type in jars of conducting material shall be supported singly, or in groups assembled in non-conducting trays, on porcelain or other suitable insulators.

Cells of the sealed type in containers of insulating material require no additional insulation except as follows:

> Cells in rubber or composition containers, if the total voltage exceeds 150 volts, or cells in glass jars if the total voltage exceeds 250 volts, should preferably be sectionalized into groups not exceeding these voltages, and such groups shall be mounted on trays or racks supported by suitable insulators such as glass, glazed porcelain, or oil type.

Rule 134. Racks and Trays

(*a*). *Racks.* Racks, as required in this section, refer to frames designed to support cells or trays. They shall be substantial and made of:

1. Wood, so treated as to be resistant to deteriorating action by the electrolyte; or
2. Metal, so treated as to be resistant to deteriorating action by electrolyte and provided with non-conducting members directly supporting the cells; or with suitable insulating material on conducting members; or
3. Other similar suitable construction.

(*b*) *Trays.* Trays refer to frames such as crates or shallow boxes usually of wood or other non-conducting material so constructed or treated as to be resistant to deteriorating action by the electrolyte.

Rule 135. Floors

It is recommended that the floors of battery rooms in which large batteries comprised of cells in lead-lined wood tanks are installed be of acid-resistive material, or be painted with acid-resistive paint, or otherwise be protected, where acid is likely to drop and accumulate.

Rule 136. Wiring in Battery Rooms

Wiring shall be in accordance with the requirements of the National Electrical Code (Storage Batteries).

Rule 137. Guarding Live Parts in Battery Rooms

(*a*) *Guarding.* The arrangement of cells and connections shall be such that any two current-carrying parts between which a voltage exceeding 150 volts exists shall be properly guarded if the parts are otherwise so exposed that persons are liable to make accidental contact with both at the same time.

(*b*) *Bare Conductors.* No bare conductor of more than 150 volts to ground shall be placed in any passageway, unless guarded or isolated by elevation.

(*c*) *Details of Guards.* Required guards shall comply with Rule 114.

Rule 138. Illumination for Battery Rooms Enclosing Batteries of the Non-Sealed Type

(*a*) *Type of Lamp.* Storage-battery rooms, in addition to daylight which is desirable when available, should be lighted only by incandescent electric lamps in keyless porcelain or composition sockets, controlled from outside the battery room if practicable.

It is recommended that portable lamps be used only in keyless sockets enclosed in holders provided with substantial guards to prevent lamp breakage and be provided with "hard service" cord.

(*b*) *Heating Appliances.* Heating appliances with open flames or exposed incandescent resistors shall not be installed.

b. Care of Rooms

Aside from the proper installation of the batteries, the care of the rooms constitutes an important factor in their successful operation. Covered cells with sprayproof vents have so largely replaced the older type of open cells that the condition of battery rooms has been greatly improved. Many installations of batteries in rooms with other electrical equipment have been made successfully. Acid spray has been practically eliminated.

Ventilation. The objects in providing ventilation for storage-battery rooms and compartments are three. The first is to carry off the gases which are liberated during the charging period and to some extent by the negative plates at other times, since the hydrogen constituent of the gas forms an explosive mixture with the oxygen of the air. The second is to preserve the insulation of the installation by carrying off the acid spray (if any is present in the atmosphere), as this is destructive to woodwork, most kinds of paint, and insulating materials. The third objective of ventilation is to cool the batteries during the charging periods and when working under heavy loads. This is of particular importance in the case of batteries in closely confined compartments, as on submarines and on certain industrial trucks. Forced ventilation is desirable in all cases where the natural draft is small or unreliable. As the gassing and maximum temperature occur near the end of the charge, it is customary in some installations to provide only moderate ventilation during the early stages of the charge and then increase the ventilation after the battery has received about 75 per cent of its charge. The full ventilation should be continued for a considerable time after the completion of the charge. A 4 per cent mixture of hydrogen in the air is dangerous. The amount present at any place should not be allowed to exceed 2 per cent.

Insulation. In addition to the ventilation, certain other precautions are necessary to preserve the insulation. The supports for the tanks should be porcelain or glass insulators with oil cups. All metal except lead should be protected against acid spray. The overhead wiring should be carried on porcelain insulators which are easily accessible so that they can be wiped off from time to time. The heads of the screws in the insulators should be covered with vaseline. In some large installations the copper bus bars and other cables are inclosed in a lead sheathing. The floors should be of waterproof material with drain at the lowest point so that they can be flushed with the hose. After the flushing, the floors should drain quickly and dry without water pockets.

c. Record Forms

Accurate records of the performance of the large stationary batteries and certain of the smaller batteries, such as motive-power and train lighting batteries, are desirable. The records indicate sources of trouble in the early stages, and they provide the necessary data for comparison of different makes and types, as well as for making an accurate computation of the cost of operation. The forms to be used will naturally depend upon the service and to some extent upon local conditions, but the following have been in successful use and are given by way of illustration.

The first (Form 1) is applicable to the batteries in industrial trucks and tractors. It was used at a large shipping depot during the war. The second (Form 2) is for a battery in stationary service. The third form (Form 3) is for a floating battery and includes the readings that should be made at the close of each equalizing charge. Form 4 is for Edison batteries.

d. Costs of Operation

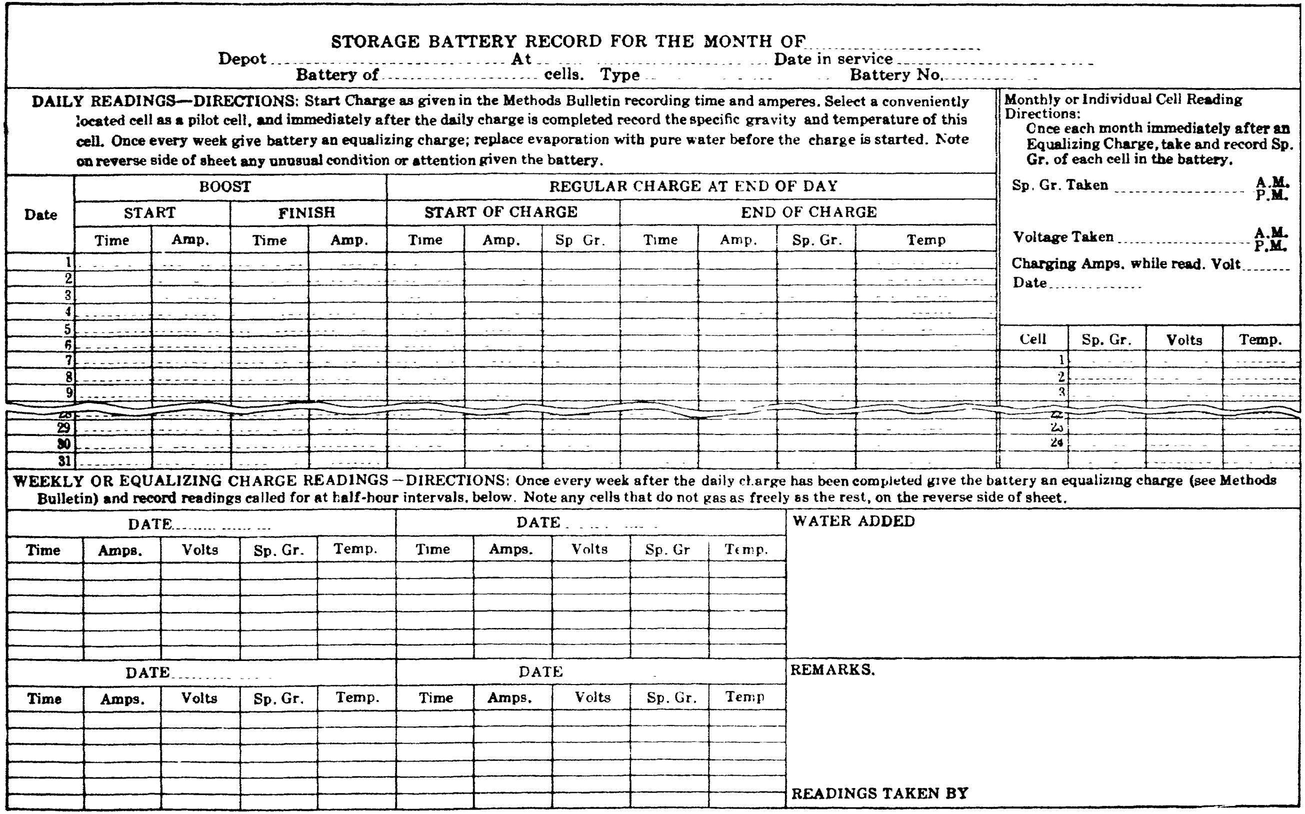
It is often important to make an accurate estimate of the cost of battery operation on trucks, tractors, or vehicles, and an outline of the general method is given below.

An estimate of the cost of operation is usually made for the purpose of determining the economy of a battery installation or of comparing one type of battery with another, to meet a given condition of service. In making such an estimate, the following items must be taken into consideration:

Equivalent batteries must be compared, that is, batteries having approximately the same watt-hour capacity at the service rate of discharge.

Interest must be paid on the investment, which is the cost of the initial battery and the renewals.

Depreciation is the amount of the capital investment to be written off per year, and is equal to the total investment in the battery divided by the number of years for which the cost of operation is to be estimated. At the close of the period, the battery last in service may have a small scrap value. The amount



STORAGE BATTERY RECORD FOR THE MONTH OF..................

Depot.............................. At.............................. Date in service..............................

Battery of.................. cells. Type.................. Battery No..............

DAILY READINGS—DIRECTIONS: Start Charge as given in the Methods Bulletin recording time and amperes. Select a conveniently located cell as a pilot cell, and immediately after the daily charge is completed record the specific gravity and temperature of this cell. Once every week give battery an equalizing charge; replace evaporation with pure water before the charge is started. Note on reverse side of sheet any unusual condition or attention given the battery.

Date	BOOST				REGULAR CHARGE AT END OF DAY						
	START		FINISH		START OF CHARGE			END OF CHARGE			
	Time	Amp.	Time	Amp.	Time	Amp.	Sp Gr.	Time	Amp.	Sp. Gr.	Temp
1											
2											
3											
4											
5											
6											
7											
8											
9											
28											
29											
30											
31											

Monthly or Individual Cell Reading Directions:

Once each month immediately after an Equalizing Charge, take and record Sp. Gr. of each cell in the battery.

Sp. Gr. Taken.................. A.M. P.M.

Voltage Taken.................. A.M. P.M.

Charging Amps. while read. Volt..........

Date..............

Cell	Sp. Gr.	Volts	Temp.
1			
2			
3			
22			
23			
24			

WEEKLY OR EQUALIZING CHARGE READINGS—DIRECTIONS: Once every week after the daily charge has been completed give the battery an equalizing charge (see Methods Bulletin) and record readings called for at half-hour intervals, below. Note any cells that do not gas as freely as the rest, on the reverse side of sheet.

DATE..............					DATE..............				
Time	Amps.	Volts	Sp. Gr.	Temp.	Time	Amps.	Volts	Sp. Gr	Temp.

WATER ADDED

DATE..............					DATE				
Time	Amps.	Volts	Sp. Gr.	Temp.	Time	Amps.	Volts	Sp. Gr.	Temp

REMARKS.

READINGS TAKEN BY

FORM 1. Record sheet adapted for use with a truck or tractor battery.

REPORT ON BATTERY PLANT

Plant of .... At ....

Number of Cells .... Type ....

Temperature of electrolyte .... °F. **of battery room** .... °F. Charging Current .... **amperes.** Voltage **readings to be taken if possible at end of charge with current still flowing. Take gravity readings immediately** after voltage **readings. If on regulation** during readings, current **fluctuations were from** .... amp. charge to .... amp. discharge

POSITIVE SIDE									NEGATIVE SIDE									
Cell	**Volts**	**Sp. Gr.**	Cell	Volts	Sp. Gr.	Cell	Volts	Sp. Gr	Cell	Volts	Sp. Gr.	Cell	Volts	Sp. Gr.	Cell	Volts	Sp. Gr.	REMARKS
1			41			81			1			41			81			
2			42			82			2			42			82			
3			43			83			3			43			83			
4			44			84			4			44			84			
36			76			116			36			76			116			
37			77			117			37			77			117			
38			78			118			38			78			118			
39			79			119			39			79			119			
40			80			120			40			80			120			

Specific Gravity Readings by .... A.M. P.M. .... (Date)

Voltage Readings by .... A.M. P.M. ....

Ampere Watt Hour Meter Reading .... Charge .... Discharge Constant of Meter ....

Water added to replace Evaporation .... (Date) ....

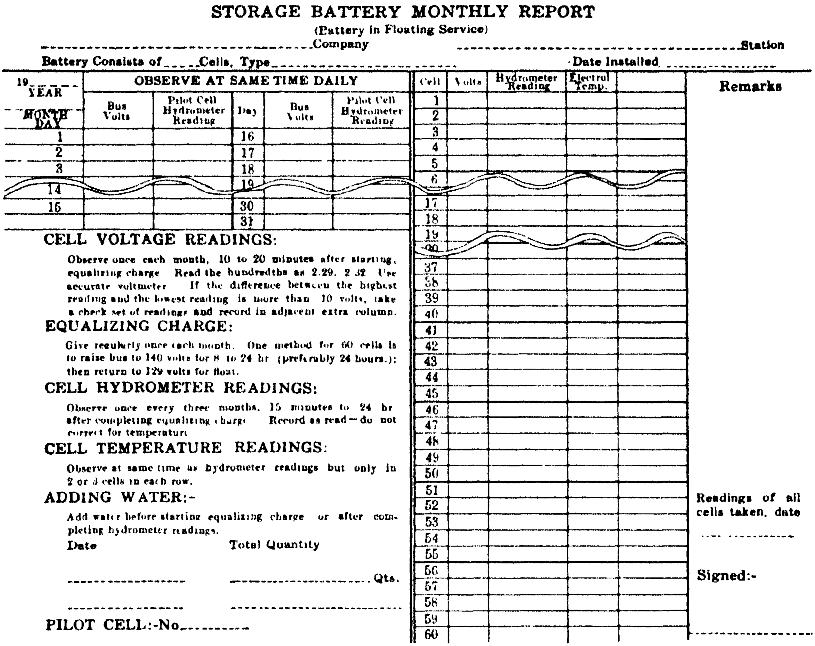
Cells late in gassing on overcharge, Positive side ....

....

Cells late in gassing on overcharge, Negative side ....

....

Form 2. Record sheet for a stationary battery.



STORAGE BATTERY MONTHLY REPORT

(Battery in Floating Service)

________________Company ________________Station

Battery Consists of____Cells, Type________________ Date Installed________

19____ YEAR	OBSERVE AT SAME TIME DAILY				
MONTH DAY	Bus Volts	Pilot Cell Hydrometer Reading	Day	Bus Volts	Pilot Cell Hydrometer Reading
1			16		
2			17		
3			18		
14			19		
15			30		
			31		

Cell	Volts	Hydrometer Reading	Electrol Temp.		Remarks
1					
2					
3					
4					
5					
6					
17					
18					
19					
20					
37					
38					
39					
40					
41					
42					
43					
44					
45					
46					
47					
48					
49					
50					
51					Readings of all cells taken, date
52					
53					________
54					
55					
56					Signed:-
57					
58					
59					
60					________

CELL VOLTAGE READINGS:

Observe once each month, 10 to 20 minutes after starting, equalizing charge. Read the hundredths as 2.29. 2.32. Use accurate voltmeter. If the difference between the highest reading and the lowest reading is more than 10 volts, take a check set of readings and record in adjacent extra column.

EQUALIZING CHARGE:

Give regularly once each month. One method for 60 cells is to raise bus to 140 volts for 8 to 24 hr (preferably 24 hours.); then return to 129 volts for float.

CELL HYDROMETER READINGS:

Observe once every three months, 15 minutes to 24 hr after completing equalizing charge. Record as read—do not correct for temperature.

CELL TEMPERATURE READINGS:

Observe at same time as hydrometer readings but only in 2 or 3 cells in each row.

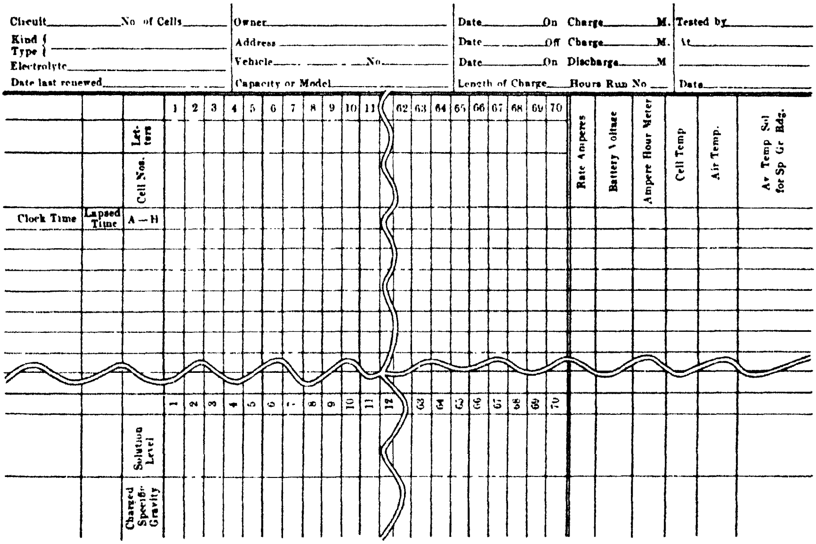
ADDING WATER:-

Add water before starting equalizing charge or after completing hydrometer readings.

Date	Total Quantity
________	________ Qts.
________	________

PILOT CELL:-No.________

FORM 3. Record sheet for a battery in floating service.



Circuit________No. of Cells________

Kind / Type ________

Electrolyte________

Date last renewed________

Owner________

Address________

Vehicle________No.________

Capacity or Model________

Date________On Charge________M.

Date________Off Charge________M.

Date________On Discharge________M

Length of Charge____Hours Run No.____

Tested by________

At________

____

Date________

		Letters	1	2	3	4	5	6	7	8	9	10	11	62	63	64	65	66	67	68	69	70	Rate Amperes	Battery Voltage	Ampere Hour Meter	Cell Temp	Air Temp.	Av Temp Sol for Sp Gr Rdg.
		Cell Nos.																										
Clock Time	Lapsed Time	A — H																										
			1	2	3	4	5	6	7	8	9	10	11	12	63	64	65	66	67	68	69	70						
		Solution Level																										
		Charged Specific Gravity																										

FORM 4. Record Sheet for Edison batteries.

of money set aside each year for depreciation is a sinking fund to amortize the debt.

The **watt-hour efficiency** of the battery is to be used in computing the costs of power for charging.

The **life** is the period of useful service, usually expressed in years.

The quantity of **electrolyte** is that required for renewal, or to replace losses by leakage, etc.

The quantity of **water** is that required to replace the losses by gassing on charge, that is, the quantity decomposed by the ampere-hours of charge exceeding 100 per cent of the previous discharge. It is, therefore, dependent upon ampere-hour efficiency of the battery.

The quantity of **power** required is that for charging, expressed in kilowatt-hours.

Cleaning for lead batteries includes renewal of wood separators, trays, and minor parts. This is seldom required now.

Labor is that required for normal maintenance. It depends on the size and kind of battery.

7. DISMANTLING AND ASSEMBLY OF LEAD-ACID TYPE

First, clean the top of the battery thoroughly.

Before starting to dismantle the battery, make a sketch or diagram showing the relative locations of cells, intercell connectors, terminals, and any other data necessary to insure the correct assembly.

a. Removal of Connectors

Connector Puller. Remove the filling plug on the cell to be dismantled and place the puller in position. With the puller vertical, press the plunger down gradually until the connector is free from the post. This method is quick and easy, eliminates boring out, but necessitates trimming the posts for reassembly of the cell.

Boring Out. Bore out the connector, using a brace and bit. The bit may be either a twist drill or a wood bit, the latter preferred, which should be at least as large as the post, usually $\frac{5}{8}$ inch (1.6 cm.) or $\frac{3}{4}$ inch (1.9 cm.). Before boring, the bit should be centered carefully on the connector. The hole should be bored to a depth of about $\frac{3}{16}$ inch (0.5 cm.). The filling plug should be in position while boring out, to prevent lead chips falling into the cell (see Fig. 95). When the hole has been bored to the proper depth, the connector will seem loose and the joint between the connector and the post can be seen. After boring out the connector, insert a screw driver between the underside of the connector and the sealing nut, if there is one, and pry firmly but gently on the connector. Repeat this operation on the other side of the post and continue until the connector is free (see Fig. 96). If there is no sealing nut which can be used as a brace for prying up the connector, place a heavy strip of wood across the top of the cell next to the post and use this as a brace. Care should be taken not to put pressure on the cover. If the boring out of the connector is not done properly—for instance, if the hole is not concentric with the post—heat can be applied gradually to the connector until the lead is softened sufficiently to permit pulling up the connector with a pair of pliers.

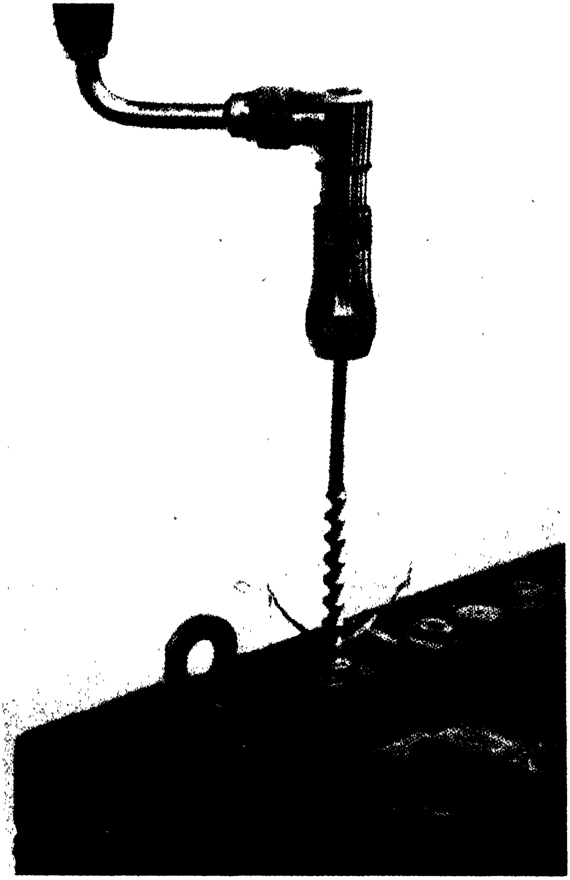


FIG. 95. Boring out the connector. The bit must be carefully centered.

In all of the above operations, care should be taken not to short-circuit the cell by allowing pliers or other tools to come in contact with both posts at the same time.

b. Removal of Cell

Grasp each post with a pair of pliers and pull vertically (see Fig. 97). If the jar sticks, a hot putty knife may be inserted around the edges. This will usually loosen the jar so that it may be pulled out easily. After the jar has been pulled out, rest it on the edge of the tray so that the pliers may be removed and the cell lifted by the hands to a position for the next operation.

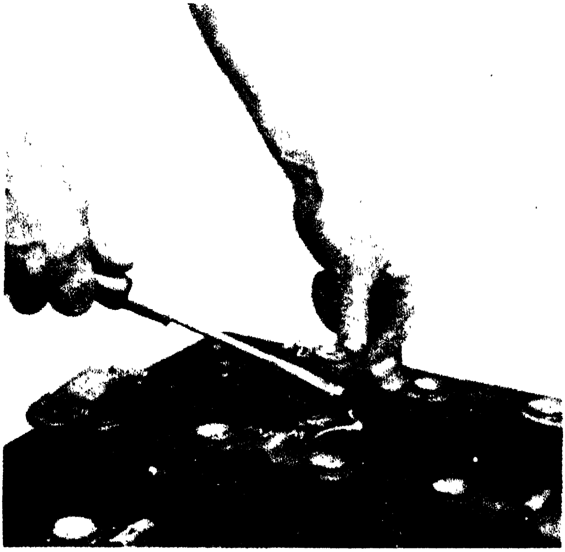


FIG. 96. Prying off the connector after boring it out. Care must be taken not to break the cover.

The sealing nuts, if used, should be removed next by means of a special wrench, unless the element and cover are to be removed together. If such a wrench is not available, use a pair of pliers, and only as a last resort use a monkey wrench or a pipe wrench (see Fig. 98). Note the shape of pliers used. The sealing nuts are sometimes held in place by scoring the threads on the post with a prick punch.

c. Removal of Element

With the filling plug out, blow the gases out of the cell. This is to reduce to a minimum the possibilities of an explosion. Warm the outside of the jar at the top with a flame and then insert a hot putty

FIG. 97. Removal of cell from the battery. If the jar sticks, a hot putty knife may be inserted around the edges.

FIG. 98. Removal of the sealing nut.

knife around the inner edge of the jar, melting out the compound to a depth of about $\frac{1}{2}$ inch (see Fig. 99). This operation should be performed as rapidly as possible, as the compound cools quickly. Next, place the finger in the filling aperture and lift vertically on the cover. If the cover does not pull readily, remove all of the sealing compound possible by means of the hot putty knife and reheat the sides of the jar before again pulling on the cover. When smaller types of batteries are disassembled, it is usually convenient to remove the element and the cover together.

After the cover has been removed, clean it thoroughly and wipe off the edges, where sealing compound is to be poured, with a cloth that is damp with dilute ammonia or bicarbonate of soda.

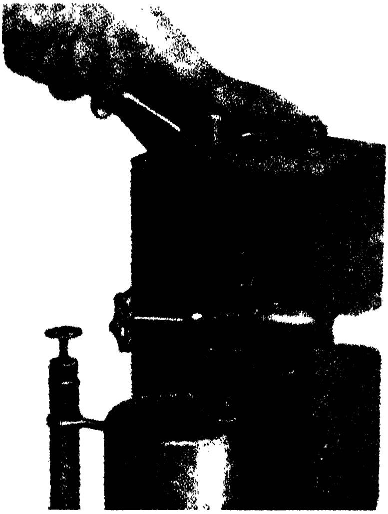


FIG. 99. Cutting out the cover with a hot putty knife. Before doing this, the gases should be blown out of the cell to avoid a possible explosion.

Place the jar, with the cover removed, on the floor with one foot on each side and grasp each post with a pair of pliers. Pull the element upward while holding the jar with the feet (see Fig. 100). When the element is nearly out, place it slightly out of plumb on the top of the jar and let it drain for about five minutes. The element should not remain out of the jar for more than fifteen minutes because of injurious heating. Should the negative plates begin to dry out and heat, sprinkle them with water until they can be taken care of.

d. Removal of Separators

Place the element on the edge of a table or bench. When it is necessary to use the separators again, it is desirable to use a special tool called a "separator inserter." The broad side is used next to the negative plate to loosen the separators so that they can be pushed and pulled at the same time from between the plates. In case the separators are not to be used again, a putty knife may be inserted between each separator and the negative plate to loosen them and then they may be pushed from the top and pulled from the bottom until free from the plates.

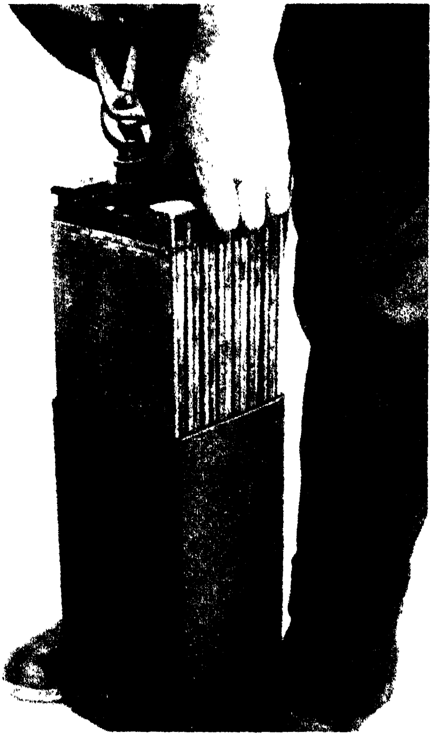


FIG. 100. Removal of the element from the jar.

Separate the positive and negative groups of plates and soak each of them in water for about twenty minutes. They are then ready to be placed away on a shelf if the battery is to be stored.

Pour the electrolyte out of the jar and wash the jar with distilled water.

e. Assembly of a Cell

To install new separators, place the elements on edge as for removal of separators. Insert the new separators from the bottom. The smooth side of the wood separator is to be placed next to the negative plate and the perforated rubber separator between it and the positive plate. (The Exide-Ironclad battery has only a smooth separator of wood or porous rubber between plates.)

Place the element on edge, projecting slightly over the edge of the bench, and place jar over the plates. Then lift the jar and plates in this position (similar to position for draining the element) to the floor and push element into position. The electrolyte may be in the jar at this time, but it is preferable not to have it so. The inside edge of the jar at the top should be cleaned of compound and wiped with a cloth dampened with dilute ammonia or soda after the element has been inserted as above. It is necessary to have the jar and cover free from all acid, as otherwise the compound will not adhere properly to the surfaces. Care should be taken that no ammonia or soda is allowed to get into the electrolyte.

Before putting on the cover, place the soft-rubber gaskets, if used, over the posts. The cover should be replaced while the jar is cold, unless it will not fit readily, in which case warm the outside of the jar with a flame until it becomes flexible enough to allow the cover to fit properly. Care should be taken not to burn the jar. Heat the compound and pour it into position, then trim with a hot putty knife until a level, smooth surface is obtained. Clean off all compound not needed to seal the cover. Replace the cell in the tray in the same position as it was in the beginning.

If there is electrolyte in the cell, first clean the posts with dilute ammonia or soda to neutralize the acid and allow them to become dry before doing anything further.

Trim each post, if a connector puller has been used, until its top is about $\frac{3}{16}$ inch below the top of the connector. This may be done by means of end-cutting pliers. Clean off the top and sides of the posts thoroughly. A file brush is good for cleaning the top, and gas pliers for cleaning the sides of the posts.

Always have the cover firmly in place and sealed before putting on the connector. If the intercell connector is not of the right length, it should be adjusted, and in no case should it be forced into position over the posts, as the jar or cover may be broken on account of undue strains.

f. Lead-Burning

This is a welding process for making a good mechanical and electrical connection between the plates and the strap and between the posts and connector. Burning is done by means of illuminating gas and oxygen, acetylene and air, hydrogen and compressed air, or an electric arc. Illuminating gas and oxygen is the most convenient of the gas methods. The gas is taken from the supply main and the oxygen from a storage tank. Care must be taken to adjust the burner properly and to prevent explosions. If the tip of the burner becomes stopped, the oxygen will flow into the gas main, owing to its higher pressure, and an explosion may follow. To prevent such an occurrence, a safety device of some sort must be used in the gas main or at each burner. Figure 101 shows a simple device which is in use at a service station for the protection of a number of burners. A similar device is obtainable in the market. The pressure of the oxygen should be about 4 to 5 pounds when used with illuminating gas. The reducing valve on the oxygen tank is usually of the diaphragm type, provided with a gage for indicating the pressure on the outlet side. The design of the valve is such as to maintain a practically constant pressure when a number of burners are being used. The pressure of oxygen is to be set at approximately the right amount by the valve on the tank when the reducing valve is partly open. The fine adjustment of the pressure is then made by opening or closing the reducing valve. Some valves are so constructed that the adjusting screw is to be turned to the right to open

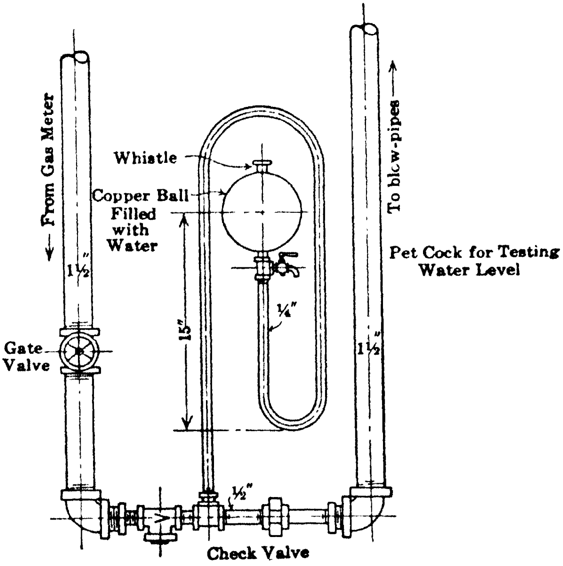


FIG. 101. Device for protecting the gas main, if the tip of the burner becomes clogged. The oxygen, which is at higher pressure than the gas, cannot flow past the check valve or a flame run back to the meter and cause an explosion.

the valve or increase the pressure. For this reason it is sometimes thought that the valve is being opened when in reality it is being closed. Use a reducing flame, as it is not desirable to oxidize the lead. Work with the tip of the inner blue flame and use a rotary motion, working from the center of the post upward and outward. The top of the post should be melted first and then fused to the wall of the hole in the connector; then lead from a piece of burning strip can be run in until the joint is flush with the top of the connector. Finish with a file and file brush. All parts must be thoroughly cleaned of dirt or foreign matter, as absolute cleanliness is necessary for successful work. Figure 102 illustrates the burning process above described.

FIG. 102. Lead burning with a flame of illuminating gas and oxygen. The cells must be blown out, the vent plugs removed, and the top of the battery covered with a damp cloth. Oxygen tank should have reducing valve, pressure at burner not exceeding 5 pounds.

The electric-arc outfit consists of a carbon holder, with connecting cable and clamp and a carbon rod about $\frac{1}{4}$ inch in diameter. The battery on which work is to be done is usually used as a source of current. From two to four cells are required, according to the state of charge. Figure 103 illustrates this method of burning. The clamp is attached to an intercell connector a sufficient number of cells away to give the proper voltage. Care should be taken to have a good connection between the clamp and connector. The carbon rod should be sharpened to a point and project about 2 inches beyond the clamp. The carbon should be brought to a bright glow by contact with the post on which work is being done. The same process as described for gas is to be followed for making the joint. The carbon should be worked with a rotary motion from the center of the post outward without drawing an arc. The carbon holder should be cooled occasionally by plunging it, with the carbon, into a pail of water. After a time the carbon may fail to work properly, owing to a film of lead oxide, which may be removed by a file or scraping with a knife. It is necessary that the operator use a pair of dark glasses to protect his eyes. If the battery is not available as the source of current, a 6-volt "starting" battery may be employed. In this case one terminal is connected to the clamp of the carbon holder and the other to the connection to be burned.

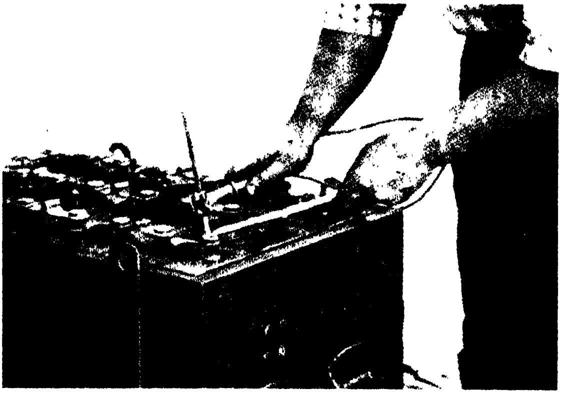


FIG. 103. Lead burning with the electric arc. The battery is being used as the source of current, voltage required 4 to 8 volts. Operator should wear dark glasses and the top of the battery should be covered with a damp cloth as in Fig. 102.

A device for lead-burning called the "pyrotip," operating on alternating current, has been put on the market in recent years. A small portable transformer reduces the 110-volt circuit to a suitable voltage. The carbon is large in diameter and terminates in a sharp point, which enables the operator to apply the heat at any place that he may desire. The alternating current may be passed through the cell without harm.

When a joint is well burned, the metal of one part fuses into the metal of the other part. This insures mechanical strength and good electrical conductivity. Imperfectly burned joints when examined under the microscope generally show void spaces, or dross. Figure 104 is a photomicrograph of two pieces of lead-antimony alloy showing complete union along the line of the burn. To the right, the alloy contains 8 per cent antimony and to the left, 4 per cent.

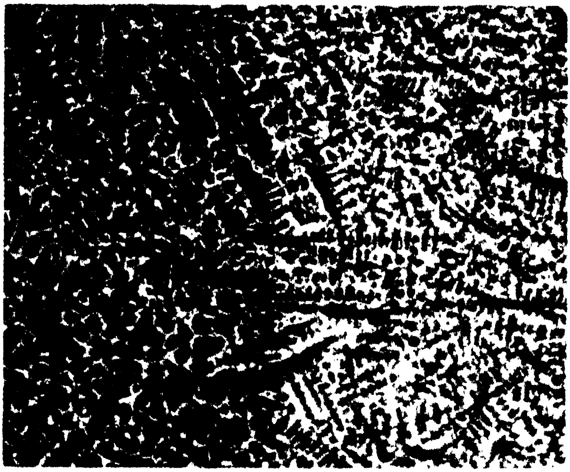


FIG. 104. Example of lead burning. A 4 per cent alloy has been burned to an 8 per cent alloy.

8. SOURCES OF TROUBLE

The most frequent sources of trouble in connection with batteries are as follows:

a. Overcharging

Overcharging produces corrosion of positive grids and excessive gassing which loosens active material in the plates, particularly the positives. This material, sifting down between the separators and the plates, is deposited in the bottom of the jar as a fine brown sediment. Overcharging also increases the temperature of the battery and in some cases may carry it to excessive temperatures which are destructive both to the plates and to the separators. Some cases of buckling of the plates are to be attributed to overcharging, although this is by no means the only cause of buckling of the plates. Overcharging, which is accompanied by excessive gassing, results in a needless loss of water, requiring constant attention to keep the cells filled to the proper level with electrolyte. Occasional overcharging is beneficial, but habitual overcharging decreases the period of useful service which the battery can give.

b. Undercharging

Consistent undercharging of the battery results in a gradual running down of the cells. This is indicated by progressively lower values of the specific gravity readings and a tendency of the plates to become somewhat lighter in color. The sediment deposited in the bottom of the jar when undercharging has been prolonged is usually a fine white powder, consisting principally of lead sulphate. Some of this material is deposited each time the cell is recharged. Consistent undercharging generally results in one or more of the cells becoming exhausted before the others, and in some cases these may become reversed by the other cells of the battery. When this occurs the most obvious remedy is to charge the battery until all the cells are again in normal condition. Equalizing charges should be a part of the maintenance schedule of all stationary batteries. Insufficient charging is one of the most common causes of buckling of the plates (see Fig. 105). The lead sulphate occupies more space than the original material and an excessive amount of it strains the plates.

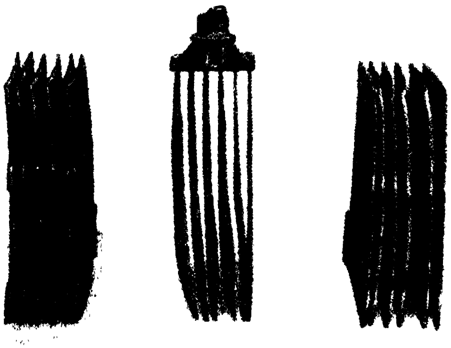


FIG. 105. Buckled plates. There are a number of causes for this, but perhaps the most common is undercharging.

c. Difficulties with the Charging System

Difficulties arising in the operation of starting and lighting batteries may in some cases be traced to difficulties with the charging system. The battery is generally held accountable for its own failures and those of the charging system also. Under normal conditions of operation of the car, the battery should begin to charge when a speed of about 10 miles per hour has been reached. Unless the generator cuts in at the proper speed, the battery will not receive its normal amount of charge. There is also the possibility of grounded circuits or partial grounds, which drain the battery and keep it in a more or less discharged condition. This can only be detected by testing the different parts of the circuit with a voltmeter. The charging system is always provided with some means of regulation which prevents the battery from receiving excessive currents when the car is being operated at high speeds.

d. Corroded Terminals

Corroded terminals often prevent the battery from delivering sufficient current for starting an automobile engine. This is because the products of the corrosion are non-conducting substances which form a layer between the terminal of the battery and the clamp connector which may be connected to it. This film will not ordinarily interfere with the charging of the batteries or the use of the batteries for lighting lamps on the car but will make the resistance too great for the passage of the large currents required during the starting period. The products of corrosion should be removed and the parts cleaned with a dilute solution of ammonia to neutralize the acid and then covered with vaseline.

e. Cracked or Broken Jars and Cases

Cracked or broken jars of inclosed batteries can ordinarily be detected by leakage of electrolyte through the tray, or, if the crack is slight, by the necessity of periodically adding more water to the cell having a cracked jar than to the others. In such a case, the electrolyte of the cell will gradually become diluted by the additions of water, and this will result in diminishing the capacity of the cell as well as in the destruction of the wooden box containing the cells. The obvious remedy is to replace the broken jar as soon as it is discovered, and to adjust the specific gravity of the electrolyte in the battery to the proper amount at the conclusion of full charge.

Cracks in the partitions between cells in composition cases result in the gradual discharge of one or two cells in the battery, the leakage path between the cells being through the electrolyte. This occurs more frequently in batteries which are eighteen months or more old. The first symptom noticed is usually the failure of the battery to hold charge. The cells are in a state of unequal charge. Sometimes the position of the crack can be determined by running the corner of a hot putty knife along the top edge of the partition. Cases having this defect should be replaced or the battery discarded.

f. Short Circuits

Short circuits within the cells may be caused by a breakdown of one or more of the separators between the positive and negative plates; by the accumulation of sediment in the bottom of the jars; or, in rare instances, by the formation of a tree-like structure of lead from the negative to the positive plates. Treeing may result from two causes: (1) Sediment, brought to the top of the electrolyte by gas, settles on the top of the plates and bridges over the tops of the separators. This is sometimes called "mossing." (2) The presence of certain materials in the grids, such as cadmium, which cause the growth of trees at the side or bottom of the element. Pure lead grids have a tendency to grow trees from the negative to positive plates. The presence of antimony in the grids, however, counteracts the tendency to treeing.

Wood separators which have become thin and perforated should be dried and examined for a silvery appearance. If this is found, it is likely that manganese is the cause of their failure.

The evidences of short circuits within the battery are: (1) continued low readings of the specific gravity even though the battery is receiving a normal amount of charge; (2) rapid loss of capacity after a full charge, and (3) low open-circuit voltage. The remedy for this condition is to disassemble the cells, wash out the accumulated sediment, and replace the old separators with new ones. The sediment in the bottom of the jars conducts metallically, and, if enough of it accumulates to touch the bottoms of the plates, a short circuit inevitably develops.

g. Worn-Out Plates

Worn-out plates are ordinarily detected by a marked decrease in the capacity of the battery when it is receiving an adequate amount of charge. If the solution in the cells quickly rises to its proper value when the cells are on charge, but only a small capacity can be obtained on discharge, the battery is worn out. This may be due either to age or to poor material used in the construction of the plates. There is no remedy except to replace the plates.

h. Electrolyte below the Tops of the Plates

If the electrolyte is allowed to remain consistently below the top of the plates, an abnormal sulphation (see Fig. 106) takes place and the plates crumble. This is generally the result of neglecting to add the necessary water to replace evaporation. Unless the injurious effects have gone too far, it is sufficient to fill the cells with water to the proper level and allow the battery to continue its normal operation.

Electrolyte should not be added under any circumstances unless it is known that electrolyte has been lost from the cell. Whenever it is necessary to add acid to the cells, the acid should be in diluted form. The cells should be placed on charge and the concentration of the electrolyte within the cells adjusted to the proper value before the conclusion of the charge.

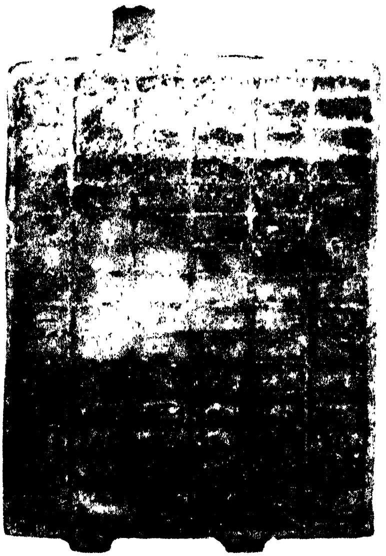


FIG. 106. Negative plate sulphated near the top, showing the effect of too low a level of the electrolyte.

i. Freezing

In some cases the freezing may be very destructive to the plates, but it is by no means certain that freezing will injure the battery. When freezing occurs, water crystals separate from the body of the electrolyte. These water crystals cause some expansion of the active materials of the plates, particularly if the pores of the plates are clogged with lead sulphate as a result of the discharged condition of the battery. The plates may become buckled and the active material may be pushed out of the grids. Experiments with small plates in a fully charged condition carried to a temperature below the cryohydric point, so that the entire mass of the electrolyte was solid, showed no destructive action on the plates. Under ordinary circumstances, however, freezing will only occur in the case of batteries which are in a discharged condition, and the results of freezing in such a case may destroy the plates.

j. Impurities in the Solution

Impurities in the solution may come from impurities initially present in the sulphuric acid, or in the plates, or from the container, or they may be added accidentally as, for example, by the use of impure water to replace losses caused by charging and evaporation. Storage batteries are particularly sensitive to certain kinds of impurities, and these have been described in Chapter III. Perhaps the most common of the metallic impurities in the storage battery electrolyte is iron. Iron produces discharge of the plates by being oxidized to the ferric condition at the positive plate and reduced to the ferrous condition at the negative plate. During this process the iron diffuses from one plate to the other, but it is not deposited upon either electrode. Unless the amount of impurities present in the electrolyte is serious, they can generally be eliminated by pouring out the electrolyte from all the cells and flushing them with distilled water, which in turn is also poured out. The cells are then to be filled with pure dilute electrolyte, which is adjusted to the proper specific gravity at the conclusion of a full charge.

k. Chipping of the Active Material

When blocks of the active material break out of the plate, as shown in Fig. 107, the effect may be referred to as chipping. There are a number of possible causes for this effect, which is observed most often with positive plates, but may occur with negatives also. Among these causes are the following: the active material may not have made good contact with the grid; the plate may not have been thoroughly dried; the plate may have been overpasted and the surface blown off by the formation of gas during charge; the active material may have been too hard and have cracked when the plate was dried or after formation; excessive sulphation may have cracked the active material. In most cases the cause of the defect is to be found in the plate itself. The obvious remedy is to replace the defective plates with those of better quality.

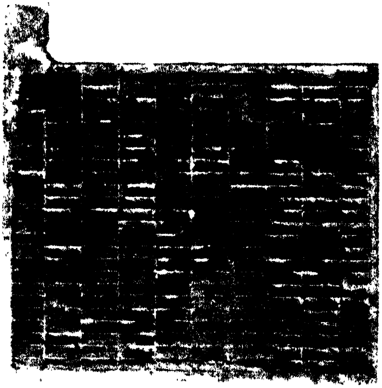


FIG. 107. Positive plate showing loss of active material as a result of overpasting.

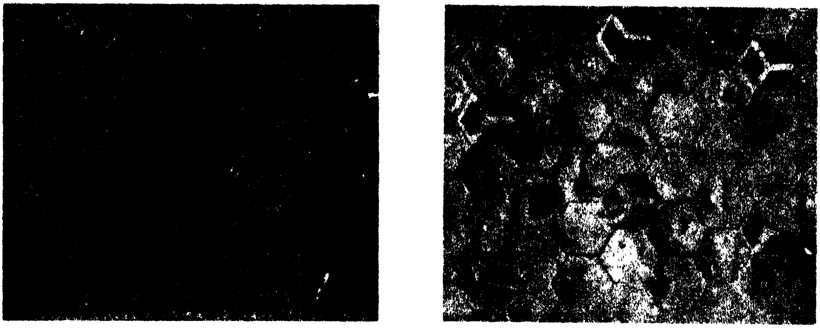
l. Sulphation.

The word "sulphation" has been used in several senses and this has led to some confusion. In general it means the formation of lead sulphate on the surface and in the pores of the active material of the plates. Sulphate forms as a natural part of the process of discharge and this fact is expressed by the chemical formula for the reactions discussed in Chapter IV. This sulphate is finely crystalline and easily reduced by the charging current. Sulphation in this sense is a necessary part of the operation of the battery and is not a source of trouble.

Lead sulphate is also formed as a result of local action or self-discharge of the plates. This is brought about by parasitic currents or by the action of the acid solution on the materials of the plates. The rate at which sulphation, in this sense, proceeds depends on the concentration and temperature of the electrolyte. It is a mistake to add acid to a cell unless it has been definitely determined that the cell when fully charged is deficient in this respect, otherwise the specific gravity will rise to an abnormally high value when the charge is completed and the sulphation may be expected to increase. The lead sulphate formed as a result of local action is easily reduced by the charging current, unless this is neglected, although the crystals are probably coarser than those formed as a result of discharging the battery. Certain impurities in the electrolyte increase the rate of sulphation of the plates.

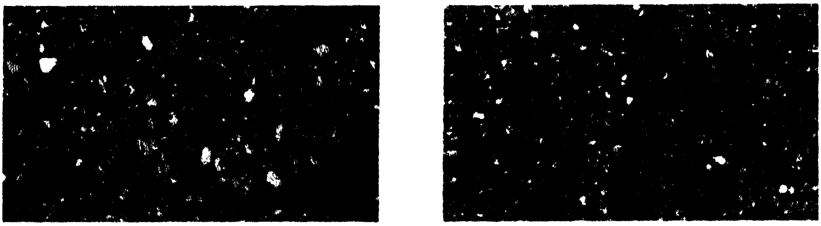
The third and perhaps most common use of the word sulphation applies to the large crystals or crusts of lead sulphate which may form on the plates as a result of neglect or misuse. Excessive sulphation of this kind is difficult to reduce and may injure the plates. As the pores of the plates become clogged with the sulphate the active material may be pushed out of the grids and the plates may buckle. The active material of the positive plates which are sulphated is frequently light in color and white spots of sulphate appear, but the color is not always a safe criterion. It may be quite dark and the presence of excessive sulphate is revealed by a hard, rough surface and the gritty feeling of the material when rubbed between the fingers. Sulphated negatives likewise are hard, expanded and gritty. They do not show a good metallic streak when stroked with a knife. Sulphation in this sense is the result of some form of abuse, as (1) allowing the battery to stand in a discharged condition for a considerable timé, (2) neglecting to make repairs when evidence of trouble within the cells becomes apparent, (3) filling the cells with electrolyte when water should have been used, (4) operating the battery at excessive temperatures, (5) persistent undercharging. Excessive sulphation can be avoided with reasonable care and it is doubtless true that the liability to sulphation of lead batteries has been exaggerated by those exploiting cures which in reality may aggravate the trouble.

When a battery stands in a discharged state the sulphate seems to harden and become more dense. Some have thought that a molecular change takes place, but of this there is no very direct evidence. The crystals of sulphate grow larger expanding the active material and in this state are more difficult to reduce by the charging current. Lead sulphate is sparingly soluble in the sulphuric acid electrolyte. The solubility increases at higher temperatures. The temperature fluctuations to which a battery may be subjected as it stands idle play an important part, therefore, in forming this hard sulphate. When the temperature of the battery is increased even slightly the smaller crystals of lead sulphate dissolve and when the temperature falls again this lead sulphate crystallizes out slowly. Some of it doubtless increases the size of crystals already present, and it is well known in general that slow crystallization results in large crystals. As a result of such temperature cycles the large crystals grow at the expense of the smaller ones. Figure 108 shows sections of positive and negative plates which were allowed to stand in a discharged condition for two years. Portions of these plates are magnified to show the crystals. Those on the posi-



(*a*) Positive, showing a fractured grid.

(*b*) Negative, showing separation of the active material from the grid.



(*c*) Magnified image of sulphate crystals on the positive.

(*d*) Magnified image of sulphate crystals on the negative.

FIG. 108. Effects of excessive sulphation of plates that were allowed to stand for two years in a discharged condition.

tive plate are larger than those on the negative plate. This is probably because they grew more slowly. Sections of the active material are pushed out of the grids and the positive grid has been fractured.

Various cures for sulphated batteries have been proposed and some of them have been patented. However, a simple and effective remedy for this condition is to pour out the electrolyte and fill the cells with water. After being allowed to stand for about an hour, the battery may be put on charge at a low rate of current, provided that the voltage at the terminals of the cells is less than 2.3 volts per cell. The resistance of the battery will be high at the start and the current initially small, but the current will increase as the sulphate is broken down if the voltage at the terminals is maintained. The cells will take the current as fast as they are capable of being charged, and the process becomes more or less automatic, but the temperature must be watched and the batteries cut off or the current decreased if the temperature reaches 43° C. (110° F.). The charging may also be done by the constant-current method at a low rate. The water which was put in the cells becomes a solution of sulphuric acid as the charge proceeds, and readings of the rising specific gravity can be made. If the final specific gravity obtained after prolonged charging becomes constant at too low a value, more electrolyte should be added. It not infrequently happens that the specific gravity of the electrolyte, initially water, will rise above the normal figure, say 1.300, and this is clear evidence that acid has at some time been added to the cells improperly, that is, when they needed only water.

FIG. 109. Positive, showing sulphation along the lines of the grid.

m. Corrosion of the Grid

This is an effect noticed with the positive plates, a sample of which is shown in Fig. 109. The trouble starts along the lines of the grid, and lines of sulphation appear. The active material becomes insulated from the grid and cannot be charged. This effect may be caused by the active material shrinking when the paste is dried, if the formula for the paste is not right, or it may be caused by the attack of organic matter and certain acids present as impurities in the electrolyte. These include nitric, hydrochloric, and acetic acids. Plates in this condition will not give satisfactory service and must be replaced. Corroded, brittle grids with soft positives and rough gritty negatives are attributed to electrolyte of excessive strength or above a safe operating temperature.

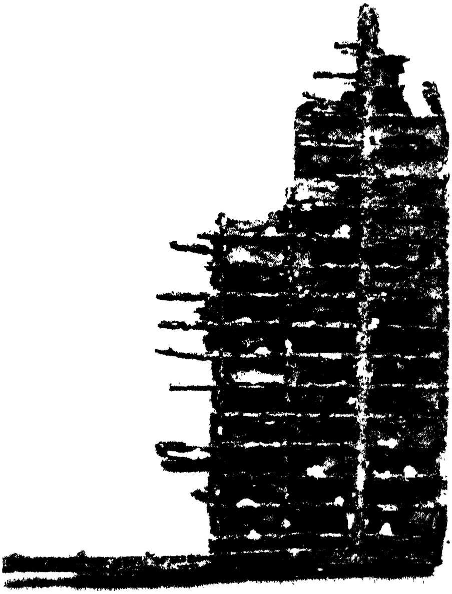


FIG. 110. Corroded grid of a positive plate, showing the effects of formation of the grid.

In aggravated cases, formation of the grid ensues. The grid is converted to lead peroxide in part and becomes very brittle, the active material is completely discharged, and the plate falls to pieces. An example of this is shown in Fig. 110.

FIG. 111. Magnified section of a reversed positive plate. The reversal is complete along the lines of the grid, but in the space between some of the original material may be seen.

n. Reversal

Reversal may be caused by the overdischarge of a cell deficient in capacity when in series with others that have greater capacity or are more fully charged; generally, however, it is the result of charging a battery in the wrong direction, in which case all cells are reversed. In Fig. 111 is shown a positive plate that has been partly reversed. The reversal became complete along the lines of the grid, but in the middle of each section some of the original brown active material can be seen. The active material has become rough. A partially reversed plate, containing both positive and negative active material is subject to strong local action. Sometimes reversal of negative plates of the Planté type is resorted to in order to restore their capacity. The sponge lead of these plates shrinks and solidifies, the plate losing a large part of its capacity. By reversing it to a positive and then again reversing it back to a negative the capacity can be greatly increased. Reversal of pasted-plate cells is not desirable.

o. Growth of Positive Plates

Planté positives gradually shed active material as they are used, and the formation of additional active material takes place. This is made from the underlying lead of the plate. If it takes place irregularly over the surface, growth and buckling result because the lead peroxide occupies more space than the lead from which it is formed. Another cause of growth is said to be the compression to which the lead sheets are subjected when they are rolled. Plates that have grown several inches in length and a less amount in width are occasionally found. Figure 112 shows a positive plate that has grown and a negative plate, the active material of which has shrunk (see next section).

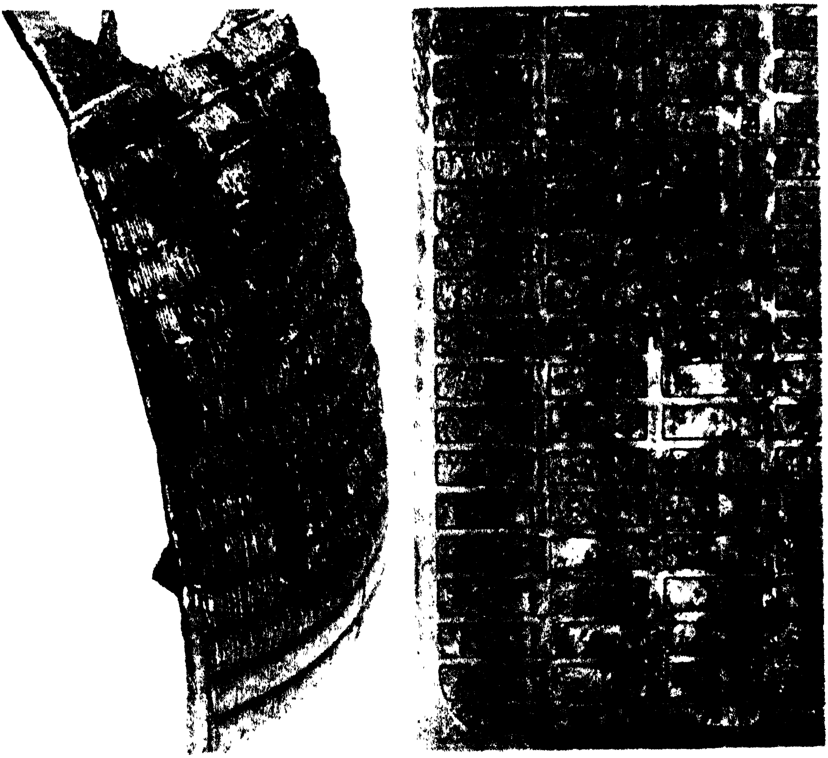
p. Shrinkage of Negatives

The surface of the negative plate is in a state of flux during charge and discharge, and as a result the sponge lead tends to solidify, that is, to shrink. This results in decreased capacity. To counteract this tendency, expanders are.added to the pastes of the negative plates when they are made as described in Chapter II. The active material of Planté plates also shrinks, losing capacity. Various treatments have been devised to retard this effect, and reversal is sometimes resorted to, as noted in the section on reversal.

q. Explosions

The gases liberated during charge are hydrogen and oxygen, which explode with violence if a flame or spark ignites them. Figure 113 shows a double-compartment battery which exploded while on charge because of a bad contact. The force of the explosion has blown out the side of the upper compartment and the seams of the carrying case have opened up along the edges.

Static sparks are usually unexpected and sometimes result in explosions. Sparks are more likely to occur when the atmospheric humidity is low. Several authors have stated that such sparks do not occur if the humidity is above 60 per cent. A person walking on a woolen rug or on insulating floor material, paper running through a printing press, leather belts on motors, contacts of silk, woolen, or fur clothing, moving vehicles on rubber tires and other conditions may result in static charges and sparks. These may seem far removed from battery operation, but battery explosions have been traced to floor materials, leather belts, and silk parachutes. Some battery attendants are instructed



(*a*) (*b*)

FIG. 112. Growth and shrinkage of the active material.

(*a*) Planté positive plate showing results of growth;
(*b*) Pasted negative plate showing abnormal shrinkage.

to ground themselves by touching a grounded metal part before working on a battery.

Sparks from other causes, such as removing clips from battery terminals or accidental short-circuits can usually be avoided by following simple and obvious rules of safety. A charging circuit should be broken before connectors at battery terminals are removed.

The discussion above relates to causes occurring outside the battery or cell, but explosions for which no probable cause can be assigned are not unknown. Some of these point clearly to the cause being within the cell. In one recent case the remaining parts of the cell revealed that corrosion of the positive terminal post, under the cover, had proceeded to the stage where only a small metallic contact remained. No one was near the battery at the time of the explosion, but it occurred at the instant that a heavy load was thrown on the battery. It seems probable that the current burned through the corroded connection above the level of electrolyte and ignited the gas within the cell.

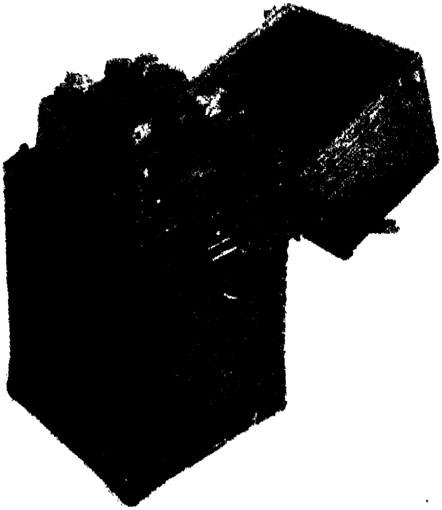


FIG. 113. Storage cells of the double-chamber type, damaged by an explosion of gas

CHAPTER VII

RESISTANCE

1. RESISTANCE OF THE BATTERY AND ITS RELATION TO THE EXTERNAL CIRCUIT

The internal resistance of a storage cell is very small and for many purposes may be neglected entirely. When large currents are required, however, as when an emergency arises in a central station, or when a tractor begins to pull a heavy load, or in cranking an automobile engine, or when a vehicle is climbing a steep hill, the resistance of the battery and its intercell connections becomes more important. In this chapter is given a simple discussion of the applications of Ohm's law and the resistance characteristics of storage batteries.

Every electrical circuit offers some opposition to the flow of electricity through it. This is called resistance, and the unit of resistance is called the ohm. For any direct-current circuit of which the resistance is constant, the current of electricity which flows is proportional to the voltage applied to it. This relation is expressed by equation (1) which is called *Ohm's Law*:

$$I = \frac{E}{R} \tag{1}$$

The current in amperes is represented by I, the voltage in volts by E, and the resistance in ohms by R.

The current flows through the external circuit from the lead peroxide plate to the sponge-lead plate, or in the case of the alkaline battery it flows from the nickel oxide tubes through the external circuit to the pockets containing the iron; that is, the current always flows from the positive to the negative terminal. The current, however, does not begin with one plate and end with another but flows through the cell as well. The resistance of the circuit is therefore not only the resistance of the external circuit but includes the so-called internal resistance of the cell or battery. We may therefore write equation (1) in the following form:

$$I = \frac{E}{R' + b} \tag{2}$$

where R' is the resistance of the external circuit, b the resistance of the cell, E is the total electromotive force of the cell or, as it is sometimes called, the "open-circuit voltage." The value of b varies somewhat with the state of the charge of the cell and other factors. It is highest when the cell is completely discharged. The current I is the same in all parts of the circuit.

Equation (2) may also be written as

$$E = IR' + Ib \tag{3}$$

That is, the total voltage drop is divided into two parts, one of which is the potential difference or voltage drop, IR', across the terminals of the resistance R' due to the current I flowing through it; the other part is within the cell itself. The quantity b is ordinarily so small in storage batteries that the product Ib may be neglected in comparison with IR'. If, however, the current I is very large, the product of Ib may amount to several tenths of a volt. The effect of this is to reduce the useful voltage of the cell.

The power developed in such a circuit is the rate of expenditure of the electrical energy or, in other words, it is the rate of doing work. The work which the electrical current does is proportional to the current, the voltage, and the time. It is expressed by a unit called the joule or the volt-coulomb, designated by W. If the time in seconds is expressed by t, the work done by the electric current is

$$W = IEt \tag{4}$$

If the circuit contains resistance only, the energy of the electric current will be converted into heat. By combining equations (1) and (4)

$$W = I^2Rt = \frac{E^2t}{R} \tag{5}$$

That is, the work done in heating the circuit of R ohms is given by equation (5), from which we may at once obtain the power expended by dividing the equation through by the time, which gives the rate at which the work is done. Letting P represent the total power expressed in watts,

$$P = \frac{W}{t} = IE = I^2R = \frac{E^2}{R} \tag{6}$$

We may consider the complete circuit as made of two parts as before, one external to the battery and the other the internal resistance of the battery itself. The power expended in each part of this circuit, considered as of resistance only, is obtained by combining equations (3) and (6):

$$P = P_1 + P_2 = I^2R' + I^2b = \frac{E^2}{R' + b} \tag{7}$$

The part I^2b is expended in heating the cell and is lost. It should be noted that this loss increases as the square of the current. This factor reduces, therefore, the watt-efficiency of the battery, particularly at high rates of discharge, and limits the useful power which the battery can give.

When several cells are connected in series, the resistance of the battery is the resistance of all the cells added together. If similar cells are connected in multiple, the resistance is reduced by a factor one divided by the number of rows in multiple. Ohm's law applied to a battery having s similar cells in series and p rows in multiple is therefore:

$$I = \frac{sE}{R' + \frac{sb}{p}} \tag{8}$$

The circuit external to the battery absorbs part of the power which is designated as P_1, in equation (7). The voltage drop across the terminals of this part of the circuit will be E' which is less than the total value of E by the amount equal to Ib which is the drop within the cell itself. If the current is I the power expended in this part of the circuit will be

$$P_1 = IE' \tag{9}$$

If this part of the circuit consists only of resistance, all of the energy will be expended in the form of heat and from equation (7)

$$IE' = I^2R'$$

Since the values of E and b are practically constant, the total power generated by the battery in a circuit consisting only of resistance will be small by equation (7) if the value of I is small, but will increase as the current increases. The maximum current is obtained when the external resistance R' is made equal to zero as shown by equation (8). In this case the power generated is a maximum, but it is all expended within the battery itself in the form of heat and no useful work is done. Between these two extreme conditions lies the maximum useful power delivered to the external circuit. The total power generated by the battery, equation (6), is $P = IE$. The power wasted in the battery (considered as a single cell) is by equation (7).

$$P_2 = I^2b$$

The power delivered to the external circuit is then

$$P - P_2 = P_1 = IE - I^2b = \frac{E^2R'}{(R' + b)^2} \qquad (10)$$

The condition that P_1 shall be a maximum is found by differentiating it with respect to R' and equating to zero;

$$\frac{dP_1}{dR'} = \frac{(R' + b)^2E^2 - 2E^2R'(R' + b)}{(R' + b)^4} = 0$$

whence

$$(R' + b) - 2R' = 0$$

and

$$R' = b \qquad (11)$$

That is, assuming E and b to be constant, the resistance of the external circuit which receives maximum power from the battery is equal to the internal resistance of the battery.

The external circuit may contain some apparatus for transforming electrical energy into something besides heat, as, for example, a motor to transform the electrical energy into mechanical energy. In this case

$$IE' \text{ is greater than } I^2R'$$

$$IE' - I^2R' = I(E' - IR') = IE'' \qquad (12)$$

The factor $(E' - IR')$ is called the counter electromotive force of the circuit. The rate of conversion of energy of the battery into mechanical energy, for given conditions, is equal to the expression $I(E' - IR')$. The useful mechanical energy obtained is equal to this multiplied by the mechanical efficiency of the motor.

The equation for the mechanical power is, therefore, (13) where C_1 is a constant.

$$P_m = C_1IE'' \qquad (13)$$

The counter electromotive force is variable, depending on the speed and the magnetization. The current delivered by the battery is

$$I = \frac{E - E''}{R' + b} \qquad (14)$$

Combining (13) and (14)

$$P_m = \frac{C_1(E - E'')E''}{(R' + b)} \tag{15}$$

From which the condition for maximum mechanical power is obtained:

$$\frac{dP_m}{dE''} = \frac{C_1(E - 2E'')}{(R' + b)} = 0$$

whence $E'' = \frac{E}{2}$

and

$$P_m = \frac{C_1 E^2}{4(R' + b)} \tag{16}$$

Equation (14) shows that the current delivered by the battery varies inversely as the battery resistance. The battery resistance, therefore, affects the torque and consequently the power which a given motor can exert, since the torque is a function of the armature current according to the equation:

$$\text{torque} = C_2 \phi I \tag{17}$$

where C_2 is a constant and ϕ the flux.

Similarly, the speed of rotation is given by the equation:

$$\text{speed} = C_3 \frac{E''}{\phi} \tag{18}$$

The product of equations (17) and (18) gives the expression for the mechanical power, equation (13), in which the constant depends on the units employed.

A battery is seldom required to deliver maximum power, but in emergencies or for short periods of time the relation of battery resistance and voltage to the outside circuit may be important.

Figure 114 shows curves, obtained experimentally, that illustrate the above statements. The battery used for these experiments was a small one, having a capacity of about 140 ampere-hours at the 5-hour rate of discharge. The voltage at the cell terminals falls to one-half its open-circuit value at about 600 amperes. This means that the drop in voltage because of the ohmic resistance of the cell is equal to the voltage drop in the external resistance when the cell discharges 600 amperes. As was shown above mathematically, this is the point of maximum power, and the curve marked "watts per cell" has a maximum at this point. The average internal resistance may be calculated from the slope of the voltage curve. It is found to be 0.0016 ohm. Other cells having different resistances would give results differing from these curves, but the principle is illustrated by this figure.

No specific statement as to the internal resistance of the many types and sizes of lead-acid batteries can be made. In general the larger sizes have the smaller resistance. Thus a small radio B battery has a resistance of about 0.1 ohm per cell; larger B batteries and small miscellaneous types have a resistance of a few hundredths of an ohm per cell; starting and lighting batteries and small motive power batteries have a resistance of a few thousandths of an ohm per cell; larger motive power batteries have a resistance of less than 0.001 ohm per cell; very large motive power batteries for locomotives have a resistance as low as 0.0001 ohm per cell.

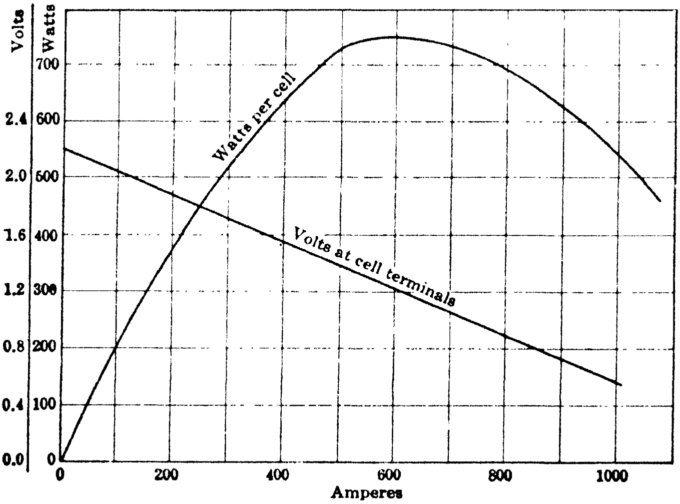


FIG. 114. Power available at various rates of discharge.

2. FACTORS WHICH AFFECT THE RESISTANCE

The first and perhaps the most obvious source of resistance in the battery is the electrolyte. Accurate data on the resistance of sulphuric acid solutions are available, and a table of values covering the range of concentrations in storage-battery practice is to be found in Chapter III. Since the resistance of the electrolyte varies with temperature as well as with the concentration, it is not surprising to find that the resistance of a storage cell varies with the temperature. Experiments by Morse and Sargent[1] on the resistance of storage cells have shown the variation with temperature to be in almost perfect agreement with the temperature-resistance curves for the acid solution of corresponding specific gravity. As the temperature rises the resistance falls.

The presence of the separators adds a small amount to the internal resistance of the cells, particularly if perforated or slotted rubber separators are also employed. The resistance of separators cut from various kinds of wood is given in Table VIII.

A third factor contributing to the resistance of the cell is the resistance of the active material and grids. The lead peroxide of the positive plates is not a good conductor, and therefore a carefully designed grid is essential. Various values have appeared in the literature for the resistivity of the positive active material, but in any case it is probably 10,000 times or more the resistivity of the grid. Crennell and Lea[2] have given the value as 0.25 ohm-centimeter. The resistivity of the sponge lead of the negative plate is given by them as 1.83×10^{-4} ohm-centimeter, increasing when in the discharged state by about 20 per cent. Comparing these figures with the resistivity of the grid metal (Table III, page 17) for the 7 per cent alloy, 2.59×10^{-5}, it is apparent that the sponge lead of the negative plate is almost as good a conductor as the grid itself, but the lead peroxide is much inferior.

The resistance of the various parts of the cell have an important bearing on the distribution of current at the plates during discharge. Crennell and Lea have found that the current density in a cell having plates 77 cm. high is not uniform over the surface. The greater part of the discharge comes from the upper portion and, further, the current density in any particular place changes during the progress of the discharge. The current density at the top of the plate is initially high, but it decreases while the low current density at the bottom of the plate increases and both approach a limiting value about equal to that maintained throughout the discharge at the middle of the plate.

The temperature coefficient of metallic resistance, unlike that of the electrolyte, is positive; that is, a rise in temperature is accompanied by a rise in resistance. The resistance due to the electrolyte of the battery is so much larger than the resistance of the metallically conducting material that the positive temperature coefficient of the latter has little effect in neutralizing the negative coefficient of the former.

Another factor affecting the resistance of a storage battery is the state of charge. Lead sulphate, which forms on both positive and

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[1] *Proc. American Acad. Sci.*, 46, p. 589, 1911.

[2] *J. Inst. Elec. Eng.*, 66, p. 532, 1928.

negative plates during discharge, is a non-conductor, and its presence materially increases the resistance to the passage of the electric current. The sulphate closes the pores of the plates when they are in a discharged condition and thereby hinders the free access of the electrolyte to the active material. It is evident, therefore, that when the cell is charged the resistance should be less than in the discharged state. This is found to be the case. The resistance of the lead-acid cell begins to increase slowly as soon as the discharge begins, and toward the end of the discharge the increase is much more rapid, reaching values from two to three times as great as the initial resistance. Morse and Sargent have found that the characteristic resistance curves for Planté plates differ somewhat in shape from those of pasted plates. The curves for the Planté plates reach higher values, and the last rapid rise is preceded by a short region of almost constant values which these authors attribute to the distribution of active material on the plate.

During the first part of the charge the internal resistance is high, but it falls gradually until gassing begins, when there may be a temporary rise in values because of polarization phenomena. The resistance may continue to fall for a time after the battery is disconnected from the charging line, because of the gradual equalization of the acid concentration, and the dissipation of the gas layer on the active material.

The resistance of the alkaline batteries also increases during discharge and falls during charge, but the reasons for this are not the same as for the lead battery. The resistance of the alkaline batteries is higher than for the acid batteries of corresponding sizes, mainly because the resistance of the electrolyte is greater.

The resistance of the electrolyte and of the plates is a definite physical quantity independent of the current flowing through the battery. There is another factor opposing the current that is not so constant or easily defined. It appears as a resistance at the surface of contact between the electrolyte and the material of the electrode. Newbery[3] has called it the "transfer resistance" and it has the peculiar property that it decreases as the current increases. This effect is particularly noticeable when gas is being liberated at an electrode. Some of the factors which affect overvoltage phenomena affect this resistance also, but the transfer resistance is not the same thing as overvoltage. The transfer resistance has the characteristics of a resistance. It decreases with increasing current, instead of increasing as a back electromotive force or overvoltage commonly does. Theories as to the cause for this effect are conflicting. Chaney[4] investigated the performance of dry

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[3] *Trans. Faraday Soc.*, 15, p. 126, 1919.

[4] *Trans. Am. Electrochem. Soc.*, 29, p. 183, 1916.

cells and concluded that the cause is a surface layer of hydrogen on the anode resulting from local action. Newbery, working with other electrolytic cells, rejected the theory of the hydrogen layer and attributed the cause to a mechanical obstruction of the ions at the transition surface.

During charging there is a back electromotive force that opposes the applied potential. The magnitude of this back electromotive force depends on the concentration of the acid in the pores of the plate and the prevalence of lead ions in the electrolyte. The difference between the impressed voltage and this back electromotive force is the effective electromotive force across the cell and this, together with the resistance, determines the charging current that flows at any instant.

3. METHODS OF MEASURING THE RESISTANCE

The measurement of the resistance of storage batteries presents unusual difficulties, because of the small values and the complications arising at the surface of contact between the electrolyte and the electrodes. A bibliography on this subject may be found in the paper by Morse and Sargent. Accidental contact resistances at binding posts and elsewhere in the measuring circuit may introduce large errors. The value for any particular cell may vary with the state of charge, the temperature, the current which the cell discharges, and the method of making the measurement. The values obtained by the use of alternating currents do not agree with those from direct-current measurements, apart from any consideration of polarization phenomena.

a. Direct-Current Methods

The numerous direct-current methods which have been proposed for measuring the internal resistance of batteries are based on the application of Ohm's law. The resistance of a cell is ordinarily defined by the equation

$$b = \frac{E - E'}{I} \tag{19}$$

The symbols have the same meaning as in the first part of this chapter. Preece [6] found many years ago that the values obtained by using the above equation vary with the values of I, the resistance becoming greater as the value of I was made smaller. This fact has been found also by many subsequent observers, and it is true for dry cells and other

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[6] *Electrician,* 15, p. 42, 1885.

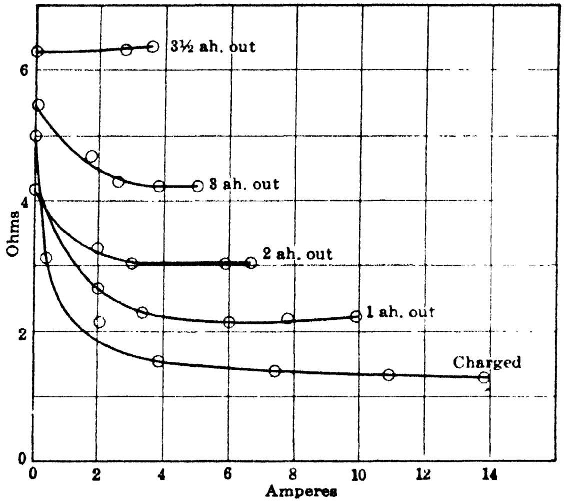

FIG. 115. Resistance of a 12-cell, 3-ampere-hour battery at various rates of discharge.

forms of primary batteries as well as storage cells. This effect is shown in Fig. 115. Whatever the cause may be, it is evident that *b* is not a true ohmic resistance, since it does not obey Ohm's law; but under specified conditions *b* is an important factor in determining the output of the cell. Northrup[6] states that *b* cannot be called anything more than a quantity which must be added to *R* to satisfy equation (2). The name "virtual resistance" has sometimes been applied to this quantity. Notwithstanding the uncertainties that attend the measurement of battery resistance, this quantity is important for both primary and secondary cells. The resistance varies, as is shown in Fig. 115, with the state of charge as well as with the

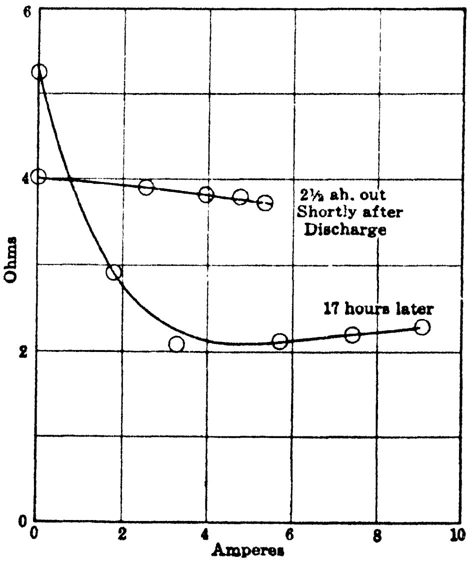

FIG. 116. Change in resistance during the period of recuperation.

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[6] *Methods of Measuring Electrical Resistance*, p. 215.

current. A small battery was selected for these experiments as a matter of convenience. The recuperation of a battery after discharge results in a decrease in resistance, as Fig. 116 shows, as well as a gain in voltage.

b. Alternating-Current Methods

In view of the difficulties of measuring the resistance of batteries by direct-current methods, the alternating-current methods, of which many have been proposed, deserve careful consideration, but only a few can be described here. It is desirable to prevent the battery from discharging through the bridge. Two methods have been proposed to accomplish this. The first and simplest is to connect two cells of like voltage in opposition and measure the combined resistance of the two. The second method is to put a condenser in series with the cell to be measured.

Nernst and Haagn [7] proposed a method which permitted measurements to be made on one or more cells which might be discharging a direct current through a local non-inductive circuit or be on open circuit as desired. This method was somewhat improved by Dolezalek and Gahl,[8] who eliminated the error introduced by the traveling contact of the bridge wire. The method is as follows:

Two known condensers, C_1 and C_2, are placed in two arms of the bridge. When balanced, the ratio of these condensers determines the ratio of the resistances in the other two arms. One of the resistances can be read directly from the slide wire, and the other, including the battery, can be calculated. If the battery is discharging through the shunt circuit, it is necessary to include in the calculation the value of the shunt resistance. A third condenser is placed in series with the source of alternating current, to prevent the battery from discharging through the circuit. All contacts may be soldered except the traveling contact, but it is apparent that irregularities in this cannot affect the measurement. This method assumes that the battery behaves as a pure resistance in an alternating-current circuit.

The Wien bridge described by Grover,[9] although designed for the measurement of capacity, can be used for the measurement of battery resistance, and it is superior to either of the foregoing bridges. A diagram of this bridge is shown in Fig. 117. The arms are designated as A_1, A_2, A_3, A_4. The condenser C_2 is of known value. The condenser

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[7] *Zeit. Phys. Chem.*, 14, p. 623, 1894.

[8] *Zeit. Elektrochem.*, 7, pp. 429 and 437, 1901.

[9] *Bulletin*, Bureau of Standards, 3, p. 378, 1907; *Sci. Paper* 64.

C_1 should be variable to compensate for the capacity of the battery, and must be calibrated. Condensers of good quality are desirable in order that the correction for absorption may be negligible. The resistances R_3 and R_4 are equal, and R_2 is a small fixed resistance. R_1 is a small variable non-inductive resistance whose magnitude will depend on the resistance of the battery and the other resistances in the circuit. The condition for a balance of the bridge is:

$$A_2A_3 - A_1A_4 = 0 \qquad (20)$$

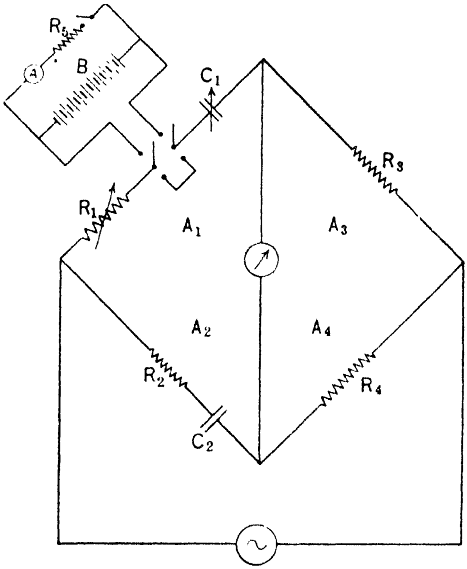

FIG. 117. Alternating-current bridge for measuring resistance of storage cells.

Since the condensers usually have some absorption that may not be negligible, Grover represents the absorption as fictitious resistances ρ_1 and ρ_2, in series with the condensers C_1 and C_2, respectively. Substituting the impedances of the various arms in equation (20) and separating the real and imaginary parts, two equations are obtained, which are as follows:

$$\frac{\rho_2 + R_2}{\rho_1 + R_1} = \frac{R_4}{R_3} \qquad (21)$$

and

$$\frac{C_2}{C_1} = \frac{R_3}{R_4} \qquad (22)$$

from which

$$\frac{\rho_2 + R_2}{\rho_1 + R_1} = \frac{C_1}{C_2} \qquad (23)$$

Assuming that the quantities ρ_1 and ρ_2 are negligible (if they are not, their values must be determined), R_1 is the only unknown quantity in the equation and its value is obtained from the solution of equation (23).

$$R_1 = \frac{R_2C_2}{C_1} \qquad (24)$$

When the battery is in the circuit, the resistance of the arm A_1 is $R_1 + b$ and the battery resistance is obtained from the difference of two measurements with the battery in and out of the bridge. The value of C_1 is different in the two measurements. If the battery is discharging through a local circuit of resistance R_5, the effect of this resistance as a shunt circuit must be allowed for in equation (24).

Another form of bridge suitable for the measurement of battery resistance, devised by the author, may be described as a resonance bridge in which the capacity reactance is balanced by an inductance and the capacitance of the battery is calculated from the change in the inductance when the battery is removed from the circuit. This bridge requires a very constant source of alternating current, free from troublesome harmonics. Some special apparatus, such as variable resistances and inductances, is also required.

When a condenser is placed in series with a battery, the impedance of the circuit is given by the expression

$$\sqrt{b^2 + \left(\frac{1}{\omega c}\right)^2}$$

where $\frac{1}{\omega c}$ represents the capacity reactance of the condenser and the battery combined. The resistance of the battery, squared, is extremely small as compared with the square of the capacity reactance. In order to eliminate the effect of the capacity, an inductance is tuned into the circuit so that

$$\omega L = \frac{1}{\omega c}$$

Whence the impedance of the circuit

$$\sqrt{b^2 + \left(\omega L - \frac{1}{\omega c}\right)^2} = b$$

Balances of the bridge should be made with the battery both in and out of the circuit, and this is therefore a substitution method. To compensate for the battery, a low variable and non-inductive resistance is required. This was supplied by a straight copper wire that could be moved at will into or out of a copper-clad glass tube, filled with mercury. Since the storage cell or any other battery possesses a large electrostatic capacity, the substitution of the mercury resistance for the battery requires a rebalancing of the inductances in the bridge.

This was accomplished by the variable inductance, and from the change in this inductance the equivalent electrostatic capacity of the battery may be computed. The cells may be on open circuit while being measured or may be discharging through a local non-inductive circuit at any desired rate. A diagram of the circuit is given in Fig. 118. R_1 and R_2 are non-inductive resistances of small values serving as the ratio arms of the bridge, R_3 is a variable resistance for balancing the bridge, C is the condenser to prevent the battery from discharging through the bridge. L is a variable inductance, B the battery to be measured, with its local circuit consisting of an ammeter and resistance. In place of the battery may be substituted a heavy link. R_4 is a non-inductive variable resistance to be used as a compensating resistance when the link replaces the battery. As a source of the alternating current a 5-watt electron tube, with loose coupling to the bridge, has been used. An amplifier has also been useful at times in the detecting circuit.

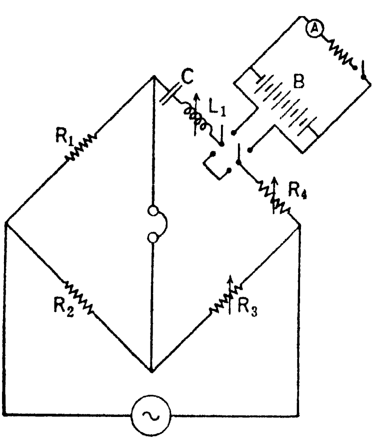

Fig. 118. Resonance bridge.

Resistances of dry cells measured by such a bridge are constant irrespective of the current and frequency, provided the latter is above 3000 cycles. The values for the resistance were always less than the lowest values obtained by any direct-current measurement. Sufficient data are not at hand to show whether the same is true for storage cells, but it seems likely.

A question naturally arises in view of the above discussion: What is the physical meaning of the resistances as determined by direct- and alternating-current methods, and which is the true resistance? It seems likely that the alternating-current values are the true resistances, but they do not represent the effective values when the battery is being used for direct-current work. The resistance determined by direct-current measurements exceeds the resistance by alternating-current measurements. Since the resistance may vary with the current which flows through the battery, any measurement of resistance, to have a real significance, must be made under service conditions.

A comparison of the alternating- and direct-current measurements of resistance of a small radio B battery of 12 cells of the lead-acid type is given in Table LI. This shows that the voltmeter-ammeter method

TABLE LI

COMPARISON OF ALTERNATING- AND DIRECT-CURRENT MEASUREMENTS OF THE RESISTANCE OF A STORAGE BATTERY

(Measurements were made on a small battery of 12 cells of about 3-ampere-hour capacity. Values are expressed in ohms.)

State of Charge	D.-C. Resistance by Oscillograph Method		D.-C. Resistance by Voltmeter-Ammeter Method	A.-C. Resistance at 1000 Cycles
	Minimum	Constant		
Charged	1.00	1.08	1.29	0.99
Partly discharged, 2 amp.-hr.	2.00	2.23	3.2	1.18
Same, after standing 45 hr.	1.52	1.60	...	1.03
Fully discharged $3\frac{1}{2}$ amp.-hr.	4.50	5.25	6.4	2.02

is too slow to catch the values obtained by the oscillograph, but probably the voltmeter-ammeter readings come the nearest to representing service conditions.

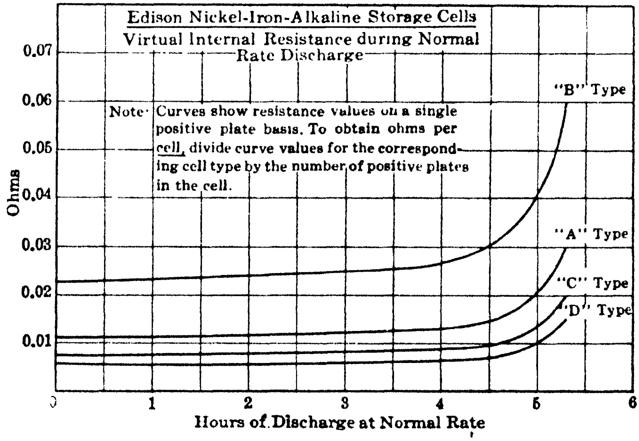

FIG. 119. Data from which the internal resistance of various types and sizes of Edison storage cells can be calculated.

The resistance of various sizes and types of Edison batteries can be computed easily from the data given in Fig. 119. These data are on a single positive plate basis. To obtain the resistance in ohms per cell, divide the values read from the curve applying to the type of cell by the number of positive plates in the cell.

CHAPTER VIII

EFFICIENCY

The efficiency of storage batteries is defined by the Standardization Rules of the American Institute of Electrical Engineers as follows:

36–300, Efficiency

The ratio of the output of a cell or battery to the input required to restore the initial state of charge under specified conditions of temperature, current rate and final voltage.

36–301, Ampere-Hour Efficiency (Electrochemical Efficiency)

The ratio of the ampere-hours output to the ampere-hours of the recharge.

36–302, Volt Efficiency

The ratio of the average voltage during the discharge to the average voltage during the recharge.

36–303, Watt-Hour Efficiency (Energy Efficiency)

The ratio of the watt-hours output to the watt-hours of the recharge.

The general expressions for efficiency will be considered first in this chapter, and then the conditions which affect the measurement of both the ampere-hour and the watt-hour efficiency.

1. GENERAL EXPRESSION FOR THE EFFICIENCY

If the current discharged by a battery at any moment be designated by I_1 amperes, the quantity of electricity delivered during an infinitesimal amount of time, dt, is I_1dt. For a longer period of time, represented by t_1 hours, the quantity of electricity expressed as ampere-hours is given by the integral:

$$\int_0^{t_1} I_1dt$$

Similarly, during the charging period, for which the current at any moment is I_2 and the length of the charge t_2, the total quantity of electricity passing through the battery is

$$\int_0^{t_2} I_2dt$$

The ampere-hour efficiency, according to the definition given above, is the ratio of these two integrals:

$$\text{Ampere-hour efficiency} = \frac{\int_0^{t_1} I_1 dt}{\int_0^{t_2} I_2 dt}$$

If the current is kept constant during both the charge and the discharge, as is usually the case, this expression for the ampere-hour efficiency reduces to the simple ratio:

$$\frac{I_1 t_1}{I_2 t_2}$$

The power delivered by a battery at any instant during its discharge is the product of the current and the terminal voltage. Expressing the latter in volts by E_1 and the current as above, the power in watts is I_1E_1, and this multiplied by dt is equal to the energy delivered during the element of time. For a discharge lasting for a period of time t_1, the energy in watt-hours is represented by the integral:

$$\int_0^{t_1} I_1 E_1 dt$$

The corresponding expression for the energy received by the battery during the charging period is

$$\int_0^{t_2} I_2 E_2 dt$$

The energy efficiency is the ratio of these two integrals:

$$\text{Energy efficiency} = \frac{\int_0^{t_1} I_1 E_1 dt}{\int_0^{t_2} I_2 E_2 dt}$$

Either the current or the voltage may be kept constant during the charge and discharge. If the current is constant, the expression for the energy efficiency may be written

$$\frac{I_1 \int_0^{t_1} E_1 dt}{I_2 \int_0^{t_2} E_2 dt}$$

To obtain the integrals $\int_0^{t_1} E_1 dt$ and $\int_0^{t_2} E_2 dt$, the time curves of the values of E_1 and E_2 are drawn and integrated. The most convenient means of doing this is with a planimeter. Multiplying the first integral by the steady value of the discharge current I_1 and the second by the charging current I_2, the watt-hours delivered and received are obtained.

If both the current and the voltage vary, as when a battery discharges through a fixed resistance, the problem is somewhat more complicated, but can be readily solved.

The current and time factors should be chosen with reference to the conditions of actual service when efficiency tests are to be made.

2. THE AMPERE-HOUR EFFICIENCY

The ampere-hour efficiency is of importance from the standpoint of the operation of storage batteries and is a step in the determination of the energy or watt-hour efficiency. The chemical reactions which occur during charging and discharging are reversible, and it is naturally to be expected, therefore, that under favorable conditions the ampere-hour efficiency should be only slightly less than 100 per cent.

The ampere-hour efficiency depends very largely upon the completeness of the recharge. A portion of the charging current is ordinarily wasted in producing gas and this reduces the efficiency. There are also accidental factors which may lower the efficiency, such as (1) the self-discharge of the plates, commonly called local action, (2) leakage of current because of faulty insulation either inside or outside the battery.

The completion of the charge is determined usually by continuing the charge at constant current until the voltage at the terminals of the battery reaches a maximum. Since this point can be determined only by carrying the charge beyond the point where the maximum is first reached, the efficiency will be low if calculated from the total amount of the charge. The ampere-hours put into the battery after the maximum is reached can be neglected, but in any case the error of an efficiency determination based on a single cycle of charge and discharge is likely to be large. It is common practice, therefore, to base efficiency determinations on a series of many cycles of charge and discharge in accordance with the normal operating conditions.

Temperature plays an important part in the measurement of efficiency, since the capacity of the battery is dependent very largely on the temperature, as has been shown in Chapter V. Temperatures below normal result in diminished capacity and efficiency, but an increase in temperature may raise the calculated efficiency to over 100 per cent. This does not mean, however, that the battery can continue to furnish more ampere-hours than it receives during charge, as a few repetitions of the experiment would quickly show. The physical significance of a calculated efficiency in excess of 100 per cent is merely that the electrolyte diffuses more readily during discharge because of its decreased viscosity at the higher temperature, and therefore more of the active material of the plates may take part in the reaction than would otherwise be the case. A standard temperature conforming to normal operating conditions should be specified when efficiency tests are to be made.

The rate of the discharge affects the capacity and, to some extent, the efficiency. The higher the rate of the discharge the lower is the delivered capacity, and a smaller number of ampere-hours are consequently required for recharging. The decrease in capacity of a battery because of increased rate of discharge is not accompanied by a corresponding decrease in efficiency. Tests on a group of vehicle batteries discharging at 45 and 90 amperes showed a decrease in ampere-hour capacity of 32 per cent at the higher rate as compared with the lower rate of discharge. Measurements of the ampere-hour efficiency of these batteries at the same rates gave 91 per cent at 45 amperes and 87 per cent at 90 amperes. The decrease in efficiency was only 4 per cent.

The following method for determining the maximum ampere-hour efficiency was suggested to the author by J. L. Woodbridge. A fully charged battery is discharged at some chosen current to a fixed cutoff voltage, careful measurement being made of the exact number of ampere-hours delivered. On the recharge the same number of ampere-hours are put back at the same current. A second discharge is then made to the same cutoff voltage as before. The efficiency of the battery is then calculated as the ratio of the ampere-hours delivered during the second discharge to the ampere-hours put in on the charge. After correcting for the slight increase in temperature as a result of the charge, the ampere-hour efficiency by this method has been found to be within the range 98 to 100 per cent. Such a measurement does not, however, represent the ordinary service conditions.

Nickel-iron batteries gas throughout nearly all the period of charge and are subject to a rather large rate of loss of charge immediately following the charging period. The ampere-hour efficiency is therefore somewhat lower than for the lead-acid batteries. By shortening the charging period, efficiencies of 93 to 95 per cent can be obtained, but the output is then less than normal. The ampere-hour efficiency of a nickel-iron battery is about 82 per cent when discharged immediately following charge, but a 7-hour charge following a 5-hour discharge at the same rate would make the efficiency 72 per cent. However, the batteries ordinarily exceed the 5 hours and this improves the efficiency.

3. THE WATT-HOUR EFFICIENCY

The watt-hour, or energy, efficiency is important because it shows the ability of the battery to return the energy which it has received. In this respect it is an important factor in determining the cost of operation. The watt-hour efficiency is affected by the same factors as the ampere-hour efficiency, and in addition to these it is affected by the voltage relations on charge and discharge.

The internal resistance of a battery is small and variable, but it cannot be entirely neglected. Assuming the internal resistance to have a value b, the decrease of voltage during discharge at a current I_1 is equal to I_1b, and during charge there is a slight increase in voltage at the terminals which is equal to I_2b. The voltage on charge is always greater than the voltage on discharge. The part of this difference which is due to the resistance of the battery is equal to the sum of the two factors $I_1b + I_2b$.

By far the greater part of the difference between the voltage of the battery while charging and while discharging is due to polarization. There is some gas polarization, but primarily it is a concentration polarization in the case of the lead battery. The battery behaves as if it contained a very dilute electrolyte when it discharges and a concentrated electrolyte while charging. This is because the electrolyte in the pores of the plates becomes impoverished during the discharge and enriched during the charge. The relation of voltage to the acid concentration has been given on page 183.

The performance curves in Fig. 76 show that the average voltage during discharge at 45 amperes was 1.95 volts per cell and during charge it was 2.28 volts per cell. The ratio of these voltages, which is sometimes called the voltage-efficiency, is $\frac{1.95}{2.28} = 85$ per cent. If the ampere-hour efficiency under such operating conditions could be 100 per cent, the energy efficiency could not exceed 85 per cent. The ampere-hour efficiency at 45 amperes discharge rate was 91 per cent and the energy efficiency was therefore $0.91 \times 0.85 = 0.77$ or 77 per cent. A fair average for the energy efficiency of the lead battery under ordinary operating conditions is about 75 per cent.

The watt-hour efficiency of the nickel-iron cells at the normal rate of discharge ranges from 55 to 60 per cent. If discharged immediately after charge, the voltage efficiency is about 73 per cent and the watt-hour efficiency about 60 per cent. After standing for a day the lower figure is obtained.

It is apparent that the better the equalization of acid within the lead cell, the less difference there will be between the average voltage of charge and discharge. High porosity of the plates and low viscosity of the electrolyte will help to accomplish this.

If the periods of charge and discharge are made very short, the concentration polarization becomes a relatively less important item. Highfield[1] gives the watt-hour efficiency of a central-station battery on lighting service during twelve months' operation as 74 per cent, but he reports the efficiency of a line battery on traction service, where the periods of charge and discharge alternated at frequent intervals, as 84 per cent. Hopkinson[2] made a series of experiments in short cycles of charge and discharge. By the time of the cycle he means the sum of the time of discharge and the time of charge. Some of his results were as follows:

Time of the Cycle	Energy Efficiency
1 minute	96 5 per cent
10 minutes	93 6 per cent
30 minutes	92 0 per cent

Bailey[3] has gone a step further in this direction and made charges and discharges in cycles as short as $\frac{1}{60}$ second. He obtained energy efficiencies as high as 98.1 per cent. The difference between this and 100 per cent is probably to be attributed almost entirely to losses caused by the ohmic resistance, because the concentration polarization must have been inappreciable at this frequency. Bailey's result is of no importance from an operating standpoint, but it is of very real interest theoretically in showing how perfectly reversible the storage cell is.

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[1] *J. Inst. Elec. Eng.*, 30, p. 1070, 1901.

[2] *Electrician*, 48, p. 211, 1901.

[3] *Electrical World*, 47, p. 829, 1906.

CHAPTER IX

TESTING OF STORAGE BATTERIES

The tests which are of primary importance are those to determine (1) the capacity of a battery at certain rates of discharge; (2) the ability of the battery to retain its charge over a period of time; (3) its ability to withstand vibration (portable types only); (4) the purity of the electrolyte; (5) its period of useful service, or life; and (6) its voltage characteristics. In this chapter is given a general discussion of the tests which apply to various types of batteries. Emphasis is laid on the nature and conditions of the tests, but fixed rules for making them are not prescribed.

1. CAPACITY TESTS

The manufacturer must determine by actual test the number of ampere-hours which any particular size and type of battery, which he makes, can deliver under specified conditions of discharge. Usually the capacity per positive plate is stated and from this he can calculate a conservative ampere-hour rating for similar batteries of other sizes. The purchaser is interested in the capacity because he wishes to know whether the battery in question can deliver sufficient energy to perform the service required of it.

The ratings made by reliable manufacturers are usually conservative, and their batteries have some margin of excess capacity. Occasional cases have arisen, however, in which batteries have been misbranded. Starting and lighting batteries and some others of the smaller types should ordinarily attain their full rated capacities on or before the third repeated cycle of charge and discharge. Stationary batteries and some motive-power batteries, however, may require as many as twelve cycles before attaining rated capacity.

In Chapter V the various factors which affect capacity are discussed in detail. The fundamental points to be observed in making capacity tests of any particular battery are: (1) rate of the discharge, (2) cutoff or final voltage, and (3) temperature.

a. Rate of Discharge

As the rate of the discharge is increased, the duration of the discharge is more than proportionally decreased. It is important, therefore, that the current should have a definite and constant value maintained throughout the test, except during intermittent tests. Storage batteries are commonly rated on the continuous discharge, "time" basis; for example, stationary batteries may be stated to have a certain ampere-hour capacity at 8 hours; and starting and lighting batteries at 20 hours for light service. Such ratings define the test current also. The ampere-hour capacity divided by the time fixes the test current. A stationary battery rated at 4000 ampere-hours for 8 hours is to be tested at 500 amperes. A starting and lighting battery having a rated capacity of 100 ampere-hours at the 20-hour rate would be tested at 5 amperes. So it is for any other time rating. Some tests of automotive and aircraft batteries are made at high current rates, such as 300 amperes, regardless of their size.

A difficulty arises in the testing laboratory when a group of batteries having slightly different ratings is to be tested. It is necessary first to determine whether the batteries are comparable and for the same kind of service. A fair average test current may then be chosen. If the batteries are to be tested in accordance with specifications which state the minimum required capacity, the problem is simplified. For example, if the minimum required capacity at the 5-hour rate is 72 ampere-hours, the test current is $\frac{72}{5} = 14.4$ amperes, although one or more of the batteries may exceed the 5-hour discharge period considerably.

b. Final Voltage

The "final" or "cutoff" voltage, as it is sometimes called, is the terminal closed-circuit voltage at which it is desirable to stop discharge. Large stationary batteries discharging at normal temperature and the 8-hour or longer rates have a cutoff voltage of 1.75 volts per cell; motive-power batteries, 1.75 volts at the 6-hour rate, and isolated plant batteries, 1.75 volts at the 8-hour rate. The cutoff voltages vary somewhat and have not been standardized except by general usage and in some cases by recognized specifications. In the absence of definite specifications, the cutoff voltages are generally determined by the shape of the discharge curve, stopping at about the knee of the curve. The capacity which may be obtained beyond this point is small and it is not economical to discharge the battery further.

When discharges are made at higher rates, the cutoff voltages are correspondingly lower. This is because of the increased voltage drop through the cell and the relation of specific gravities of the electrolyte within the plates to that outside. The determining factor in fixing the cutoff voltage is the concentration of acid in the pores of the plate. The values for starting and lighting batteries are as follows:

RATE	CUTOFF VOLTAGE
20-hour, 80° F.	1.75
20-minute, 80° F.	1.50
300-ampere, 0° F.	1.00

Care must always be taken in measuring these voltages to make the measurements at the cell terminals and avoid losses in leads and inter-cell connectors.

c. Temperature

The temperature of a battery under test is ordinarily specified as the initial temperature of the electrolyte, since this is under control of the laboratory. Standard temperatures for most portable batteries are 80° F. or 25° C. (77° F.). The difference is small and may be neglected. The standard temperature for stationary batteries is usually 70° F. The final temperature, which is not under control, is really more important in its effect on capacity. Permissible limits of the ambient temperature should be stated. A battery should always be near the standard temperature when a test is made, to avoid large corrections. Corrections may be calculated from Fig. 62 in Chapter V. The temperature correction varies with the rate of the discharge.

d. Accuracy

The accuracy of the measurements made in any determination of capacity deserves especial mention. To attain a satisfactory accuracy of 3 per cent or better, the current must be held constant to within close limits by regulation. Hand-operated rheostats are suitable for regulation if the steps are small, but carbon resistances afford the best means for continuous regulation. The ammeter chosen for the test should have a scale permitting readings to be made directly to 1 or 2 per cent of the test current, and it should be calibrated. The time is easily measured to 1 per cent, except in the case of high-rate discharges such as the 300-ampere test for automobile batteries or the 5-minute rate for aeroplane batteries, for which especial precautions must be taken.

When the end of the discharge is approaching and the knee of the voltage curve is reached, the voltage may change so rapidly as to make it difficult to maintain the current constant at the time when it is most important to do so. To overcome this difficulty, recourse may be had to the use of "booster batteries." The battery under test is connected in series with a battery of larger capacity which serves to maintain the current and decrease the percentage change in voltage in the circuit. For example, if the drop in voltage of the test battery is 0.2 volt per cell, or 10 per cent of the voltage of the cell, the use of nine booster cells in series with this will reduce the voltage fluctuation to 1 per cent, provided the latter are of sufficient capacity. The proper number of booster cells to be used during test is determined mainly by convenience; even a few are of assistance, and ordinarily the ratio would not be as high as 9 to 1.

Careful and systematic records throughout the measurement of capacity are important. The records should include the following: date of previous charge, date of the discharge, number of the cycle, initial specific gravity and temperature of each cell, initial open-circuit voltage of each cell, closed-circuit voltages at appropriate intervals with record of the time in each case (the intervals being shorter as the end of the experiment is approached), the cutoff voltage for the battery and the exact time that it is reached, final specific gravities and temperatures for each cell. It is often worth while to repeat the final specific gravity and temperature measurements after several hours because equalization of the specific gravity of the electrolyte within the pores of the plate with that outside takes place slowly.

Since the capacity of new storage cells increases rather rapidly from one cycle to another, it is necessary that a new battery be given several preliminary cycles of charge and discharge before determining the capacity. The capacity at any particular rate is influenced by the previous discharges (p. 223), and therefore when changing to a different rate of discharge a preliminary cycle at the new rate should precede the measured experiment. In testing any battery it is desirable to determine the capacity at several rates of discharge, although the final judgment of its performance may be based on the results at the normal rate.

e. Causes of Failure

Batteries which fail to meet capacity tests often require special attention, since it is always desirable for a testing laboratory to report the cause of failure as well as the fact. Experience is the best guide, but, if the observations have been carefully made, an analysis of them may suggest the cause of failure. The following items are suggested as a guide to the general procedure:

1. Compare the open-circuit voltages before discharge with Table XXXVI. Appreciably low values may indicate internal discharge due to short circuits through a split separator, excessive sediment, or similar cause.
2. Examine voltage readings throughout run and see if they progress regularly except for the "*coup de fouet*" (see p. 252) at the start. Erratic readings may be an indication of bad contacts, loosely burned plates, internal short circuits. In case of 2-volt changes occasionally observed, the reversal of one cell is indicated.

FIG. 120. Racks for testing small types of storage batteries.

3. Examine the gravity readings to see whether the range is normal for the type of cell under test. If the range is too small, and the plates are in good condition, the indication is that the electrolyte does not circulate freely. Causes for this are high-resistance separators, separators without corrugations, wrong side of separator next to positive plate, or the addition to the electrolyte of some foreign substance which increases the viscosity. If the gravity range is abnormally great, the amount of electrolyte may be too small. Estimate the total amount

of electrolyte if possible, and make use of Table XVI, which will show the possible output for the amount and range.

4. The capacity of the cell is usually limited by the positive plate, but in some cases the negative plate may be deficient. The plate capacities can be determined by the use of the cadmium electrode (see p. 231) which will indicate whether either plate is deficient.
5. By dismantling the cell or battery, and examining the plates and structural details, defects arising from poor manufacture or abuse are often revealed. Chemical tests of the electrolyte may reveal impurities that produce excessive local action.

Two test racks for making automatically controlled tests of small types of batteries are shown in Fig. 120. The current is regulated by carbon resistors and ballast lamps (iron filaments in hydrogen). The latter may be seen above the rack in the foreground. Each rack is provided with a recording ammeter and ampere-hour meters for both charge and discharge circuits. The switches are operated by a program machine not shown in the illustration.

2. TEST FOR RETENTION OF CHARGE

Besides determining the capacity of a battery, it is desirable to determine its ability to retain the charge over a considerable period of time. The Federal specifications for automobile batteries require that a battery must not lose more than 25 per cent of its capacity during a standing period of four weeks. This is an average loss of about 1 per cent per day. The test is made as follows: After a careful determination of the capacity at a specified rate, as outlined in the preceding section, the battery is fully charged and allowed to stand on open circuit at room temperature for a period of four weeks, following which it is discharged under the same conditions as before and the percentage loss in capacity computed as the ratio of the decrease in ampere-hours delivered to the original capacity in ampere-hours.

The loss in capacity will depend on the specific gravity of the electrolyte, the temperature, and the purity of the electrolyte. The amount of the loss allowed by the specifications is liberal and should cover any battery of reliable quality containing electrolyte not exceeding 1.300 in specific gravity. Lower specific gravities should result in smaller losses. On test of seventeen different makes of batteries, the smallest loss observed was 4 per cent and the largest 85 per cent; the average of the batteries which complied with the specification was 13 per cent.

One reason for the relatively small loss in capacity in some cases is the fact that the negative plates at which the greatest local action occurs usually exceed the capacity of the positives by a large amount, and it is possible in such cases, therefore, for them to be considerably affected without materially changing the battery capacity. A continuation of the test for an additional period may show greater losses.

The causes for loss in capacity while standing idle are local action and internal short circuits. The normal rate of local action is shown in Tables XX and XXI of Chapter III. Local action is accelerated by the presence of certain impurities in the electrolyte or on the plates. Antimony on the negative plates is a cause of local action, particularly in old batteries. Iron is a common impurity which can be eliminated in part at least by pouring out the electrolyte. Platinum, although rarely found, is exceedingly destructive even in amounts of only one part in 10,000,000. Among the causes of internal short circuits are excessive sediment, defective separators, metallic particles falling into the cells through the vents and, in rare cases, porous sealing compound. Stationary batteries, if not properly cared for, may lose charge because of poor insulation.

3. VIBRATION TEST

This test applies particularly to automobile and airplane batteries, but may be used with other portable types to develop possible defects in lead-burning, sealing of terminal posts, vent-plug design, and shedding of active material.

Figure 121 shows a vibrating board driven by a cam on a motor at the left. The board vibrates in a simple harmonic motion of 5 millimeters' total displacement (battery position) with a frequency of 1000 cycles per minute. Any departure from a simple harmonic motion changes the maximum acceleration value and modifies the test. For this reason a short connecting rod cannot be used.

The battery is fastened to the vibrating board by hold-down clamps and vibrated for one hour, during which time it is discharging at any convenient rate (5-hour rate generally used). It must maintain a steady voltage and current during this time. Fluctuations are generally due to plates breaking loose from the straps, as may happen if the lead-burning is not properly done. Failure occurs most commonly at the terminal posts, which may become loose and allow the electrolyte to flood the top of the battery; vent plugs, if not provided with baffle plates, will usually allow electrolyte to escape. Excessive sediment may be produced. A battery of good design and workmanship should pass this test without difficulty. At the conclusion of the tests the cells are examined for broken plates, connectors, straps, and sediment in the bottom of the battery jars.

This test is considered superior to a bumping test, because the batteries in service are subjected to vibrations; also the test is easily specified in simple mathematical terms.

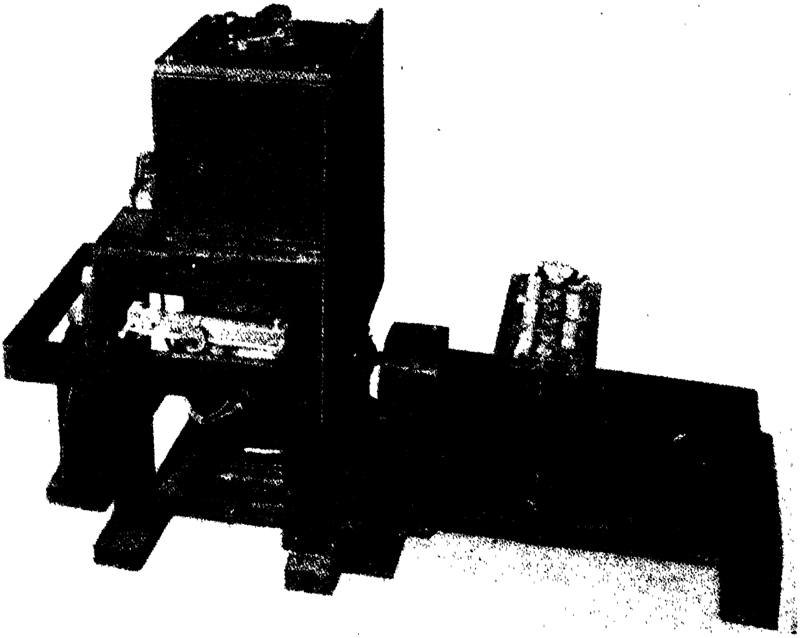

FIG. 121. Vibrating board for testing automobile and airplane batteries.

4. TESTS FOR PURITY OF THE ELECTROLYTE

Tests for the purity of the electrolyte form an important part of the complete test of a storage battery but cannot be made satisfactorily when suitable chemical laboratory facilities are lacking.

The presence of some of the impurities can be readily detected by inspection of the cells. Antimony and some of the more noble metals cause excessive gassing of the negative plates. This may be observed when the cells are on open circuit, if the cells are contained in glass jars, or a sample of the negative plates may be removed and placed in a beaker containing a solution of pure sulphuric acid. It is to be observed, however, that gassing will be somewhat in evidence even in a normal battery, particularly after the termination of a charging period. Negative plates which are contaminated will continue to gas until they are completely discharged. When manganese salts are present in the electrolyte they may ordinarily be detected by the characteristic permanganate color which appears at the positive plates when the cells are on charge. Hydrochloric acid and acetic acid, if present in any considerable amount, may be detected when the cells are on charge by the characteristic odors of chlorine and acetic acid, respectively.

Chemical methods for the detection of impurities in storage-battery electrolytes follow more or less the general procedure for analytical determinations, but they present the special difficulty that the impurities are present normally in small amounts in a fairly concentrated solution of a strong mineral acid.

Tests for the purity of sulphuric acid, both concentrated and diluted to 50 per cent are described in detail in the Federal Specification for sulphuric acid, O-A-111. This is obtainable from the Government Printing Office. The maximum limits for various impurities as given in the specification are included in Table XXVIII of Chapter III. With some modifications the tests for these can be applied to samples of electrolyte removed from batteries. These tests, however, are of the type to determine whether the impurities in the test sample exceed the permissible limits of the specifications. Reference should be made to the complete specification for details of these tests.

Very briefly, the methods and reagents employed are as follows: For organic matter, charring when heated to fumes; for iron, ammonium thiocyanate; for substances oxidized by permanganate, potassium permanganate; for arsenic and antimony, Gutzeit test with modifications to distinguish between them; for manganese, potassium periodate; for nitrates, ferrous sulphate; for ammonium, Nessler's reagent; for chlorides, silver nitrate; for copper, ammonium hydroxide; for zinc, hydrogen sulphide; for selenium, iced sample overlayed with hydrochloric acid containing a little sodium sulphite—no red color to develop at zone of contact (selenium is found occasionally in acid from Oriental sources); for platinum, residue after evaporation is taken up in a little aqua regia and absorbed in asbestos paper, ignited, and while still hot tested in a stream of illuminating gas for incandescence.

A very useful method for volatile acids (acetic, formic, etc.) not included in the specifications was described by Craig.[1]

The choice of the methods for the detection of impurities in storage-battery solutions depends, first, upon the possibility of making the determinations quantitative, second, upon the accuracy which can be

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[1] *J. of Research*, 6, p. 169, Bureau of Standards, 1931.

obtained by the method, and third, upon the presence or absence of certain impurities which may interfere with the results of the test. In order to determine the presence or absence of these impurities, preliminary tests are sometimes desirable before deciding upon the method of test to be used for the quantitative detection of any particular impurity. The accuracy which can be obtained will depend very largely on the care with which the reagents are prepared and the preparation of the colorimetric standards for comparison. It is not possible within the scope of this treatise to give in detail the considerable number of tests which are used for the determination of the various impurities and the conditions under which any one test is to be preferred to others.

Aside from chemical tests for the purity of the electrolyte, it is possible to determine the presence of impurities of the noble metals by spectroanalysis of material removed from the surface of negative plates. This method has been applied particularly for the detection of small amounts of platinum, since it is possible to effect a concentration of the impurity, even when present in very small amounts, by scraping the surface of the negative plates. A quantitative estimate of the amount of impurities can in some cases be made from the relative intensities of the spectrum lines.

Such impurities as platinum and other metals which deposit on the negative plates can seldom if ever be detected in electrolyte drawn from the cells, since these impurities are left behind on the plates.

5. LIFE TESTS

A storage-battery life test for automotive batteries, generally known as the S.A.E. test[2] (Society of Automotive Engineers' test) consists of four cycles of charge and discharge in each 24 hours. Each cycle consists of discharge for one hour at 40 amperes followed by charge for 5 hours at 10 amperes. Automatic control of the charges and discharges may be accomplished by a time switch or by an ampere-hour meter. The former is referred to as type A and the latter as type B equipment. For wiring diagrams of the circuits reference should be made to the current S.A.E. *Handbook*.

Batteries to be tested are first given a freshening charge at 5 amperes until three successive readings of a hydrometer at hourly intervals (corrected for temperature) are constant. The batteries are then given a complete measured discharge to 5.1 volts. Following this they are recharged by manual control until each has received a charge

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[2] *Handbook*, Soc. Automotive Eng., p. 107, 1939.

amounting to 125 per cent of the previous discharge. Having determined the initial characteristics, they are ready for the automatic cycling process, although periodic measured discharges and charges must be made at intervals of about a week.

Each battery circuit should be provided with a double-throw, double-pole switch and a fixed resistor. In the "down" position of each switch the battery and its resistor are connected in the circuit, but in the "up" position the continuity of the circuit is preserved when no battery is being tested on that particular portion of the circuit. An ammeter, having a scale of 25–0–50 amperes, is in series with the batteries and their resistors.

The resistors and wiring are designed to discharge the batteries by 40 ampere-hours in one hour. Initially the current will be about 45 amperes and this will taper off to about 38 amperes at the end of the hour. The average should be 40 amperes. The charging rate for the automatic control should be adjusted to start at about 12 amperes and this should finish at approximately 8 amperes, the average being 10 amperes. Each cycle is completed in six hours and there are, therefore, 4 cycles per day, except on the days when measured charges and discharges are made. On such days there will be two cycles. The total is 26 cycles per week. Requirements of the S.A.E. standard for various types and sizes of batteries range from 234 cycles to over 500 in the case of some of the larger batteries of the heavy-duty type. Occasionally the batteries are removed from the apparatus for a test at 300 amperes, 0° F. Each of these tests is counted one cycle, along with the others. When the ampere-hour output of a battery falls below 40 per cent of the manufacturer's rating at 20 hours, the test of that battery is discontinued.

With type A equipment the ampere-hours are calculated from the time, assuming the average current. With type B equipment the ampere-hours are exact, but the time may vary slightly from the schedule if irregularities in the line voltage occur. Numerous details for conducting these tests are given in the S.A.E. handbook and the latest edition should always be consulted, as it is not possible to give all the details here. These tests have attained general recognition, but they are not considered a part of the S.A.E. standard battery specifications.

Data on the useful life of large stationary batteries, train lighting, and some motive-power batteries may be obtained from actual installations of these batteries. In such cases it is necessary that they receive proper care and that systematic records of performance be kept. A life test made in a laboratory may lead to incorrect results unless details of the charge and discharge are carefully worked out to simulate the working conditions.

The details of a life test will depend upon the kind of battery to be tested, but in any case it will consist of cycles of charge and discharge under conditions that approximate service conditions. Not all the discharges need be made at the same rate, a group of discharges at a low rate may be followed by a group at a high rate. As such a test involves a large amount of routine work, it is helpful to plan the schedule of charges and discharges for the week. The length of time that the life test will last will normally depend upon the type of battery tested. Airplane batteries may last only 50 to 75 cycles; starting and lighting batteries several hundred cycles; and submarine batteries may last over a thousand cycles, requiring two years and a half to complete.

At the conclusion of a life test the positive plates are examined for loss of active material, corrosion of the grid, color, buckling, texture of the active material and breaks in the grids. The negative plates are examined for color, expansion or contraction, and texture of the active material whether firm, spongy, or sandy. The amount of sediment in the bottom of the jars is estimated or weighed, and its color noted. The separators are examined for strength, degree of action of acid, and oxidizing effect of the positive plates, and particularly for splits or holes. From such an examination it should be possible to form an opinion as to the worth of the various parts and the probable cause of failure.

6. VOLTAGE TESTS

The speed of a motor, the light from an incandescent lamp, and other services depend on the available voltage at the terminals of a battery under specified working conditions. These conditions will ordinarily indicate the kind of test to be made. One test, which has become recognized in the industry, is described in the *Standards* of the S.A.E. and in the *Federal Specification for Automotive Batteries*, W-B-131b. These specifications provide for a voltage test at 0° F. (−18° C.), when the battery is discharging at the rate of 300 amperes. The measurement of voltage is made 5 seconds after beginning the discharge. To comply with the specification, the battery must have a voltage above the minimum specified for its type and size. This test is sometimes called the "5-second voltage test."

7. LOW-TEMPERATURE TESTS

Batteries which are subject to low temperature conditions, as those in automobiles and airplanes, are usually tested at low temperatures in addition to the capacity tests at ordinary temperatures. The "300-ampere, zero-degree test" is now well recognized, but there is a tendency to go to lower temperatures. Ten years ago 10° F. was considered low enough, but now some prefer −10° F. The S.A.E. specifications and the Federal specification for automotive batteries describe the conditions for the test. After the battery has been cooled to 0° F. during a 24-hour period, it is discharged at 300 amperes. The voltage of the battery must be above a specified minimum at the end of 5 seconds, and the current must be maintained for a specified number of minutes without the voltage falling below an average of one volt per cell.

8. EFFICIENCY TESTS

The measurement of battery efficiencies has been discussed at length in Chapter VIII, and little remains to be said about it at this place. Efficiency tests are of secondary importance, and quite often the results are an indication of the efficiency of the experimenter as well as that of the battery.

The ampere-hour efficiency is calculated as the ratio of the ampere-hours output of the battery to the ampere-hours put in during charge, and usually expressed as a percentage. The conditions of charge and discharge should be carefully chosen and adhered to in all the tests. Since the charging current, besides restoring the active materials of the plates, may produce gassing, the efficiency will be lowered in proportion as the quantity of gas produced is increased. By eliminating gassing altogether and correcting for temperature, it is possible to show that the current efficiency very closely approaches 100 per cent. This is seldom the normal condition of operation, however, as some gassing almost inevitably occurs. In making an efficiency test, therefore, it is necessary that the operating conditions be clearly defined. The chief factors affecting the current efficiency are gassing, temperature variation, and the rates at which the battery has previously been discharged (see p. 223). Preliminary discharges, at the rate which is to be used for the final series of tests, should always be made.

The watt-hour or energy efficiency is of greater importance than the current efficiency because it is a factor in computing the cost of operation of a battery. The watt-hour efficiency is equal to the ampere-hour efficiency multiplied by the ratio of the average voltage during discharge to the average voltage during charge. The average voltage is obtained from the time integral of the voltage curve.

The watt-hour efficiency is affected by the same factors as the ampere-hour efficiency, and in addition by the factors that affect the voltage, namely, polarization, internal resistance, and, to a small extent, temperature.

9. OTHER TESTS

a. Tests of Intercell Connectors

Batteries intended for discharge at high rates must be provided with adequate intercell connectors. A table is given in Chapter X, showing the power losses in intercell connectors of motive-power batteries. Specifications for automotive batteries [3] provide that the voltage drop in intercell connectors shall not exceed 20 millivolts per inch of distance between post centers when the battery is discharging 300 amperes, the temperature being 80° F. The test is made by "stabbing" the post centers with sharp metallic points connected to a suitable millivoltmeter through flexible leads while current is flowing from the battery at the prescribed rate.

The voltage of Edison batteries which are used for oil circuit-breaker installations and other purposes requiring heavy currents should be calculated on a basis allowing for voltage drop in the intercell connectors and jumpers. Voltages shown in Table LVI of Chapter X are the voltages per cell. From these values should be deducted 0.006 times the multiple of normal rate to obtain the effective voltage per cell at the battery terminals. Tests of any particular battery can be made to find whether it meets this condition.

b. Tests of Container Material

Test specimens (not including seams) are cut from the sides and partitions of the container as shown in Fig. 122. The specimens are immersed in water at 70° F. (21° C.) for at least one hour and then may be broken in a testing machine, provided this is not done until 12 hours after the specimens have been cut. According to the *Federal Specification* W-B-131b, the material from rubber cases of automotive

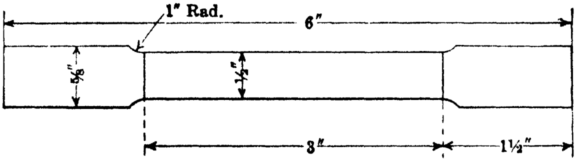

FIG. 122. Test specimen of container material for tensile-strength tests.

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[3] *Federal Specification for Ignition, Lighting, and Starting Batteries,* W-B-131b, obtainable from the Government Printing Office, dated 1939.

batteries is subject to rejection if its tensile strength is less than 1300 pounds per square inch, or if the elongation (before rupture) is less than the following minimum requirements for corresponding tensile strength.

TENSILE STRENGTH (Pounds per Square Inch)	ELONGATION (Per Cent)
1300	6
1350	5
1425	4
1525	3
1700	2
2000 or more	1

Rubber containers for motive power, motorcycle, and some other types of batteries are usually subject to requirements of greater tensile strength.

Tests for acid absorption are made by measuring and weighing specimens (3 by 3 inches) after immersion in sulphuric acid solutions of 1.300 sp. gr. at 75° F. (24° C.). The containing vessels are placed in an oven at 155° F. (68° C.) 7 days. When the specimens are removed from the solution, they are quickly rinsed in water, dried on the surface, and weighed. The material is subject to rejection if the increase in weight exceeds 1.5 per cent or if blisters or cracks are observed, or if the dimensions are increased 2 per cent. In this, as in other tests covered by the specifications to which reference is made, the full details should be obtained from the specification.

c. Tests of Glass Jars

Specifications for the quality of glass storage-battery jars may be found in the manual of the Signal Section of the Association of American Railways.

CHAPTER X

PRESENT-DAY USES FOR STORAGE BATTERIES

1. TELEPHONE BATTERIES

Storage batteries form an important part of telephone power-plant equipment. The requirements of telephone service are very exacting and much care and engineering skill have been devoted to perfecting the design, installation, and operation of these batteries. The large, and most of the small, telephone central offices in cities are operated on what is called the common-battery system in distinction from smaller offices in rural communities where each telephone may have its own local battery of dry cells. The storage batteries with their associated generators at the central offices furnish current for transmitting, signaling, switching, and various miscellaneous services. In addition, the batteries serve as electrical noise absorbers, preventing crosstalk between simultaneous messages and reducing the circuit noise of motor-generators, rectifiers, or other equipment used to transform the incoming power supply to a form suitable for use on telephones. The storage battery is admirably adapted to this purpose by reason of its low resistance and impedance.

Besides the normal continuous uses for these batteries, they are required in times of emergency to carry the entire load of the central office. Batteries with sufficient reserve capacity are provided, therefore, to permit operation of the central office to continue for some time if failure of the outside power supply should occur.

a. Historical Developments

Battery development in the telephone field has been stimulated by the rapid development in this system of intercommunication. Bell's first telephone apparently employed a primary battery to energize an electromagnet, but he discarded the battery shortly thereafter, preferring an instrument in which the feeble current induced in a coil of wire by a diaphragm of iron vibrating in the field of a permanent magnet served as the "talking current." The voice of the speaker was the source of power and this has been estimated to be of the order of 1×10^{-5} watt. The receiver, which at this time was a duplicate of the transmitter, converted the varying electrical current into corresponding vibrations of its diaphragm, thus producing sound waves heard by the listener. Early in 1878 the first commercial exchange was established in New Haven, Conn., without the use of batteries.

Following the invention of the carbon transmitter, of which there are several forms, battery-operated circuits became indispensable. Various voltages were tried, but little was gained by increasing the voltage above limits which are familiar today. The phrase "24-volt talking battery" which is applied somewhat indiscriminately to batteries of 10, 11, or 12 cells probably originated with an installation of 12 cells at Worcester, Mass., about 1896. About 1900, dry cells replaced other types of primary batteries in individual instruments, but the trend was strongly toward common-battery circuits in the larger communities. An early telephone power plant of 1893 is shown in Fig. 123.

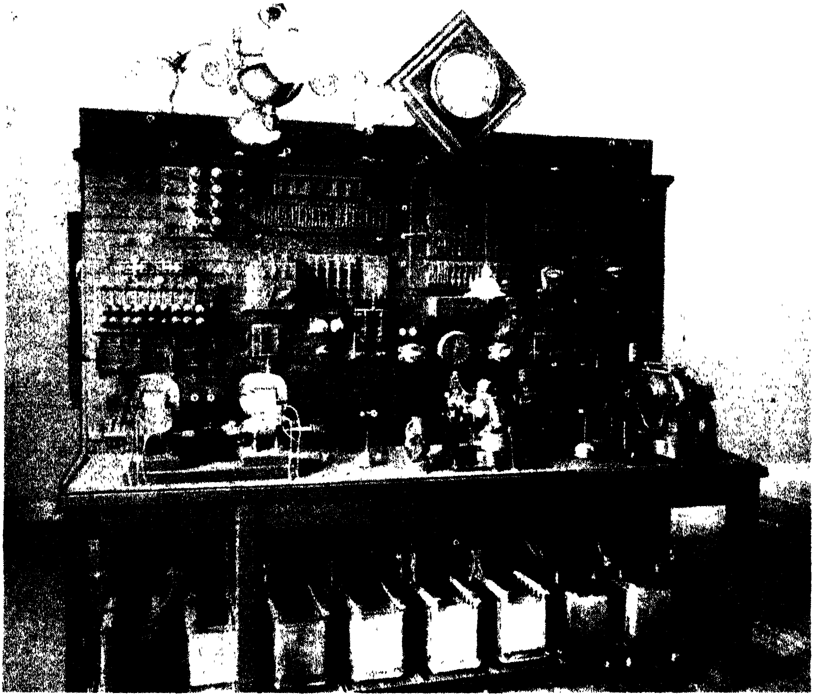

FIG. 123. Early telephone power plant, August, 1893. Four 4-volt batteries, two of them tapped at middle point; cells are of the Manchester box-type; charging machines, ringing machines, and tone-generator are mounted on a wood bench. The "switchboard" above is really made of boards.

The evolution of the common-battery system has produced two types of central offices, manual and automatic-switching offices. The latter are often called dial offices. Automatic-switching offices may be further classified as (1) motor-driven panel offices, (2) step-by-step switch offices, and (3) the all-relay offices of which the new crossbar system is one type. Obviously, any detailed description of these would be out of place here.

For many years, batteries of 11 cells have been standard in manual offices, with an additional battery of 11 cells connected in series with the first group to provide for toll calls and long-distance messages. The actual voltage of the 24-volt battery, however, ranged from 20 to 28 volts when no attempt was made to regulate the voltage. With the introduction of panel equipment about 1920 and the adoption of the continuous floating system of operation, 12-cell batteries again became common practice, and one emergency cell was added to hold up the voltage upon discharge. An additional battery of 11 cells in series with the first battery constituted the "48-volt battery" group to which were added 3 emergency cells. The limits of voltage variation have been narrowed by the use of automatic regulators until 25.75 ± 0.25 volts is commonly found today in dial offices, while large repeater offices run a little lower at approximately 23.5 volts. The regulation of the 48-volt battery is similarly held to 49.5 ± 0.5 volt.

More recently, the practice most commonly used in dial offices is to have one large battery of 23 cells with its floating generator, and with 4 emergency cells in reserve, to provide the major load which is nominally at 48 volts. The 24-volt load is then provided through counter cells if small, or by a separate battery and floating generator if large. The single 48-volt battery may of course be made up of two or more strings of cells in parallel.

b. Many Power Supplies Needed

While the 24- and 48-volt storage batteries are the principal ones in many telephone central offices, both manual and dial offices require a variety of other sources of power. These include, in various offices, (1) direct-current circuits of 4, 6, 16, 24, 38, and 48 volts for talking, signaling, message registers, and other purposes; (2) 110-volt positive and negative circuits for coin collection and return; (3) 24, 34, 48, and 130 volts for repeaters, teletypewriters and d.-c. telegraph circuits; (4) 20-cycle, 110, 85, and 77-volt alternating currents with direct current supplied by storage batteries superposed for manual and machine ringing circuits; (5) a variety of frequencies such as 4, 135, and 1000 cycles for testing or signaling; (6) several frequencies from motor-generators to provide "dialtone" and other tones to indicate the condition of the telephone circuits; and (7) twelve-frequency machines for carrier telegraph.

Most of these voltages and frequencies are obtained from generators driven by motors on the commercial power circuit, some are obtained from rectifiers and some from oscillators, while certain of the direct-current voltages are obtained from dry cells. Some essential equipment within the office is provided in duplicate as a safeguard against interruption of service.

The main batteries are connected directly to a bus, to which are also connected the large motor-generators. Normally the batteries float on this line, except in some types of offices when the load conditions are too light to warrant running the machines. The reserve capacity required of the battery in each case is estimated on the basis of load conditions and the probable reliability of the power supply. Although commercial power services in duplicate are obtained where possible, in addition to these, in many offices engine-driven generators are provided as stand-by protection, because times of emergency are usually periods of heavy load and continuous telephone service is of particular importance. Recent floods and wind storms have demonstrated the value of this reserve engine and battery equipment in maintaining telephone service during intervals when outside power was lost.

c. Direct-Current Loads

The amount of electrical energy required for the transmission of a single message is very small. About 35 ampere-seconds are required in a manual office to build up and restore connections and about twice this amount for each 100 seconds of actual conversation. Similar figures for dial offices are small also. In the aggregate, however, the current requirements for an office of 10,000 lines or more may be surprisingly large, amounting to hundreds of amperes.

In manual offices the 24-volt battery carries a heavier load than the 48-volt battery, since the latter is limited principally to the transmitter supply on long-distance or toll messages and to supplying P.B.X. batteries over cable pairs. In automatic-switching offices, however, operation of the intricate mechanism constitutes a heavy load on the 48-volt battery and this battery furnishes the greater part of the current. Approximate figures for certain multi-unit offices of 17,000 to 20,000 lines illustrate this difference.

TYPE OF OFFICE	BATTERY	HEAVY LOAD AMPERES (DAY)	LIGHT LOAD AMPERES (NIGHT)
Manual	24-volt	300 to 500	50
Manual	48-volt	50	5
Automatic switching	24-volt	250 to 300	100
Automatic switching	48-volt	600 to 900	200

Power-plant loads are frequently greater than the above, particularly in large cities where several offices may be housed in one building and these offices may supply current for many private branch exchanges.

Peak loads in residential districts usually occur about 9 A.M. and again in the early evening. In business centers, the peak load is fairly well sustained during customary business hours, showing some decrease during the luncheon period. In long-distance repeater offices there is generally no distinct peak since most of the equipment operates 24 hours daily.

The size of cells in the main batteries will naturally depend on the traffic to be handled and whether the battery is assembled as a single series connection of cells or by paralleling strings of smaller cells. When parallel batteries are used they may be connected either through switches or by solid bus bars across the ends of the groups, and in some cases additional cross-connections have been made within the groups to insure equalization of the load. As many as 8 paralleled strings of cells are sometimes employed.

d. Open Type Cells

The larger cells are usually of the open lead-lined tank construction mounted on oil insulators (Fig. 124). The plates may be of the G-size, $15\frac{5}{16}$ by $15\frac{5}{16}$ inches or the H-size, $15\frac{5}{16}$ by $30\frac{3}{4}$ inches. The number of plates per cell varies with the requirements of the particular installation, but space is often provided in each cell for the addition of more plates to meet the needs of increased traffic, the plates being burned on to bus bars through connecting lugs at the top. The bus bars on terminal cells, or on intermediate cells where taps are taken off, have heavy copper bars cast in the lead bus bars. The capacities of G-cells with Manchester positives and box negatives range from 800 ampere-hours at the 8-hour rate for the 11-plate size to 6720 ampere-hours for the 85-plate size. Larger batteries, containing H plates, range from 3200 ampere-hours at the 8-hour rate for cells containing 21 plates to 13,440 ampere-hours for 85-plate cells at the same rate. For the largest and busiest central-office power plants supplying several office units, even this is not sufficient and installed capacities up to nearly 35,000 ampere-hours have been reported.

Open-tank batteries are installed in ventilated rooms having floors and walls protected by acid-resisting paint. One terminal is grounded, this being the positive, originally adopted to reduce the possibility of electrolytic corrosion of open-wire subscriber's lines. With this arrangement there is also less likelihood of corrosion of the lead linings of the tanks which might result from accidental grounds on any part of the system, combined with a leak at the tank. With modern installations these corrosion troubles are not experienced. The substantial reduction in gassing and spraying under the continuous floating routine

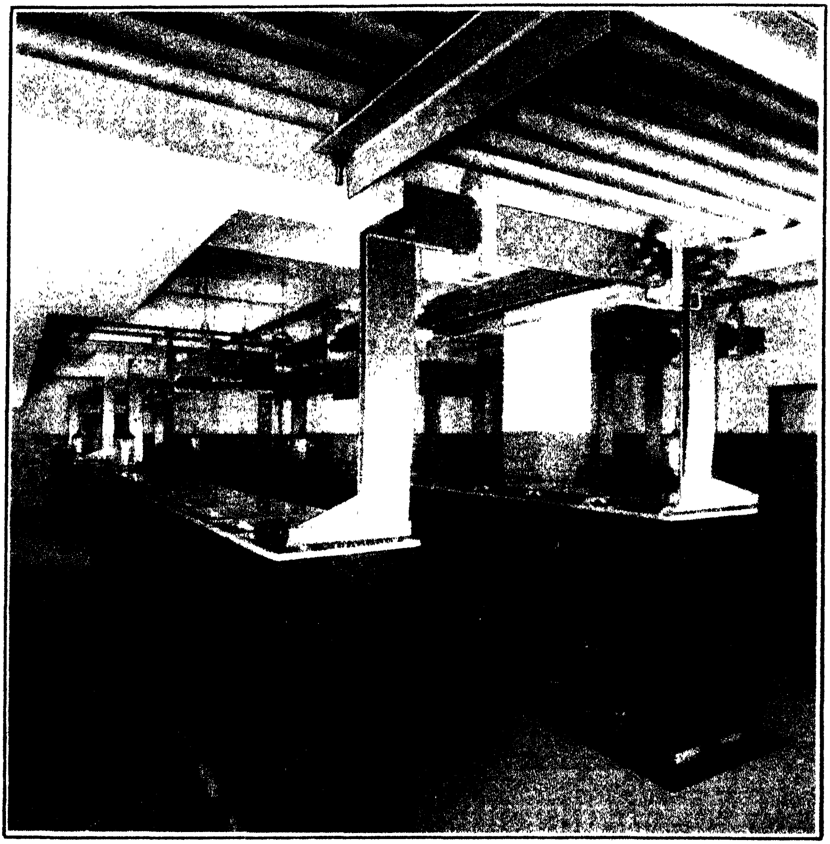

FIG. 124. Main batteries in a multi-unit telephone office; type H-21 3200 ampere-hours; 46 regular and 8 emergency cells, with low-type insulation to facilitate maintenance (1931).

common for these batteries has reduced acid attack to a point where protective paint rather than the former expensive acidproof floor construction is satisfactory and economical.

e. Sealed-In Cells

Increasing use is being made of sealed-in glass-jar cells which are provided with vents designed to prevent effectively the escape of spray from the cells. These cells are naturally smaller than the massive open-tank cells, but sufficient capacity for rather large central offices can be obtained by paralleling a number of strings of series connected cells (Fig. 125). These sealed glass cells contain either Manchester positives and box negatives (Fig. 22 in Chapter II) or flat-pasted plates having heavy reinforced grids designed for floating service, such as the Floté or Tytex types (Figs. 20 and 21). The individual cells contain plates of the F size, approximately 11 by $10\frac{1}{2}$ inches, or of the smaller E size. The capacities range from about 1155 down to 80 ampere-hours per cell at the 8-hour rate. The sealed glass-jar cells are usually shipped filled and charged. They are, therefore, ready for immediate installation, which is much simplified as compared with open types requiring assembly and initial charge. Another advantage, which is perhaps of more importance, is the possibility of installing them in rooms with other telephone equipment including switching and power-plant apparatus.

These cells were developed with the needs of telephone service particularly in mind and certain accessories to facilitate operation and maintenance are available. These include floating charge indicators, which show at a glance the approximate amount of charge in each cell, thereby permitting early discovery of any irregularity in spite of the less frequent readings now being taken. Thermometers in wells are also provided for pilot cells, and explosionproof vent caps are available, through which specific gravity readings and addition of water to replace evaporation can be made (Fig. 126). Explosive gas during charging is a greater hazard with enclosed cells than with open, and possible ignition by static electricity collected on an attendant or by a spark from a tool or by opening of a circuit near a cap must be guarded against. The cells are available with either thin or thick plates, the latter giving long life under continuous floating routines where they normally get little or no working. Steel racks are used instead of impregnated wood formerly employed, since attack by acid has been eliminated. These racks are ordinarily located in machine rooms with the rest of the power plant, but battery rooms intended for open-type cells are also utilized. This gives substantially increased flexibility of floor-plan arrangement as compared with the use of open-tank or open-glass-jar cells.

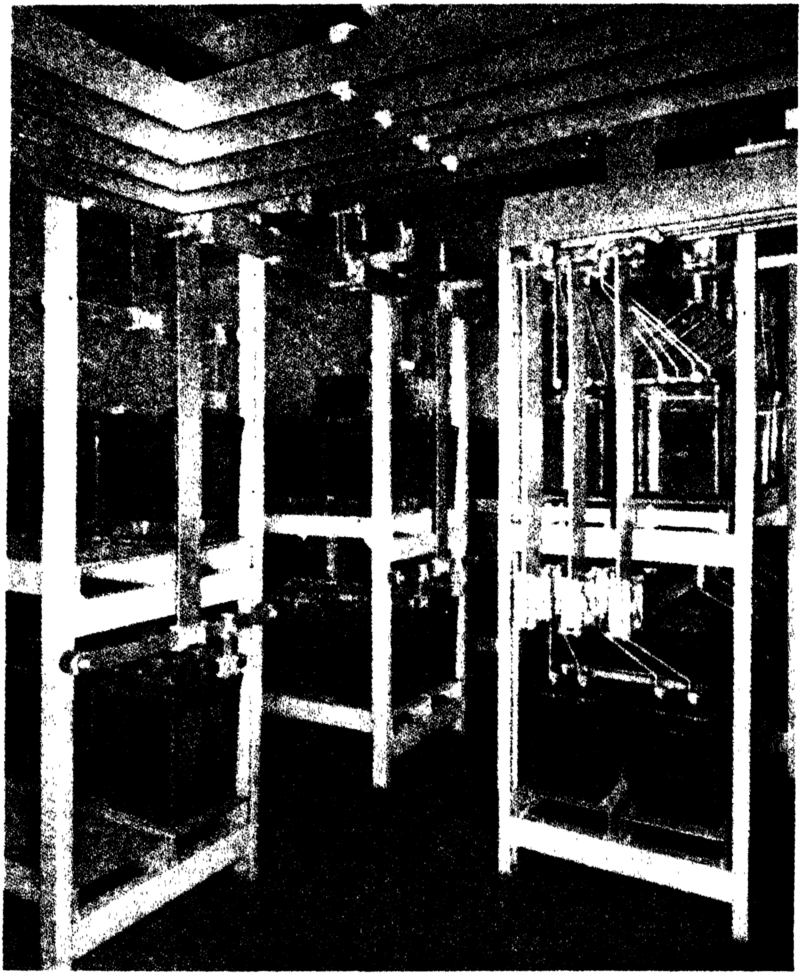

FIG. 125. Main batteries in a standardized telephone power plant for medium-sized metropolitan dial office; parallel strings of 1056 ampere-hour cells with emergency cells and 200-ampere nickel-alkaline counter cells, mounted on metal stands; connected by aluminum bus bars (1939).

The specific gravity of electrolyte in most telephone batteries when they are fully charged is 1.210 to 1.230. The specific gravity being low, local action is reduced to a minimum and the deterioration of separators is also reduced. Use of double insulation, that is, both wood and rubber separators, contribute to long life and freedom from trouble.

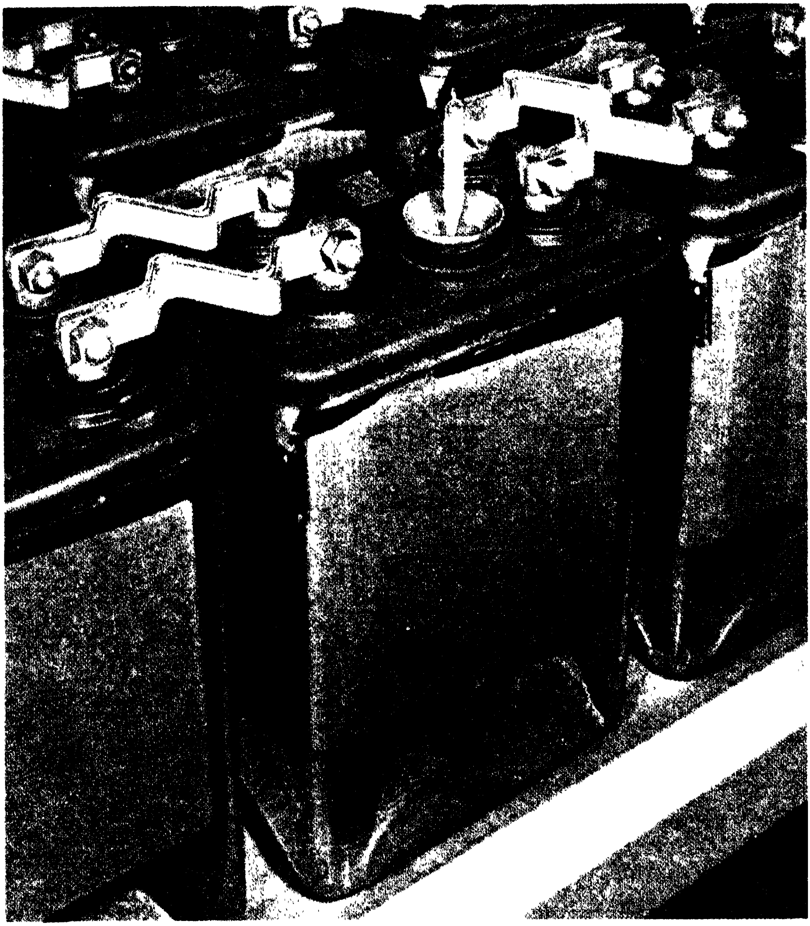

FIG. 126. Sealed glass-jar telephone battery, thin plates, 684 ampere-hours, equipped with floating-charge indicators, explosion-proof vents and thermometers (1936).

f. Operating Routines

Most central offices now operate on floating batteries which are, therefore, fully charged at all times except during an emergency discharge. The floating voltage is preferably 2.15 volts per cell. At this voltage the batteries absorb sufficient current to keep them in proper condition, but periodic equalizing charges are part of the program of maintenance. The load of the office is really carried by the primary source of power, but the battery serves the double purpose of providing reserve power for emergencies and improving the transmission of speech.

Where the size of the installation, or light load during the night, or the absence of continuous supervision makes it uneconomical to float continuously, various intermittent charging routines are used, some manual and some automatic. The intention is to carry as much of the 24-hour load as is practicable from the charging equipment which improves operating efficiency and extends the battery life.

Charging generators which were formerly of a special type with smooth armatures and windings banded on the surface as a means of reducing the noise level have now been largely superseded by the use of commercial-type generators with filter circuits. The latter consist of choke coils of high impedance and low direct-current resistance together with electrolytic condensers of high capacitance. Each electrolytic condenser has 1200 microfarads capacitance or more at 24 volts, or approxmiately half this amount at 48 volts, and several condensers in multiple are used. Similar but smaller condensers are also available for 130 volts. Both liquid-type and "dry"-type condensers are used.

g. Batteries for Miscellaneous Uses

As indicated above, there are various miscellaneous batteries of small capacity which are required in addition to the main batteries. One of these is for operation of message registers in manual offices. Thirty-nine volts are required with an allowable variation of plus or minus 2 volts. For this purpose, a battery of 19 cells is provided and kept charged by floating continuously through an automatically controlled two-rate charging circuit from the 48-volt central-office battery. For operating coin-collecting devices on telephone lines, two batteries of 55 small storage cells each are provided at many of the larger central offices, while dry cells are used in small offices, the negative side of one battery and the positive side of the other battery being grounded. Connection being made to one or the other of these batteries, the operator is enabled to collect or return the coins which have been dropped into the slots at the pay-station telephone. These batteries seldom exceed 6 ampere-hours in capacity. Later ti was found practicable to design a double-current generator, which in addition to 20-cycle and other signaling energy, provides the currents for controlling coin boxes. Certain types of ringing systems commonly used have small storage batteries of 8, 16, or 22 cells to superimpose a direct-current voltage upon the alternating-current ringing voltage. This aids in tripping and improves the wave shape for ringing the bells.

In main offices where large groups of telephone repeaters are located for use in long-distance transmission, separate storage batteries and generators are provided primarily for the operation of the vacuum tubes. The current which heats the filaments is usually derived from a motor-generator set with automatic voltage control floating upon a 24-volt battery. The plate circuit needs 130 volts and this is also usually provided by a generator floating upon a storage battery. In the largest combined repeater, long-distance and telegraph installations loads are heavy, approximating 5000 amperes at 24 volts and 500 amperes at 130 volts.

In telegraph offices, batteries for two systems are employed. For grounded telegraph these usually consist of two parts each of 61 cells plus 8 emergency cells and 9 counter-electromotive-force cells, furnishing regulated 130 volts on the positive and negative sides of a neutral ground wire. For metallic telegraph two batteries of 16 cells each furnish plus and minus 34 volts. In both systems motor-generators or rectifiers float the batteries continuously.

h. Counter Cells and Emergency Cells

Counter cells of both the lead-acid and nickel-alkaline types have been employed for battery regulation within limits of their rating. Thus in dial P.B.X. equipment requiring regulated voltage, counter cells are introduced into the discharge circuit to keep the voltage at the distributing point below the upper limit during the time the battery is being charged. They are used in connection with plate voltages for repeater circuits and for telegraph circuits to prevent excessive voltages during charging of the batteries. They are also used to obtain lower voltage current from higher voltage battery, such as 24-volts from 48-volts. In these and various other uses counter cells may be in the circuit for brief periods or continuously.

The nickel-alkaline counter cells (Fig. 94 in Chapter VI) use several thin plates of nickel with glass separators and a solution of treated sodium hydroxide. Another form uses stainless steel (Ni–Cr–Fe) plates with sodium hydroxide solution. These counter cells have displaced the lead-acid type, because they do not build up objectionable capacity with continued use and can be short-circuited during switching without causing heavy currents to flow. They also have a longer life. The counter electromotive force of these cells for various percentages of their rated current is as follows:

PER CENT OF RATED CURRENT	COUNTER EMF IN VOLTS
10	1.95
25	2.0
50	2.1
75	2.2
100	2.3

Counter cells are generally used in the ratio of one counter cell to from 7 to 12 active cells, depending upon the charging methods used and the voltage limits which must be maintained.

"Emergency cells" are regular storage cells arranged to be cut into the circuit when the battery voltage is being reduced by an emergency discharge. They are kept fully charged during idle periods by small rectifiers which replace the internal losses.

i. Private Branch Exchanges

Private branch exchanges are large users of storage batteries. These exchanges vary greatly in size, from those having one trunk line and a few stations to those which have switchboards like large central offices and handle several thousand extensions. They are of two main types: (1) the private manual branch exchanges known as P.B.X., and (2) the private automatic branch exchange, sometimes known as P.A.X. or dial P.B.X. since the telephones are equipped with dials. The community dial exchange, using equipment somewhat similar to a large dial P.B.X., is a small central office attended only at intervals. In these offices alarm circuits are provided to call an attendant from an attended office in the event of major trouble.

All these exchanges require storage-battery power for calls to the central office and for local messages. Voltages range from 14 to 26 volts for the smaller exchanges to 48 volts for the larger dial boards. Most of the private exchanges are too small to warrant a resident maintenance personnel and, as a result, the maintenance of the local storage batteries, when provided, must be largely automatic. Small batteries are ordinarily charged over cable pairs from the central office, but those in the larger exchanges and in the dial type are charged locally by rectifiers or by motor-generators. This charging goes on during use so that the batteries are relieved of a substantial part of the load.

In small P.B.X.'s the batteries are trickle-charged continuously, and it has been found practicable to have a maintenance man visit the exchange only at extended intervals when addition of water is needed, while in the meantime the P.B.X. attendant will call for a plant man if a charge-indicator ball drops below a white line. Water-level charts are being introduced to assist in charging rate readjustments.

Ampere-hour meters were once used in dial P.B.X. power plants to control the amount of charge, being arranged to start and stop a rectifier as needed to let the battery take a 10 to 20 per cent discharge. The charging rate was set so that the rectifier worked most of the time during the day's load period. Recently voltage control in conjunction with a two-rate floating-charge system has found increasing application in automatic operation of these batteries. Several kinds of temperature-compensated relays are available for the purpose. The primary function of relay, type 253, for example, is to select either of two charging rates, high or low, depending on the state of charge of the battery. If the battery is in need of considerable charging, the high rate will be used first. As the voltage of the battery rises to approximately that of full charge, the relay operates to remove a short-circuit from part of the resistance in the circuit and the charging rate decreases to a trickle-charge rate. Compensation for changing room temperatures is accomplished by a bimetallic strip which alters the tension of the spring of the relay, thereby changing the voltage at which the relay operates.

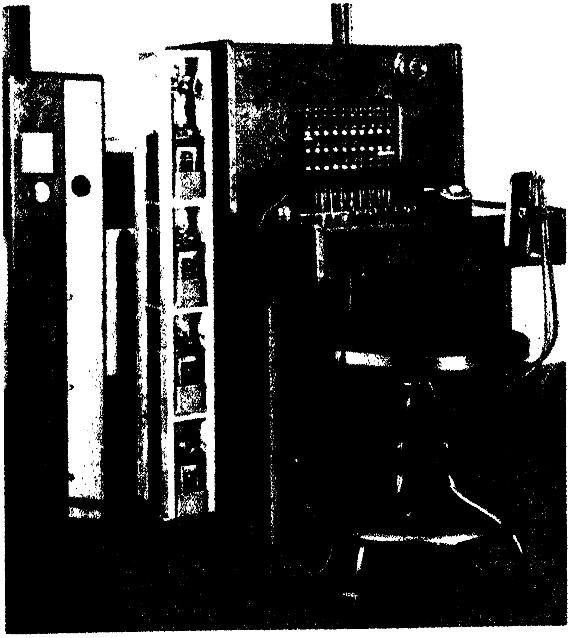

FIG. 127. Battery for a private branch exchange.

Grid-controlled tubes afford another means of close automatic voltage regulation of rectifiers continuously connected to storage batteries. If only direct-current commercial power is available, small motor-generators are provided.

The batteries are universally of the sealed-in type but may be in either glass or rubber jars, the former now predominating. A battery plant widely used in small single-position P.B.X.'s has four 2-cell units (Fig. 127), each unit being mounted in a rubber cup and placed upon a separate shelf in a tall narrow cabinet matching the exchange switchboard to which it is attached at one end. The charge-indicator balls in the top unit are conveniently in view of the attendant through an opening in the cabinet. The assembly comes from the factory wired and equipped with a fuse panel, thus greatly reducing the installation work upon the premises. Two-cell batteries in single glass jars are available in small capacities, and also similar 3-cell units in larger capacities approximating 100 ampere-hours.

Counter cells are provided, if necessary, in the larger dial P.B.X.'s and these, together with a voltmeter relay and other control equipment, maintain the bus voltage automatically within the proper range. Automatic power plants to meet widely varying needs of private branch exchanges and small central offices have been so skillfully designed and constructed in compact units that relatively infrequent visits of the maintainer are required. He can tell by the state of charge of the battery and the amount of water which it needs at the time of his visit, whether the installation is properly adjusted to the particular conditions of service.

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2. STORAGE BATTERY APPLICATIONS IN RAILWAY SERVICE

a. Railway Signaling

Track and Signal Circuits. A report of the Block Signal and Train Control Board of some years ago contained the statement: "Perhaps no single invention in the history of the development of railway transportation has contributed more toward safety and dispatch in that field than the track circuit. By this invention, simple in itself, the foundation was obtained for the development of practically every one of the intricate systems of railway block signaling in use today wherein the train is, under all conditions, continuously active in maintaining its own protection." The closed track circuit was invented by Dr. William Robinson, August 20, 1872. This invention grew out of his previous invention of the open-track circuit, which proved to be unsatisfactory. The closed-track circuit differs from the open-track circuit in the essential particular that a small electric current flows continuously through a section of the track, and, when the track is clear, a signal indicates it to be so.

Signals are installed along railroad tracks to space trains properly and to instruct them when to proceed or stop. The distance between signals is dependent upon the character of the country, the concentration of traffic and the allowable speed of trains in the particular locality. As a general average, a track circuit is about a mile long.

Almost every modern automatic-signaling system employed on steam roads involves some form of battery power for the various control, lighting, and operating circuits. Both primary and storage batteries are widely used for these important services. Railway signaling is one of the most exacting applications of storage batteries, because the highest degree of dependability is required and because maintenance of batteries scattered along many miles of track is a difficult matter.

For some purposes, the batteries furnish the entire direct-current power requirements, but where circuits are normally fed directly or through rectifiers from a power line, a battery is usually installed as a stand-by or reserve power supply to insure uninterrupted service in case of failure of the normal power supply.

Operation of automatic block signaling equipment is in most cases controlled entirely by the movement of trains. This is accomplished through track circuits, the track being divided into sections which are electrically insulated from each other. Within each section adjoining rails are bonded together to provide a continuous low-resistance circuit. At one end of the circuit a "track battery" is located and at the other end a relay, which in turn controls a second or signal circuit (see Fig. 128). As long as no train is in the block, the relay is energized and the signal is held in the clear position. When a train enters, its wheels and axles shunt the primary circuit of the track relay, causing the armature to drop and thereby interrupt the signal circuit. The signal then changes to a restrictive indication, shown by a semaphore or by the position or color of lights. Broken rails or battery failure automatically result in a signal for trains to stop.

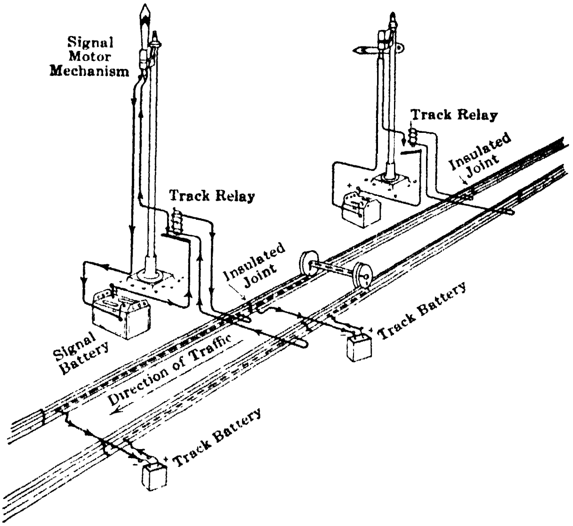

FIG. 128. Track and signal circuits.

The voltage applied to track circuits is from ½ to 2 volts. It is purposely kept low to minimize leakage of current from rail to rail across the ballast. The current flowing in the rails when the track is

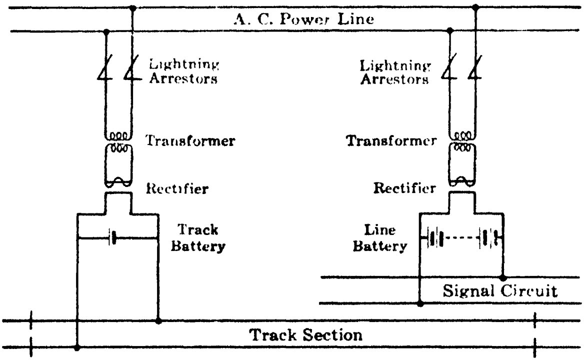

FIG. 129. Floating battery system for track and signal circuits.

clear ranges from 200 to 500 milliamperes and, when occupied, from 500 milliamperes to 2 amperes, depending on the type of battery and the resistance in series with it to limit the current when a train enters the section. A single storage cell of 60 to 80 ampere-hours is generally sufficient for the track circuit, but if primary batteries are used the capacity is necessarily larger.

Block signals are of three general types, described as semaphores, color lights, and position lights. In most cases they operate on 8 to 12 volts. Semaphores require a steady current of about 40 milliamperes for holding the arm in the clear or caution position and 2 to 3 amperes for about 10 seconds to operate the motor when the signal arm changes from a restrictive to clear position. If semaphores are equipped with electric lamps, an additional current, which may be as much as 1.5 amperes, is needed. Color-light signals require from 0.5 to 2.25 amperes and position-light signals from 2 to 5 amperes, depending on the number and wattage of the lamps. Sometimes the lamps are lighted only when trains are approaching, in order to conserve power. Batteries for the signal circuits range from 80 to 300 ampere-hour capacity.

Although several methods of maintaining storage batteries in a charged condition can be used, the floating battery system (Fig. 129) is commonly employed at the present time. An alternating-current transmission line along the railroad's right of way furnishes the power, and connection is made at each battery location through a transformer and rectifier. The output of the rectifier is adjusted to cover the average current required by the service, plus a small additional amount to compensate for local action in the battery. Other charging arrangements include trickle charging at various rates through rectifiers or periodic replacement of the discharged battery by one freshly charged.

At highway grade crossings, various automatic protective devices, including flashing lights, wigwags, stop-and-go signals, and barriers of several kinds, are employed to warn or stop vehicles when trains are approaching. Power requirements for these range from 8 to 12 volts and from one to 20 amperes. At many crossings these protective devices are operated by alternating-current power either directly or through rectifiers with a battery as a stand-by source of power.

Both lead-acid batteries and nickel-iron alkaline cells find use in various signal applications. The type of cell and its capacity must in any case be determined by the character of the service. A cell of the lead-acid type commonly used for railway signaling is shown in Fig. 22 (Chapter II). The nickel-iron cells are Edison cells of the types A or B, the former being shown in Fig. 35. Storage batteries of either type are required to meet specifications covering construction and performance of the Signal Section of the Association of American Railroads.

b. Interlocking Plants

Signaling facilities and switch mechanisms for governing the movements of trains at terminals, junctions, grade crossings, and drawbridges are usually interconnected and controlled through mechanical, electro-pneumatic, or all-electric interlocking plants in order to expedite traffic and to avoid conflicting routes and signal indications. The interlocking machine is installed in a tower overlooking the tracks. Power for the control machine, switch-operating mechanisms, and, in some cases, for signals within the range of the plant is generally supplied by a storage battery of 10 to 120 volts, depending on the type of plant. The capacity of the batteries ranges from 75 to 150 ampere-hours. The batteries may be floated on a rectifier from an alternating-current line with provision for increased rates of charge following emergency discharges. At some interlocking plants engine-driven generators are provided for battery charging. The service requirements vary widely with the type of equipment and with the distance from the control tower. The cells are of the same types as those used on signal circuits.

c. Centralized Traffic Control

One of the most recent developments in automatic signaling is centralized traffic control. As its name suggests, it is a method by which an operator in a convenient location can control the switching and movement of trains throughout a wide territory, extending 20 to 30 miles in either direction. The operator sits before a panel board such as that shown in Fig. 130. Pilot lights on the board indicate the location of trains, the position of switches, and the indications of signals throughout his territory. By levers on the control board he can route trains, permitting fast trains to pass slower trains at passing sidings, or arrange for trains in single-track territory to meet and pass at sidings with a minimum of delay. Trains move on signal indication without the necessity of written train orders. This system increases track capacity and thereby postpones the necessity for increased trackage with increased traffic under older methods of operation.

Signaling and switch mechanisms are actuated through coded impulses for which power is supplied by storage batteries of relatively high voltage but small capacity. The voltage used depends on the length of the coded circuits. At each remote switch, a relay tuned to its special code responds to its signal and actuates a secondary circuit controlling the mechanism. The power supply for the signals may be the same as in any automatic block signaling system, but switch mechanisms usually operate directly from a local storage battery of 100 to 150 ampere-hour capacity.

d. Car Retarders

In railroad classification yards, mixed car consignments are received with each incoming train. The cars must be shifted and reclassified according to routes and trains. A locomotive will do the shifting from a "hump" by allowing cars to glide from a running start on to the proper track, but the cars must be retarded at the proper time to avoid colliding with other cars. This was formerly done by hand brakes, but the use of electric or electropneumatic retarders and switches has done much to expedite the movement of cars through the yards. Car retarders are mechanical shoes along the rails which contact both faces of the car wheels and slow the cars down to the proper speed for traversing the yard tracks and for coupling to other cars. The retarders are controlled from a high tower overlooking the switching area. Power is furnished by storage batteries of 120 or 240 volts having an average capacity of 120 ampere-hours. The batteries are usually floated on rectifiers or motor-generators. The types of cell employed are the same as for signal service.

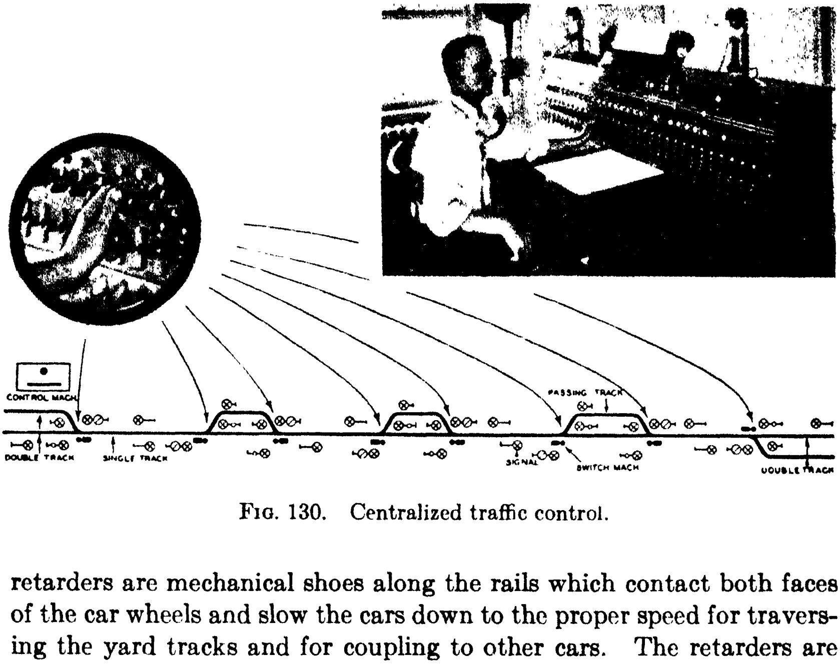

Fig. 130. Centralized traffic control.

e. Multiple-Unit Cars

In and around large cities, rapid transit facilities must be provided for moving large numbers of people. Mass transportation has been accomplished most effectively by electrified lines on which the cars are a modification of the standard railway coach. Each car, or car and trailer as a unit, has its own propulsion motors and other facilities, in contrast to a railway coach which depends on a locomotive for power. These cars operate in trains without a locomotive. In a sense they are trolley cars joined together and operated by one man at the control position at the head of the train, hence the name multiple-unit cars or MU cars. The number of cars in a train varies with the expected traffic density at the time of day. This varies through wide limits from rush hours to the light traffic of the early morning.

The controller is essentially a switching device that operates the power switches by electromagnets. The control circuit is independent of the main propulsion current and is of lower voltage, that most commonly used being 32 volts. It provides the power supply to actuate motors and brake equipment. It supplies power also for door mechanisms, safety interlocks, marker lights, and emergency lights. Storage batteries are the indispensable source of power, protecting these vital services. The capacities which are needed vary from 50 to 300 ampere-hours. When lead-acid batteries are used, they are assembled in rubber jars and contain electrolyte of a relatively low specific gravity, 1.225. Nickel-iron-alkaline batteries of the Edison type for 32-volt systems consist of 24 to 27 cells, depending on service requirements. Charging is accomplished by a motor-generator or by connecting the battery to the grounded side of the air-compressor motor with a shunting resistor to control the charging rate. The latter has been used on subway and elevated lines.

f. Electric Locomotives

Electric locomotives have control circuits similar to those found on MU cars, the principal difference being that the current-carrying contactors must be much heavier and that additional loads are often put on the control circuits. These include cab lights, headlights, cooling fans, blowers, train-control equipment, and general, rather than emergency, lighting. The size and voltage of the battery depends on the choice of the locomotive manufacturer and the connected load. Some locomotives are provided with 32-volt batteries having a capacity of about 300 ampere-hours and others with 76-volt batteries and a capacity of 425 ampere-hours. The storage batteries are floated continuously across a motor-generator set.

g. Gas-Electric Rail Cars

Service on branch lines is likely to be more economically handled by light-weight rail cars than by the conventional equipment and steam locomotives. These cars are driven by electric motors which receive their power from gasoline-engine-generator sets. This gas-electric equipment, as it is generally called, has advantages over straight-engine drive because of the flexibility of electric control and the elimination of gear-box transmission. The first cars were equipped with two or more automotive bus engines, but increased power requirements led to the design of special heavy-duty engines. More recently the trend has been toward Diesel engines.

Both 32- and 64-volt systems are employed, using batteries of 16 or 32 lead-acid cells or of 24 or 48 cells of the nickel-iron-alkaline type. Charging is accomplished by a small exciter mounted on the end of the main generator shaft, or by a separately driven engine generator set, or by the main generator when the engine is idling. Some bus-type generators have been used also. The batteries have a capacity of 200 to 300 ampere-hours. They are used to crank the engines, light the cars, and provide current for the control circuits.

h. Switching Locomotives

In the field of heavy traction, several types of electric locomotives have been put in operation for switching service and as a substitute for steam locomotives in city streets where the use of steam locomotives is objectionable. Effective electrification of railroad yards and sidings thus becomes possible in many localities without the necessity of supplying trolley or third-rail systems. A saving in capital charges and operating costs may be effected and the risk of fire reduced when the battery locomotives operate into, and out of, buildings. The battery locomotive possesses characteristics which make it well adapted to switching service. The load is fluctuating and the peak loads are high, but the average demand is relatively low. The battery serves as a reservoir of energy which can be supplied in large quantity for starting and accelerating trains.

Switching locomotives may be classified as (1) straight storage battery locomotives for which the battery is the sole source of power; (2) combination battery and trolley (or third-rail) locomotives which may operate either on the battery or on external power; (3) three-power or battery-oil-electric locomotives which operate on the battery alone, or the battery and internal-combustion engine together or on external sources of power; (4) Diesel-electric locomotives.

The straight storage-battery locomotives vary in size from 2 to over 100 tons. They are adapted to service where the total energy required in the course of a day can be furnished by a battery of reasonable size and where sufficient time (usually night time) is available for charging the batteries. Such locomotives are relatively simple in construction and economical to operate; they are free from fumes; they have a high overload capacity for starting and accelerating trains of cars; and they avoid the necessity for trolley wires and bonded tracks.

Combination battery and trolley locomotives are applicable to situations where the work to be done would preclude installing batteries large enough for a full day's work, or where the work is so continuous that sufficient time is not available for battery charging, or where it is impracticable to install trolley wires or third rails on the complete trackage which is to be covered. The batteries in these locomotives are proportionately smaller than in straight battery locomotives, because the main part of the load is on external sources of power. The trolley or third rail is used when the locomotive is on main tracks, but the battery supplies current when it is within buildings or on tracks which are not electrified. The size of the battery, therefore, must be determined for each individual installation, depending on traffic conditions. The batteries on these locomotives can be charged by current from the trolley.

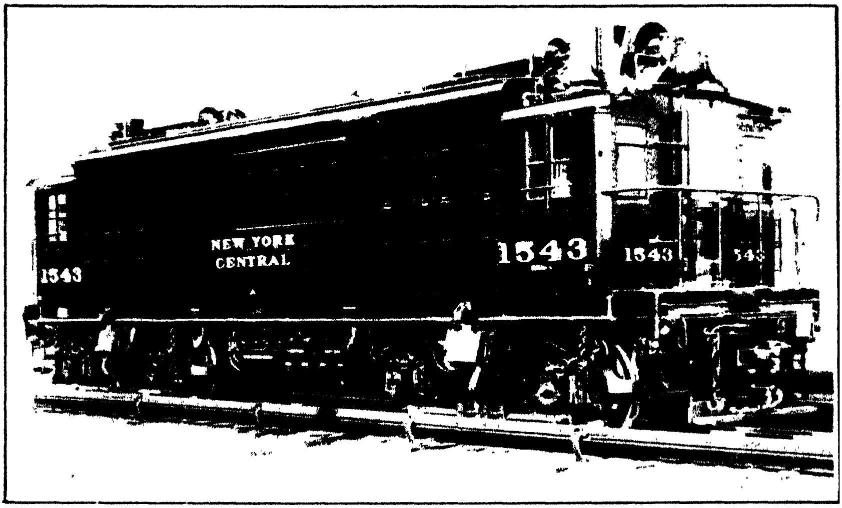

FIG. 131. Battery-oil-electric locomotive for switching service.

Battery-oil-electric locomotives of 1000 horsepower, sometimes called three-power locomotives, have Diesel engines directly connected to generators of suitable characteristics to supply current to the four traction motors and at the same time operate in parallel with the battery which floats across the terminals. If the locomotive is operating over electrified tracks, current is supplied from external sources through a trolley, pantograph, or third-rail shoes. Much of the time, however, these locomotives operate on the battery and engine combined or on the battery alone. These locomotives are of 128 tons and they are provided with 300-horsepower Diesel engines and 300-kilowatt batteries.

These locomotives are provided with batteries of 240 cells of the Ironclad type, TLA-27, rated at 650 ampere-hours at the 6-hour rate. A locomotive of this type is shown in Fig. 131.

The Diesel engine is cranked by power furnished by the battery through the main generator, which for the time being functions as a motor. The generator is compounded to permit full-load application of power before power is drawn from the battery. The battery aids the generator when accelerating trains, but it is charged by the generator when the traction load is less than the capacity of the engine generator. Provision is made for periodic equalizing charges of the battery by raising the generator voltage. The operating characteristics of one of these Diesel-oil-electric locomotives are shown in Fig. 132. The division of the load between battery and generator depends on the voltage. This is entirely automatic and the engine-generator is not overloaded.

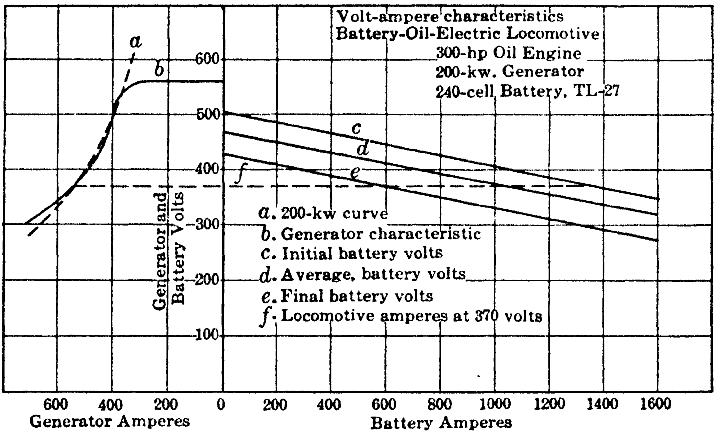

FIG. 132. Operating characteristics of a battery-oil-electric locomotive.

Diesel-electric locomotives of 600 to 1000 horsepower are now in common use for switching service. They are economical to operate. The Diesel engines are connected to the main generator and usually have a separate exciter mounted on the same shaft. A starting winding is put in the generator to crank the engine from the storage battery.

The electrical requirements vary, but the breakaway torque requirements may amount to 1200 to 1600 amperes. The cranking batteries vary from 64 volts and about 300 ampere-hours to 110 volts and about 200 ampere-hours.

i. Diesel Locomotives for Passenger Service

Originally applied to switching service, Diesel-electric locomotives are now operating successfully on main-line high-speed passenger service. Since 1935 the development of these has been rapid. One of the larger manufacturers has standardized on 900 horsepower engines, installed as two engines in each cab. As many as three cab units have been coupled together as a single unit, controlled by one man in the head end of the first unit. Two units, having 3600 horsepower are commonly employed on high-speed streamlined passenger trains. Each cab unit has a 64-volt, 425-ampere-hour storage battery for engine cranking, control, and fuel-pump services. In order to start the Diesel engines, a special winding is put in the main generator so that it may be cranked by the battery. The breakaway torque requirements are commonly 1200 to 1600 amperes.

j. Car Lighting and Air Conditioning

The earliest attempts at lighting railway cars by electricity were made in 1881 with a straight storage-battery system. The Pennsylvania Railroad is said to have equipped eight parlor cars with batteries in 1885 and the Central Railroad of New Jersey installed the first axle-generator system of which there is record, in 1894. Electric car lighting is confined to passenger trains or trains made up of express, mail, or baggage cars.

One of the important factors which has contributed to the rapid development of railway train lighting in recent years has been the introduction of metal-filament electric lamps. In the earlier days lamps were rated at 60 to 64 volts, but with the introduction of axle-generator systems and tungsten lamps this was reduced to 30 to 32 volts. This reduction was made possible because of decreased line drop and increased efficiency of the lamps. The voltage of train-lighting systems, with few exceptions, has been less than 110 volts because it is desirable to keep the number of cells in the battery as low as possible. In some foreign countries, voltages as low as 24 volts are found.

The traveling public has been educated in recent years to expect higher intensity of illumination than was previously acceptable. Four to six foot-candles which were once satisfactory have been increased to 8 to 12 foot-candles. To provide this without glare, indirect lighting or special light-diffusing fixtures have been used. Some roads have used spectrum lighting and other decorative effects. The effect has been to increase the demands on the battery for lighting and still more for the newly developed air conditioning.

The straight storage system was the earliest system developed. It consisted of a battery on each car to provide current for the lights on that car irrespective of the other cars of the train. Charging was done at terminals or division points during the layover period. An advantage of the system is simplicity, but extensive charging equipment is required at terminals, cars must be "spotted" for charging, and they are unproductive of revenue while this is being done. The straight storage system is said to be the most expensive in spite of its simplicity and is seldom, if ever, used at the present time.

Head-end systems consist of a generator on the baggage car or locomotive, driven by a reciprocating engine or turbine supplied with steam, at reduced pressure, from the locomotive. The earliest forms did not include a battery. Failures were frequent and were necessarily caused each time the cars were parted or the locomotive uncoupled. For this reason, batteries were added with voltage regulators to avoid excessive voltages at the lamps when the batteries were charged. Head-end systems found their chief applications on trains having long runs without change in make-up, but the axle-generator system was more commonly employed. With the advent of stream-lined trains operating as a unit, several cases of alternating-current or direct-current generators supplying current for lights and air conditioning have been reported. These are 110-volt systems.

Axle-generator systems are most commonly used. Each car is provided with a battery and a generator to charge it. The latter is driven by the axle of the car. As used in the United States, the axle-generator systems are mostly of the 32-volt type. The essential parts are: First, the generator of the inclosed type, shunt wound and provided with some form of pole changer, unless of constant polarity, in order that the terminal voltage may have the same polarity irrespective of the direction in which the car may be traveling. Second, an automatic switch, usually of the solenoid type, to connect the generator with the lighting system and batteries when the car attains a predetermined speed. Third, a regulating device to control the voltage supplied to the lamps and current to the batteries. Fourth, the battery itself, consisting of 15 or 16 cells of the lead-acid type, or 24 to 25 cells of the alkaline or Edison type. The necessity for some regulating device may be seen from the fact that a 16-cell battery, when discharged to 1.8 volts per cell, has an effective voltage of 29, but the same battery near the conclusion of a charging period will have a terminal voltage of 2.5 to 2.6 volts per cell or 40 to 42 volts for the whole battery. Increasing the voltage from 29 volts at the end of discharge to 34 means doubling the illumination from the lamps. Regulators are normally adjusted to limit the voltage to 32 volts at the lamps. Some axle generators supply a constant current to the batteries and others charge the batteries at constant potential. When the train is standing the battery must carry the load, but charging commences when the train has reached a predetermined speed.

Before 1932, it was standard practice to use a 32-volt axle-generator system together with a storage battery whose size was determined by the electrical load and the protection period required in the opinion of each railroad electrical engineer. Railroad men thought in terms of 8 to 10 hours as the necessary protection periods during which the battery would be required to carry the load in the event of a failure of the generator equipment. It was common practice to provide 150- to 250-ampere-hour batteries on baggage cars, 200- to 400-ampere-hour batteries on mail cars, and 300- to 500-ampere-hour batteries on coaches, dining cars, and Pullmans. Since then the addition of air conditioning has so increased the load that protection periods of 10 hours are no longer considered, partly because the generating equipment has been developed to a higher state of perfection and partly because it was unwise to increase the battery to a size that would have provided equivalent protection periods. The changes in power requirements that began in 1932 as a result of air-conditioning cars were so marked that this date may be considered a beginning of a new era in the railroads' use of batteries. The electrical load, however, depends to a large extent on the type of air conditioning employed.

Air conditioning has been defined as the simultaneous control of all or at least the first three of the following factors affecting both physical and chemical conditions of the atmosphere within any structure. The factors include temperature, humidity, motion, distribution, dust, bacteria, odors, toxic gases, and ionization.

Three basic systems of cooling the air have found general application in railway passenger service. These are (1) mechanical-compression systems, sometimes subdivided into direct-mechanical (axle) and electromechanical (motor) systems; (2) steam ejector systems; and (3) ice-activated systems.

In the mechanical compression systems, the refrigerant (dichlorodifluoromethane, commonly called "Freon") is in a liquid state under pressure on one side of an adjustable expansion valve. Through this the freon passes to a much lower pressure, vaporizing and absorbing heat from its surroundings as it expands. The gas is compressed, which heats it, then from the compressor it is passed through a condenser which returns it to the liquid state, and the cycle is repeated. Air for the car is cooled by contact with the cold pipes. The capacity of the cooling system is usually measured in terms of tons of equivalent ice manufactured in 24 hours. Thus we speak of 5-; 6-, or 7-ton refrigerating equipment.

The compressor represents the largest load and it may be driven by an electric motor, by a gasoline engine, or by mechanical drive direct from the car axle. In the case of electromechanical systems (motor-driven compressors) the power requirement for cooling alone will vary from 8 kilowatts for 5-ton units to 13 kilowatts for 7-ton units. The battery capacity can be supplied within a reasonable space and it is common to find 32-volt batteries of 1000 to 1200 ampere-hours installed on the cars (Figs. 133 and 134). However, the current requirements are large and the electrical conductors must be large. To decrease the expense and weight of the copper cables, some railroads

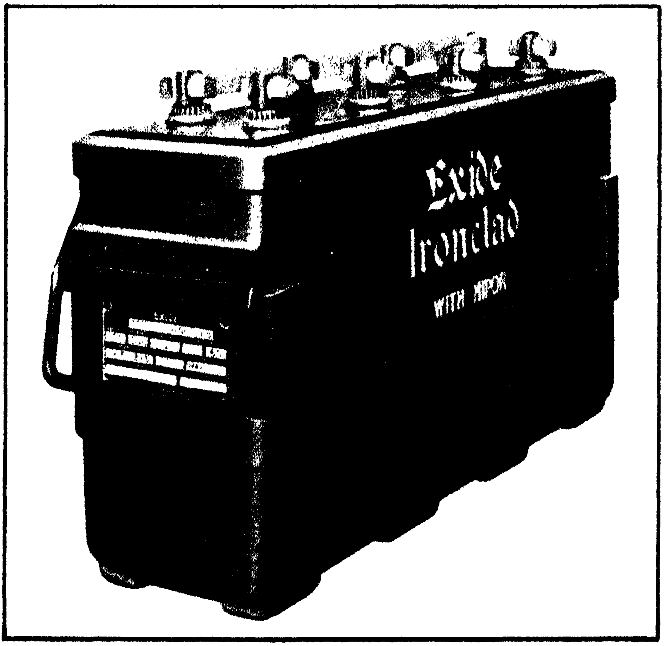

FIG. 133. A 2-cell unit of an Exide Ironclad battery for railway-car lighting and air conditioning. The complete battery consists of eight of these units.

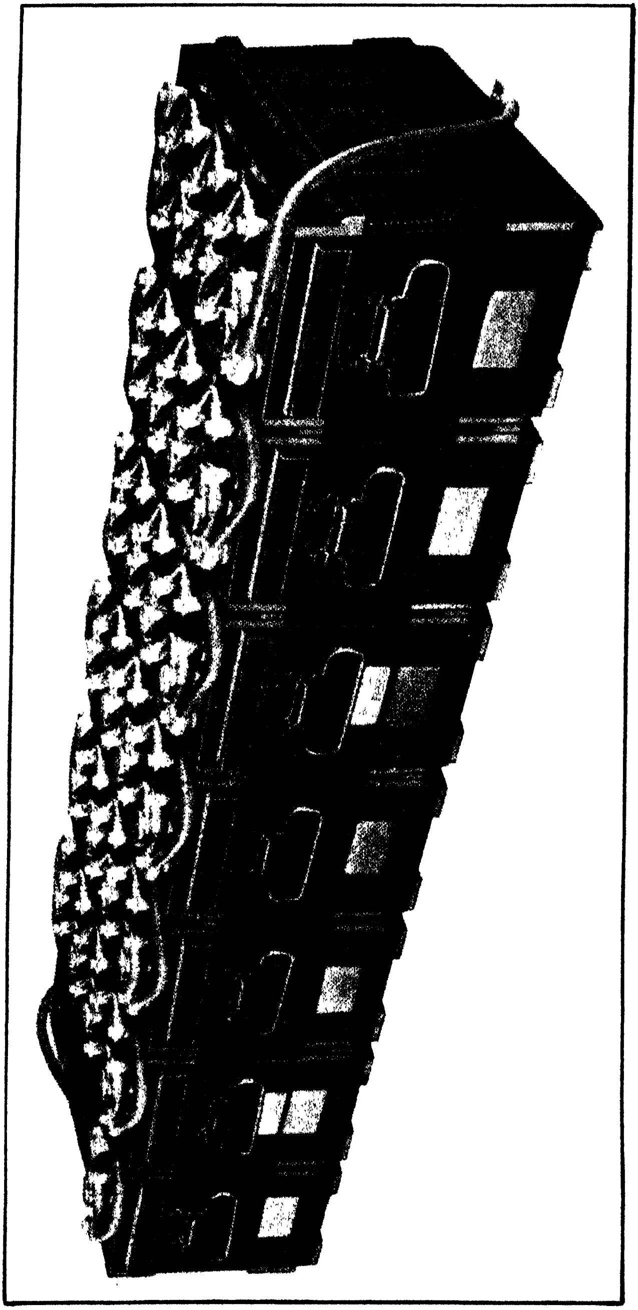

FIG. 134. Car-lighting and air-conditioning battery of the Edison alkaline-type, consisting of 25 cells, size A20H.

are turning to 64-volt systems which means doubling the number of cells in the battery and halving their capacity. One railroad is using a 110-volt direct-current system and a battery of 88 nickel-iron-alkaline cells of 300-ampere-hour capacity.

In the direct mechanical system the compressor is driven by a slip clutch from the car axle. Here the only additional electrical load is that required for circulating fans and pumps. The Pullman Company which uses this system is said to have standardized on batteries of 550- to 600-ampere-hour capacity at 32 volts.

In the steam-ejector system of cooling, water is the cooling medium. Live steam is passed through the ejector and its velocity produces a vacuum in the evaporator tank which entrains the water vapor. The mixture of steam and water vapor then passes into a condenser and is liquefied. The cooling effect is brought about in the evaporator by part of the water boiling off at reduced pressure, which lowers the temperature of the remaining water. The cold water is then pumped to the air-cooling unit, and the water vapor entrained by the steam is replaced from the condenser. The electrical load consists of motors to drive the condenser fan, cooling-coil fan, condenser pump, and cold-water pump. The total power consumption is about 4 kilowatts. The size of batteries applied to passenger cars using the steam ejector system is 600 to 1000 ampere-hours at 32 volts.

In ice-activated systems, the water which is cooled by ice is circulated through coils over which the air to be cooled passes. This is probably the cheapest in first cost, but it presents a serious servicing problem. Bunkers mounted under the car carry the large blocks of ice. Water is sprayed over these and the cooled water is circulated through tubing with fins which in turn cool the air. The increase in load on the battery over that required for car lighting is small. Consequently, little, if any, additional capacity of the battery is required. While this system can be installed at a relatively low cost, extended tests reported by the Division of Equipment Research of the Association of American Railroads, 1937, have shown that under some conditions the total operating costs may considerably exceed that of the other systems.

Irrespective of the additional load conditions on the batteries, the installation of air conditioning on cars has meant an additional load on the locomotive which is the primary source of power. There is one type of equipment, however, in which the battery is charged from a propane-gas engine-generator.

In axle-generator systems (Fig. 135) when the car is traveling at slow speed (below 16 to 18 miles per hour) the complete power requirements are taken from the storage battery. As the train increases speed a "cut-in" switch connects the generator to the electrical system for supplying the electrical load plus charging current for the battery. Regulators protect the generator against overloads and limit the voltage to a setting whose average value will maintain the battery in charged condition. Since the maximum voltage of the generator system would be too high for the lamps, the lighting load is passed through a voltage regulator. When the generator is cut out, the terminal voltage of the battery is lower. An unsatisfactory condition can be avoided by supplying a battery of sufficient capacity, maintaining it in a charged condition, and providing adequate wiring.

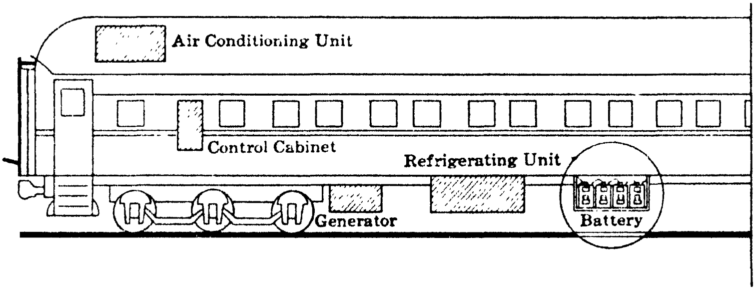

FIG. 135. Diagram of an air-conditioning unit on a railway passenger car.

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3. DIESEL-CRANKING BATTERIES

Diesel engines belong to the class of internal-combustion engines. Like other engines of this class, they require a starting system to put them in motion before they can operate under their own power. Various systems for starting Diesel engines are employed, including (1) electric starters, (2) compressed-air starters, (3) small gasoline engines connected for the moment through reduction gears, and (4) the introduction of explosive mixtures which can be fired in the cylinders. Electric starters are used commonly on the smaller types of engines, and modified forms of electric starters are employed on larger types, such as are found on Diesel locomotives. The voltage and current requirements of the battery exceed those for comparable gasoline engines.

The present Diesel engines are modifications of the type proposed originally by Rudolph Diesel. They operate on the principle that air compressed in the cylinders nearly adiabatically to about 500 pounds per square inch attains a temperature sufficient to cause ignition of the fuel which is injected at the proper moment near the end of the compression stroke. Spark plugs to provide ignition are not necessary.

Diesel engines are an economical source of power because they burn relatively cheap grades of oil, but further economies are possible because they operate at high compression which increases the efficiency of using the fuel. Other fuels than oil might be used, and, in fact, Diesel proposed the use of coal dust.

Comparison of Diesel engines with the more familiar gasoline engines shows some points of similarity, but there are essential differences which distinguish one from the other, as shown in the following outline of four-stroke engines.

STROKE	GASOLINE ENGINE	DIESEL ENGINE
1. Suction stroke	Air and gasoline vapor enter cylinder together	Air alone enters cylinder
2. Compression stroke	Mixture is compressed to 90 to 150 lb. per sq. in. temperature 400° to 500° F.	Air is compressed to 400 to 500 lb. per sq. in. 830° to 920° F.
Beginning of combustion	Spark ignition near top of stroke, developing pressure of 200 to 400 lb. per sq. in.	Fuel injected near top of stroke, ignited by temperature of air in cylinder, developing pressure of 500 to 850 lb. per sq. in.
3. Expansion stroke	The gases burn	The gases burn
4. Exhaust stroke	The burned gases are expelled from cylinder	The burned gases are expelled from cylinder

It is apparent from this outline that the starting problem is more difficult in the case of Diesel engines than gasoline engines. Higher pressures in the cylinders must be overcome, but fortunately this is partly offset after the engine has begun to rotate by the expansion of air previously compressed in other cylinders. Because high compression is required in Diesel engines, the clearances between pistons and cylinder walls must be small and friction is, therefore, a relatively large factor. Leingang[1] has estimated that 60 per cent of the power expended in starting the engine is used in overcoming friction between pistons and cylinder walls. The remaining 40 per cent is expended in overcoming compression and the friction of bearings and valve mechanisms. The Diesel engine must be turned fast enough to provide nearly adiabatic compression of the air. Otherwise the temperature attained on compression stroke may be too low to ignite the fuel. If the compression were strictly adiabatic, the temperature attained as a result of compression of the air to 500 pounds per square inch would be about 1050° F., but in ordinary practice the cooling effect of the cylinder walls lowers the temperature to about 900° F. High cranking speeds are necessary also to avoid losses of pressure resulting from "blow-by" past the piston heads. This effect is greater in the smaller sizes of engines.

Many sizes and kinds of Diesel engines are available for a variety of uses. The advent of small sizes and the decrease in weight per horsepower as a result of improved design and materials has stimulated the demand for Diesel engines during the past few years. Some of their more important uses are: (1) portable power units for industrial service; (2) electric generating units including stationary and marine types; (3) marine propulsion and auxiliaries; (4) compressors and drilling equipment; (5) motive power on trucks, tractors, and buses; (6) industrial and railroad locomotives.

The larger sizes usually operate at lower speeds. Diesel engines may be classified approximately according to speed as follows: Slow speed, up to 400 rpm; medium speed, 400 to 800 rpm; high speed, 800 to 2000 rpm. Cranking speeds are lower, of course, than these figures, but must be high enough to produce ignition.

Climatic conditions are important. Diesel engines in transportation service, and perhaps other services as well, may be exposed to temperatures of 0° F. or below. Obviously the engines are more difficult to start under such conditions and much depends on the viscosity of the lubricating oil. Some manufacturers of Diesel engines provide glow plugs or air-intake heaters to assist starting under low-temperature conditions. The former heat the ante-combustion chambers so that the atomized fuel attains a higher temperature, while the air-intake heaters supply heated air to the cylinders. Both of these auxiliaries for the starting process are an added drain on the battery. They

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[1] *Diesel Power and Transportation*, 16, p. 136, 1938.

require considerable current for perhaps a minute before the cranking operation is begun. With proper preparation the engine should start in not more than 30 seconds.

Some of the larger Diesel engines which are directly connected to generators are started by the use of auxiliary field windings in the generators, which for the time being operate as motors, current being supplied by a battery of 32 or 56 cells. On engines of 1000 horsepower the breakaway current to be supplied by the battery may be as high as 2000 amperes and the rolling current 1200 amperes. When the engine has attained a predetermined speed, the starter circuit is opened.

Recent applications of high-speed Diesel engines to bus transportation and other services have necessitated the development of starting systems somewhat analogous to those used on gasoline engines. The electric motors used for Diesel-engine starting are of the series-field type for which the torque increases with the current and the speed depends on the voltage. Starting motors for engines up to 300 horsepower are relatively small and they are usually mounted on the side of the engine. Connection between the motor and the engine during the starting period is provided by a sliding pinion or Bendix drive which meshes with a ring gear on the flywheel at a ratio of about 10 to 1. The electric motor must therefore rotate at high speed.

The fundamental condition for satisfactory battery performance is that the battery must be able to furnish currents of the order of 1000 amperes or more at sustained useful voltages for several minutes, if necessary. Batteries used for starting purposes on trucks, tractors, and motorboats are usually required to furnish in addition the current for lighting, but they are not needed for ignition. The capacity and voltage of the battery must be chosen with a view to the service required of it. In particular it is necessary to know the engine displacement, the voltage, the time, and the temperature conditions.

Starting systems of 12, 24, 30, and 32 volts are commonly employed on the light-weight high-speed Diesels, but because of the size and weight of the batteries they are assembled in units of three or four cells. Since the cranking speed of the engine is dependent on the voltage applied to the starting motor, the resistance within the battery circuit must be small. Conductor cables are usually 0 to 0000 (B and S gage) and they should be as short as possible. Aside from keeping the resistance of the circuit low, it is equally necessary that all conductors have a safe current-carrying capacity.

The batteries contain from 9 to 45 plates per cell. The plates are about $5\frac{5}{8}$ by 5 by 0.90 to 0.156 inches. The separators are porous rubber or wood. Figure 136, from the paper by Leingang, shows the normal discharge characteristics of positive plates of a Diesel starting battery at 80°, 32°, and 0° F. The characteristic is shown as the number of minutes of discharge to a final voltage of 1.00 volt per cell for current rates from 20 to 80 amperes per positive plate. The number of plates per cell is chosen on the basis of engine displacement, time, and expected temperatures. The displacement in cubic inches may be calculated from the formula: $3.14 \times \left(\frac{\text{bore}}{2}\right)^2 \times (\text{stroke}) \times$ (number of cylinders). Figure 137, also from the paper by Leingang,

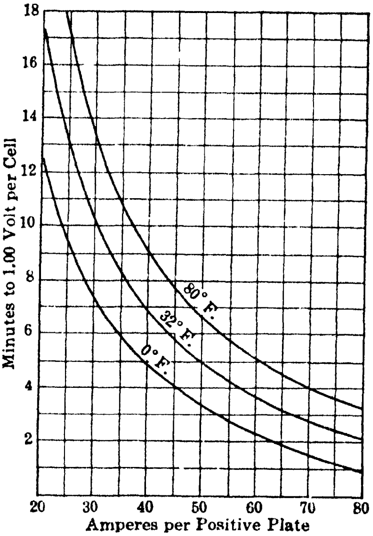

FIG. 136. Discharge characteristics of a Diesel-starting battery at 80°, 32°, and 0° F.

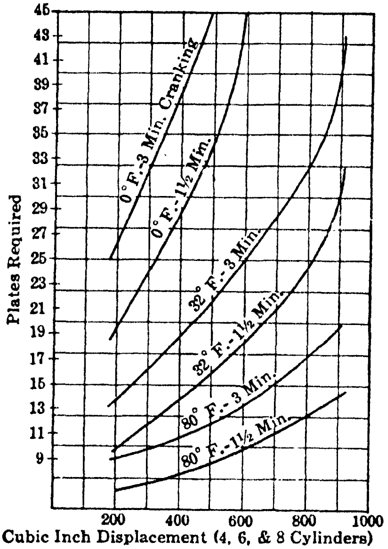

FIG. 137. Relation of size of battery to engine displacement, time and temperature, 24-volt system.

gives data for 24-volt systems. Two curves are given for each temperature. These are for cranking times of 1½ and 3 minutes, respectively. For starting systems of other voltages reference should be made to his original paper. Assuming that the engine is equipped with the proper starting motor and gear ratio, the cranking speeds should be about as follows:

ENGINE DISPLACEMENT	SPEED, RPM.
200 cubic inches	175
300 cubic inches	150
400 cubic inches	125
600 cubic inches	100

If abnormal heater loads are applied, or some other service is required of the battery, or the engine is difficult to start at low temperatures, the 3-minute rate should always be chosen. If batteries of the required number of plates are not available, the next larger size of battery should be chosen.

Figure 138, which was furnished through the courtesy of H. C. Riggs, shows two oscillograms of the starting of internal-combustion engines. The first is for a 6-cylinder gasoline engine of 300-cubic-inch displacement, and the second is for a 6-cylinder Diesel engine of equivalent size. Each was cranked when the temperature of the lubricating oil was 32° F. The curves show the comparative starting times, currents, and voltages. The effect of compression is shown by maxima in the current curves and minima in the voltage curve. On the basis of this oscillogram the following comparisons can be made.

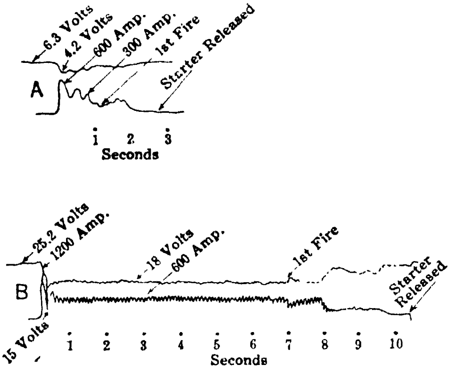

FIG. 138. Comparative oscillograms of starting gasoline engine (*A*) and Diesel, engine (*B*), each having 6 cylinders 300-cubic-inch displacement, temperature 32° F.

	Gasoline Engine	Diesel Engine
Open circuit battery voltage, volts	6.3	25.2
Maximum break away current, amperes	600	1200.0
Minimum voltage, volts	4.2	15.0
Rolling current, amperes	300	600.0
Cranking speed, rpm	90	180.0
Average voltage (rolling), volts	5	18.0
Time to first fire, seconds	1	7.0
Time to starter release, seconds	2.6	10.5
Approximate watt-hours to start, watt-hours	0.6	21.0

Diesel engines are usually equipped with a generator for charging the batteries when the engine is running. These are similar more or less to the generators on gasoline engines.

In discussing batteries for starting Diesel engines and in comparing Diesel engines with the more familiar gasoline type of internal-combustion engines, the thought has been to present the facts in such a manner that they may be easily understood. The fact that Diesel engines are difficult to crank should stand as a challenge to the battery manufacturers. It should not be interpreted as in any way diminishing the usefulness or importance of this type of engine.

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4. MARINE APPLICATIONS

Storage batteries find many uses on board ship. These range from the simplest applications on ignition circuits of internal-combustion engines of small craft to the complex circuits of the largest and finest ships. The batteries assure continuity of power for radio, lights, and essential auxiliaries. They carry the peak loads of pumps, hoists, and compressors. On naval vessels they provide for gun firing and for the propulsion of submarines when submerged.

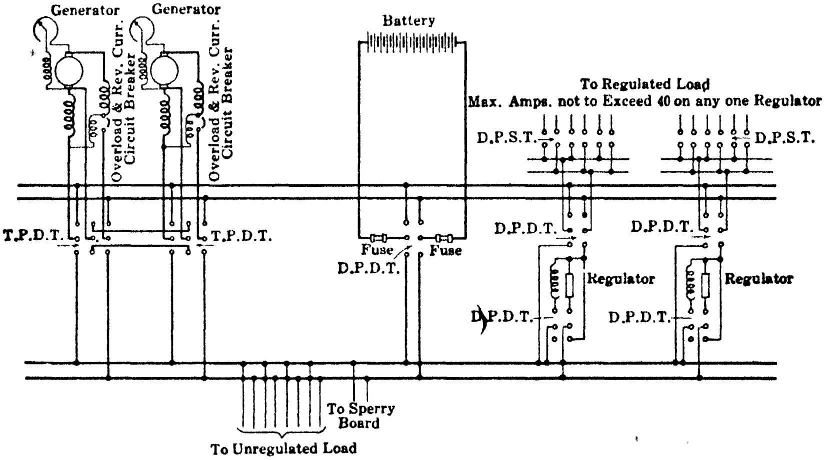

FIG. 139. Diagram of the Exide floating-battery system.

Ordinarily the storage batteries float on the power line (Fig. 139). They are maintained, therefore, in a fully charged state ready for emergency service. The relation of battery voltage to line voltage, however, involves several interesting problems. The generator must have a drooping characteristic if the battery is to assume the load in excess of the generator capacity. This is especially necessary if the generator is driven by an internal-combustion engine, as such engines have relatively little overload capacity. When it is necessary to charge the battery, the generator voltage is raised from time to time in order to maintain the desired charging rate. This is essentially a constant current charge until the generator reaches a maximum voltage of 135 volts for a nominal 115-volt system. It provides an average voltage of 2.4 volts per cell for a 56-cell lead-acid battery. This is enough for a rapid charge of the battery, but it is too high for incandescent lamps, radio tubes, and gyrocompass. There must be a regulated portion of the voltage supply for these services. The unregulated portion of the bus is satisfactory for motor-driven auxiliaries which have largely replaced the steam-driven hoists and winches of some years ago. After the generator voltage has reached 135 volts, it is held at this point and the charge is continued as a constant-potential charge. The current through the battery then falls gradually until the charge is completed, when the generator voltage is reduced to normal value and the battery again floats on the line. About 90 per cent of the charge can be given before the charging current begins to decrease. The time of charge up to this point is about 10 hours.

The electrical load on board ship is a fluctuating load, and the battery improves the conditions of operation by absorbing part of the fluctuations. A smaller generator than would otherwise be required can be used because the battery automatically carries the peak loads. The battery, on the other hand, must be large enough to carry the entire load for a specified time, which may be either to cover an emergency or to carry the night load on smaller ships, particularly yachts, if it is desirable to stop the generators for reasons of economy or personal comfort.

Another method of operation for 110- to 120-volt marine requirements is by series-paralleling the two halves of the battery. Under normal operating conditions the generator supplies the ship's load and charges the two halves of the battery, but, if the generator voltage should fail, the two halves of the battery are automatically connected in series and assume the load. The principles of this system are illustrated in Fig. 140. Transfer of the load is accomplished by an automatic contactor when the line voltage falls below a predetermined setting. The contactor which connects the battery in series operates rapidly enough for the direct-current motor starting boxes in the load circuit not to be released and for no interruption in the current to occur. This system is used with Edison alkaline batteries. By dividing the battery, ample voltage for charging is provided, but when the batteries are in series the voltage may be too high for the lamp load and a voltage regulator must be provided. This is a carbon pile, subjected to pressure that varies inversely with the voltage. It is similar to voltage regulators used on the lighting circuits of railway cars. The heavy motor loads can be separated from the emergency and lighting loads by use of a disconnect circuit breaker that divides the bus. This has the advantage of relieving the generator of overload and of protecting the lamp load from large fluctuations. In full automatic control, loss of generator voltage causes the main disconnect contactor to open which de-energizes the battery charge contactor and the series-parallel contactor operates immediately to put the battery on discharge as one series-connected unit. The proper current for charging the batteries can be set on the manually operated charging rheostats. Normally 50 cells (Edison type) are used in each half of the battery.

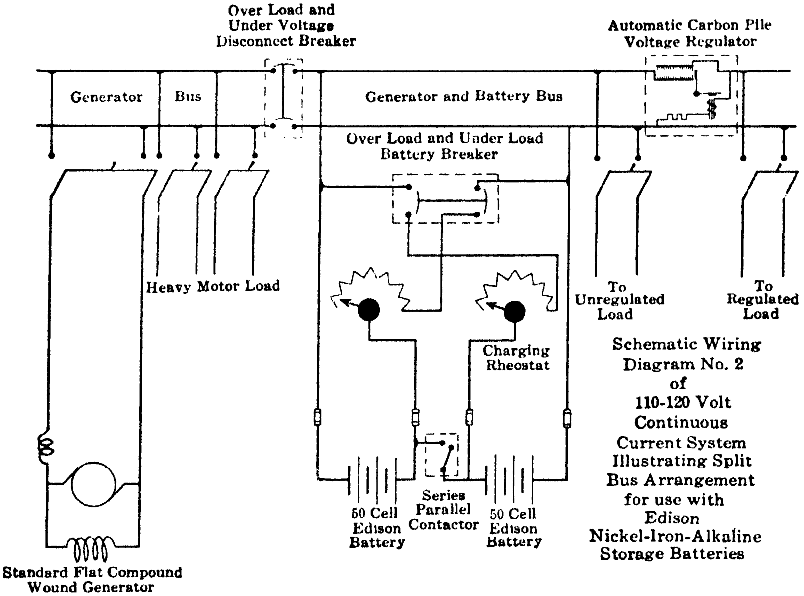

FIG. 140. Diagram of the Edison continuous-current system for marine use.

Regulations prescribed by the Bureau of Marine Inspection and Navigation of the Department of Commerce for new vessels provide that two or more generating sets shall be installed so that, if one breaks down, there will be sufficient remaining capacity to carry the "peak sea load." Passenger vessels over 1600 gross tons are to be provided also with an independent emergency source of power. The final emergency source for lighting and auxiliary power is specified to consist of one or more Diesel-engine-driven generating sets of sufficient capacity and fuel to carry the full emergency load for at least 36 hours, supplemented by a storage battery as a temporary emergency source capable of continuous operation for at least 1½ hours. The capacities of the temporary and final emergency sources are based on circuit conditions such that the temporary emergency circuits will provide for continuous lighting and communication during the interval between failure of the main source and the starting of the emergency generators. Passenger vessels of less than 1600 gross tons are to be provided with an emergency source of lighting and power consisting of a Diesel-engine-driven generating set or a storage battery, either of which shall have capacity to carry the emergency load for at least 12 hours. The emergency source of lighting and power in either case must be located above the bulkhead deck. The battery voltage when first connected to the line for supplying emergency power shall not exceed the normal rated generator voltage by more than 5 per cent and at the end of a discharge period shall not be less than 12½ per cent below normal rated generator voltage. Capacity and voltage of lead batteries when fully charged are based on a specific gravity of 1.210 to 1.220 at 25° C. Manually operated charging may be permitted, but full automatic equipment is recommended. For the details and latest requirements of these rules, reference should always be made to official sources of information.

Thirty-two- and 110-volt systems are available for auxiliary yachts and motor cruisers. Some of these are used for cranking the engines. The battery receives its charge from a generator operated by the main engine. However, if the main engine is seldom used, a small separate generator driven by some other means is generally supplied. The battery should have sufficient capacity to provide for several hours continuous operation of the lights and all the auxiliaries which operate automatically, such as refrigerators, bilge pumps, etc. Heavier loads, such as electric cooking, hoisting the anchor or sails, may be provided for either by installing a larger battery or by starting the main engines, after which the main generator supplies the necessary current. The service is intermittent and some thought should be given to selecting convenient times to charge the battery adequately. The batteries are either 16 cells of lead-acid type or 25 cells of the Edison nickel-iron type for the 32-volt systems. At higher voltages, 55 or 60 lead cells, or 100 cells of the Edison type may be needed.

With the development of Diesel engines for tugs and other small commercial craft, a need has arisen for electric power to replace steam formerly used for auxiliaries. Shaft-driven generators, somewhat like railway carlighting equipment, have found increasing use. The smaller installations are usually 32-volt systems up to about 10 kilowatts.

Larger units of 115 volts are employed in sizes up to 40 kilowatts or more. On many of the older installations it was the practice to call for two Diesel-engine generator sets of the same capacity, one being held in reserve, but more recently a shaft-driven generator of equal capacity has been used to replace one of the Diesel sets. When the main engines are operating, the auxiliary unit can be shut down.

The essential parts of a shaft system include: (1) A generator, the voltage of which will remain constant over a wide variation of the shaft speed. (2) A belt or chain drive from the propeller shaft, from which the system gets its name, "shaft-driven generator system." (3) A voltage regulator to maintain constant voltage and protect the generator from overload. (4) A reverse current relay to disconnect the battery and load from the generator when the terminal voltage of the generator is too low for battery charging. (5) A battery of the lead-acid or alkaline type which floats on the bus from the generator or which is charged in paralleled halves. The battery assists the generator on peak loads, carries the emergency load, and provides for the lighting load at such times as the main engine and generator are shut down. (6) A lamp voltage regulator to protect the lighting units from voltages above their rating. On some installations a pole changer may be necessary to prevent reversal of polarity when the motion of the shaft is reversed.

The types of batteries used for marine service include various sizes of Exide-Ironclad batteries ranging from 57 to 1136 ampere-hours at the 8-hour rate. Five sizes of plates are available. Flat-plate batteries of the lead-acid type, assembled in rubber cases of two to four cells, are used also. These contain relatively thick plates, because space and weight limitations are of less importance than durability. Edison batteries in four sizes of plates are available in capacities from 18 to 900 ampere-hours at the 5-hour rate.

It is desirable that marine batteries should be rugged and durable enough to give long service. They are subject to continual vibration and the safety of the vessel and its passengers may depend on their proper functioning under adverse conditions.

5. TRUCK, TRACTOR, AND VEHICLE BATTERIES

a. Economic Importance

We have reached a point in industrial development beyond which greater efficiency in the methods of handling goods must play a large part in reducing the cost to the ultimate consumer. There is abundant opportunity for increased efficiency. Obsolete methods of handling goods, whether in transport or within the factory, are industrially wasteful. It is difficult and perhaps impossible to estimate the yearly burden of waste that results from inadequate methods of handling the raw materials, the parts, and the finished products. Many important industrial concerns, recognizing this fact, have installed modern methods that are highly remunerative. These methods lessen the cost of manufacture, relieve congestion, and give advantage in close competition.

Efficiency in the handling of materials depends partly on speed and the amount of goods which a truck can carry, but it depends also on how long a time must be spent in loading and unloading operations. There are practical limits to the speed of trucks from the standpoint of safety, and there may be limits to the amount transported at one time, depending on the rate of production, the weight, or the physical dimensions of the vehicle which are allowable. The earliest trucks and tractors were loaded and unloaded by hand. This often required considerable time, but it is characteristic of modern equipment that its measure of transportation service has been increased by the rapidity with which it can be loaded and unloaded by its own power. There is a variety of equipment available now from which to choose the type best adapted to some particular service. In this respect the modern equipment is more specialized than formerly. Needless handling of goods is avoided.

b. Classification of Trucks, Tractors, Vehicles, and Locomotives

Industrial trucks were originally designed for use in railway terminals for the transportation of baggage. These trucks combined in a single unit the battery for motive power and the loading space. The next step was to divide the functions of these platform trucks. The load to be transported was placed upon trailers drawn by a tractor, which is a short, sturdy unit with rubber-tired wheels carrying only the battery and the driver.

Tractor-Trailer System. The tractor draws a train of trailers (Fig. 141). It may collect these at different points and may deliver them to various destinations. Having done so, the tractor may be detached from the trailers and pick up another load. This system is adapted to moving large quantities of goods which are to be distributed to various points. Loaded trailers are sometimes taken directly into the freight cars in which the goods are to be shipped. With an adequate number of trailers, loading of a number of cars may be systematized and needless handling of the goods avoided.

Skid-Lift-Truck System. The platforms of these trucks may be raised, permitting them to pick up loaded skids. The truck can pick up its load in a few seconds and can deposit its load in an equally short time. The truck is provided with two motors, one for travel and the other for elevating the platform. A modification of this type of truck is found in the "high-lift" trucks which can raise the load to a considerable height for stacking loaded skids in tiers. Sometimes the skids accompany the consignment of goods for quick unloading at their destination by similar lift trucks. Crane trucks in combination with platforms (Fig. 142) are adapted to general utility work.

Fig. 141. Tractor pulling a train of trailers. Note how the trailers are following the path traversed by the tractor.

Pallet-Fork-Truck System. The pallet is essentially a skid platform with thin stringers instead of legs or a double platform with stringers between. This is picked up by the fork on the truck and tilted to a safe angle for stability while the load is being transported. This truck can lift the load to a considerable height for stacking goods in tiers (Fig. 143). The fork truck usually has three motors, one for travel, another for lifting the load, and a third for tilting the load. By taking the pallet with the goods into a car or into the hold of a ship,

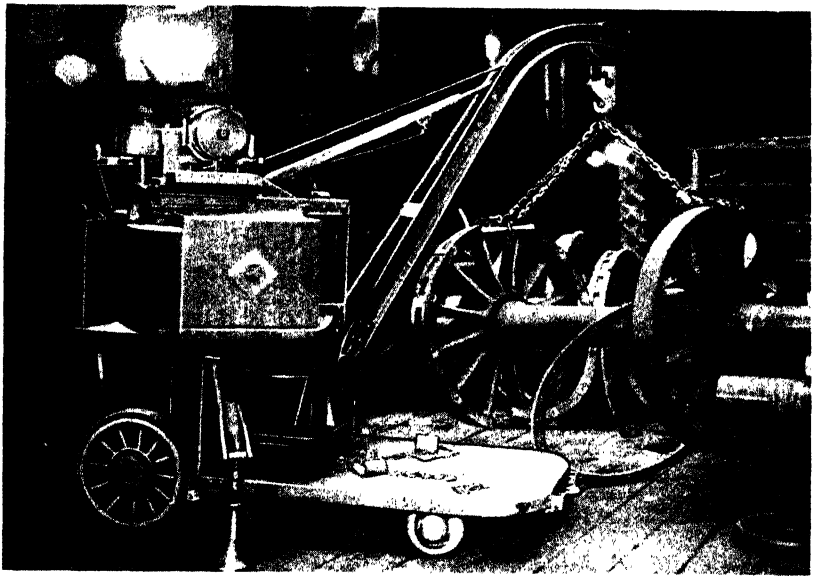

FIG. 142. Electric platform truck with crane.

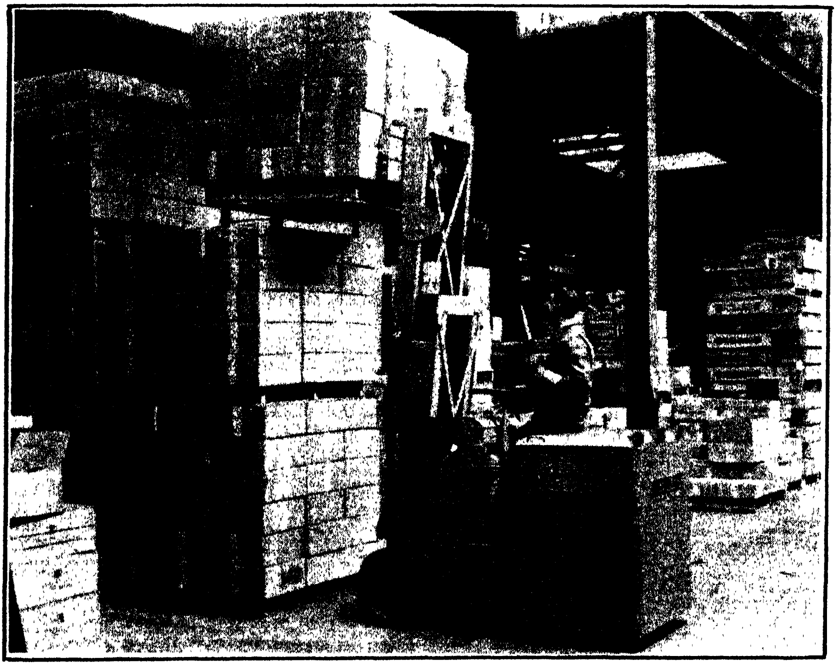

FIG. 143. A fork truck lifting a loaded pallet, stacking materials in tiers.

rehandling of the goods at point of shipment and at destination is avoided.

Other Systems. Special types of trucks have been developed for handling materials of particular shapes, such as large rolls of paper, coils of steel-strip (Fig. 144), wire, or bundles of sheet metal. Decreased time for loading and unloading usually means that the truck is operating a greater percentage of the time.

Mine Locomotives. A locomotive is distinguished from a tractor by the fact that it runs on rails, while a tractor usually has tires, and a steering mechanism. Mine locomotives are compact units of minimum height which carry a battery for motive power (Fig. 145). They are capable of pulling a train of loaded trailers and are rapidly replacing other means of transportation, including the animals which were commonly used for transporting material within mines. No trolleys are needed and the rails do not require bonding. With no voltage drop in a long line, the operating voltages can be lower than when a trolley is used.

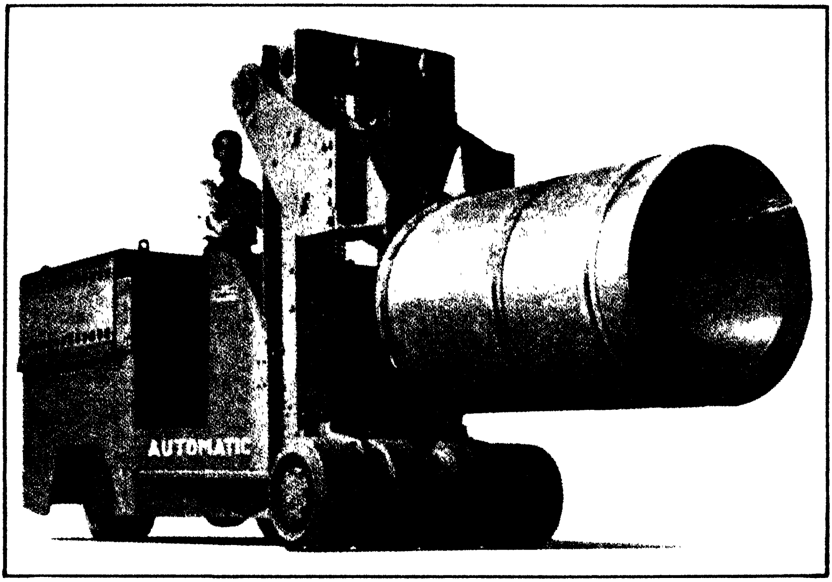

FIG. 144. A heavy-duty ram truck, capacity 30,000 pounds, handling strip-steel coils.

In gaseous atmospheres which are present in some mines the storage-battery locomotive is the safest form of motive power. Types approved by the U. S. Bureau of Mines are permissible in such atmospheres.

In the field of heavy traction, several types of battery locomotives are employed for switching service or as a substitute for steam locomotives. Battery locomotives of this class are described in the section on railroad applications of batteries.

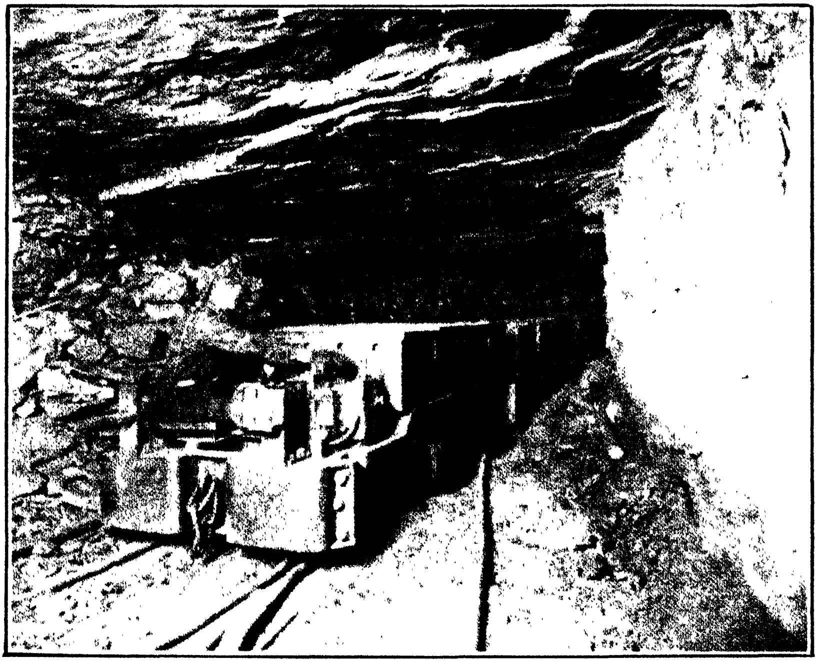

FIG. 145. Mine locomotive operated by storage batteries. The battery is in the compartment beyond the operator, who is wearing a cap lamp for which a small battery is attached to his belt.

c. The Batteries

The batteries used for propelling trucks, tractors, and vehicles are of either the lead-acid or the nickel-iron type. Typical batteries of these kinds, for use in trucks, are shown in Figs. 146, 147, and 148. The lead-acid batteries contain plates which are usually $5\frac{3}{4}$ inches in width (14.6 cm.) by $8\frac{5}{8}$ inches (21.9 cm.) or more in height. The positive plates vary from .43 inch (1.09 cm.) to .13 inch (.33 cm.) in thickness. The negative plates vary from .20 inch (.51 cm.) to .11 inch (.3 cm.). The negative plates are naturally made thinner than the positives.

For certain types of vehicle service, thin-plate batteries have been extensively used. The thin plates in these cells do not have a greater capacity per plate than the thick plates of the same length and width.

The capacity of the thin plates is actually less, but because a larger number of these plates can be used within a jar of given size, the capacity of the cell at the higher rates of discharge is considerably greater.

Connections between individual cells of a tray are made by intercell connectors, and similarly the connections between the trays are intertray connectors. These may be either burned or bolted to the terminals. Burned-on connectors are generally preferred, since the acid may creep in between the contact surfaces of the bolted connection and cause corrosion, which will destroy the joint electrically.

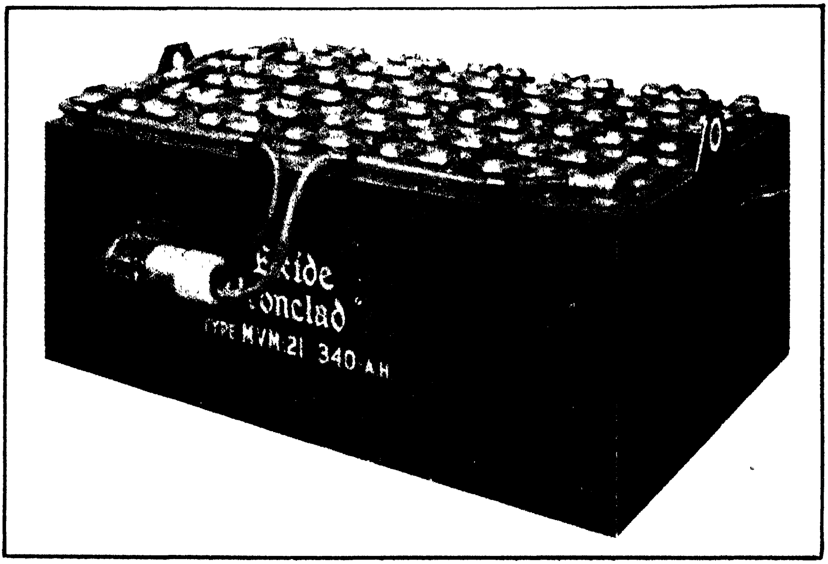

FIG. 146. Exide Ironclad battery for industrial tractors and locomotives. The cells are assembled in a steel tray.

The intercell connectors may be either copper straps heavily lead-plated or solid connectors of lead-antimony alloy. The copper straps, which are sometimes subject to corrosion, have the advantage of flexibility and high conductivity. A loop in the middle of these straps allows for expansion and for a slight movement of the cells without danger of cracking the covers. The design of the intercell connectors is a matter of considerable importance, since the drop in voltage when the battery is subject to large current drains may become an appreciable part of the total available voltage of the battery. The power which is lost in the intercell connectors increases with the square of the current which the battery delivers. This power loss for low rates of discharge is entirely negligible, but at high current rates such as may be required when a tractor is pulling a heavy load up a steep ramp, it may amount to $\frac{1}{2}$ horsepower or even more. Table LII shows the power loss for intercell connectors on a battery of excellent design. This table shows a hundredfold increase in the power loss as the discharge current is increased from the normal value of 45 amperes to 10 times the normal rate, or 450 amperes.

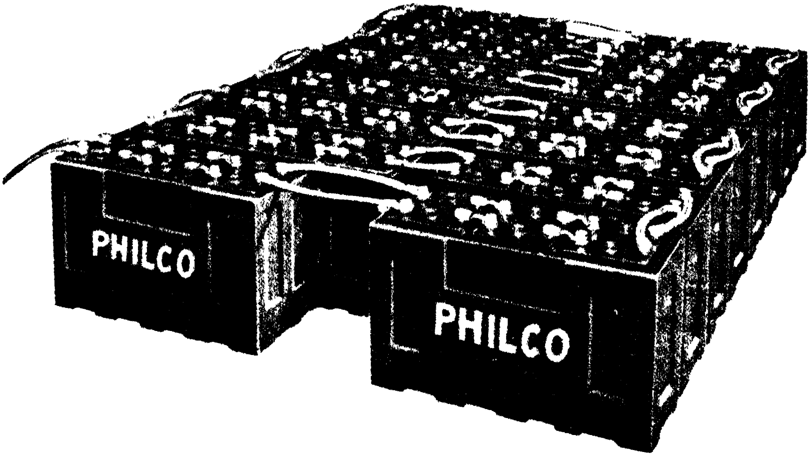

FIG. 147. Philco locomotive battery of 54 cells.

TABLE LII

POWER LOSS IN INTERCELL CONNECTORS

Type and Number of Cells	Discharge Current	Drop in Voltage	I^2R Loss, Watts
Lead-acid batteries, 12 cells (11 connectors)	45	0.053	2.38
	90	0.106	9.5
	225	0.264	59.0
	450	0.528	237.6

A wider variety of types and sizes of motor-power batteries is available now than in former years. It is obviously impossible to give detailed operating data for these, but their general characteristics may be found in Tables LIII and LIV. The first of these applies to lead-acid batteries having 21 plates per cell. This size of cell was arbitrarily chosen because each cell contains 10 positive plates, facilitating computations of other sizes on a decimal basis. The various types and kinds are not strictly comparable because of variations in size and kind of plates, in their spacing, and in the separators employed. These data were compiled from catalogs which should be consulted for detailed information.

Table LIV applies to the nickel-iron type, Edison cells. All cells are of the sizes ending in 6, that is, each cell contains six positive plates and the capacities of other cells can be calculated as fractions or multiples.

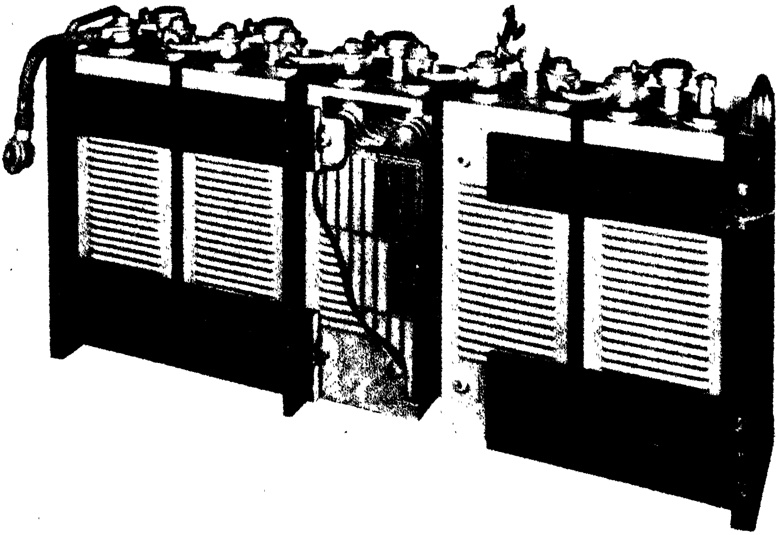

FIG. 148. Edison battery for trucks, tractors, and vehicles; type A8.

Figures 149 and 150 show the variation of capacity of lead-acid batteries with time of discharge and the relation of power delivered to the discharge current. Similar curves for Edison batteries are given in Figs. 66 and 151. These apply to the type A. Values for other types can be estimated by recalling that the B plate has half the ampere-hour capacity of the A size, the C plate once and a half more, and the D plate twice as much.

The connections between the cells of Edison batteries consist of heavy copper wire swaged into steel lugs having an inside taper which fits the taper of the terminal posts of the cells. More of these connec-

TABLE LIII

DATA ON SOME TYPES OF BATTERIES FOR MOTIVE-POWER SERVICE

(The data are given on the basis of 21-plate cells, which contain 10 positive plates, to facilitate estimates of current and capacities of other cells of their respective types. Motive-power cells are often discharged at relatively high rates. By using the ampere-hour capacities at the 6- and 8-hour rates which are given, computations may be made of the capacity at any other rate by using the equation given on page 209. All cells have double or triple insulation.)

	Exide—Ironclad Cells					Cells with Flat-Pasted Plates						
											Gould Kathanode	
	MVM-21	ML-21	TLM-21	MEH-21	FLAM-21	Exide MVA-21	Philco 21 XV	Philco 21 XVL	Philco 21 XL	Philco 21 AMH	KMD-21	KHD-21
Number of positive plates per cell	10	10	10	10	10	10	10	10	10	10	10	10
Normal 6-hour discharge, amperes	56.7	63.9	83.3	166.7	300	47.5	56.7	63.3	91.7	166.7	56.7	83.3
Capacity, ampere-hours	340	383	500	1000	1800	285	340	380	550	1000	340	500
Capacity, watt-hours	660	739	966	1910	3420	553	666	743	1070	1910	674	990
Voltage, initial, volts	2.04	2.03	2.02	2.01	2.00	2.04	2.05	2.05	2.04	2.03	2.06	2.07
Average, volts	1.94	1.93	1.93	1.91	1.91	1.94	1.96	1.95	1.94	1.91	1.98	1.98
Final, volts	1.76	1.75	1.74	1.70	1.72	1.76	1.75	1.75	1.75	1.75	1.75	1.76
Eight-hour discharge, amperes	45	50.6	66.5	133.1	237.5	38.5	45	50.6	73.1	133.1	45	66.3
Capacity, ampere-hours	360	405	532	1065	1900	306	360	405	585	1065	360	530
Capacity, watt-hours	704	786	1034	2045	3670	600	707	794	1140	2045	713	1050
Dimensions, length, inches	8⅛	8⅛	8⅛	8¼	10 1/16	6⅞	8	8	8⅛	8¼	8⅛	8⅛
Width, inches	6¼	6¼	6¼	8 13/16	11 9/16	6¼	6¼	6¼	6¼	8¾	6¼	6¼
Height, inches	15 3/16	15 11/16	20⅜	28⅝	35¼	15 3/16	15 3/16	15 3/16	20¾	28⅝	15¼	20¾
Charge rate, 8 hours, start, amperes	......	... .	..				51	57	81	150	56	85
Finishing rate, amperes	22	23	25	50	100	19	17	19	27	50	22	35
Electrolyte, specific gravity	1.280	1.280	1.280	1.280	1.280	1.280	1.280	1.280	1.280	1.280	1.280	1.280
Weight per cell, pounds	15.5	16.6	21	45	74	13.5	14.0	14.0	29.4	42.5	......	......
Weight, complete cell, pounds *	71	75	98	188	290	60.5	73	80	108	201.5	......	......
Battery, per cell, pounds *	82	86	113	228	440	69.5	86	94	127	242	95	129

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* The weight of the battery per cell, frequently called "the trayed weight," varies considerably with the construction and the amount of reinforcing.

TABLE LIV

DATA ON EDISON STORAGE BATTERIES FOR TRUCK, TRACTOR, AND OTHER SERVICE

(Since only the B-type cells are made in a one-plate (positive) size, the electrical and physical characteristics are given for comparison on the 6-positive-plate size for the 5 motive-power types of cell. Ratings are based on 5-hour discharge for types A, B, C, and D; and on 3⅓-hour discharge for type G, all to one volt per cell. Normal charge is 7 hours for types A, B, C, and D; and 4¾ hours for type G.)

	Type B6	Type G6	Type A6	Type C6	Type D6
Number of positive plates	6	6	6	6	6
Normal discharge rate, amperes	22.5	45.0	45.0	67.5	90.0
Capacity, ampere-hours	112.5	150.0	225.0	337.5	450.0
Capacity, watt-hours	135.0	180.0	270.0	405.0	540.0
Voltage, initial, volts	1.45	1.45	1.45	1.45	1.45
Average, volts	1.20	1.20	1.20	1.20	1.20
Final, volts	1.00	1.00	1.00	1.00	1.00
Normal charge rate, amperes	22.5	45.0	45.0	67.5	90.0
Average volts, 95° F	1.704	1.704	1.704	1.704	1.704
Maximum volts, 95° F	1.845	1.845	1.845	1.845	1.845
Dimensions,* length, inches	3.85	2.93	3.85	3.85	3.79
Width, inches	5.07	5.13	5.13	5.13	5.07
Height, inches	8.81	13.41	13.41	19.16	25.83
Electrolyte,† pounds per cell	2.55	3.36	4.12	5.99	8.30
Resistance, mean effective, ohms	0.004	0.002	0.002	0.0013	0.001
Weight of battery,‡ per cell, lb	13	17.5	22.4	34.4	45.6
Single positive plate data:					
Normal discharge rate, amperes	3.75	7.50	7.50	11.25	15.00
Capacity, ampere-hours	18.75	25.00	37.50	56.25	75.00
Capacity, watt-hours	22.50	30.00	45.00	67.50	90.00
Voltages as above					

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* Length and width dimensions are, respectively, the dimensions along and across the tray axis.

† Electrolyte is for cells of normal height, "high" and "high-wide" cells require more.

‡ Weights are for cells completely assembled in trays, including trays, connectors and electrolyte.

tors are necessarily used for the Edison battery than for the lead type, since 21 Edison cells correspond approximately in voltage to 12 cells of the lead type. In spite of this fact, however, the drop in voltage within the connectors exceeds that for the lead cells by only a slight amount. The Edison cells are assembled in hardwood crates which are provided with recessed hard-rubber buttons into which fit the bosses on the individual cells. They are therefore held rigidly in position with a slight space between each cell to provide the necessary insulation and ventilation.

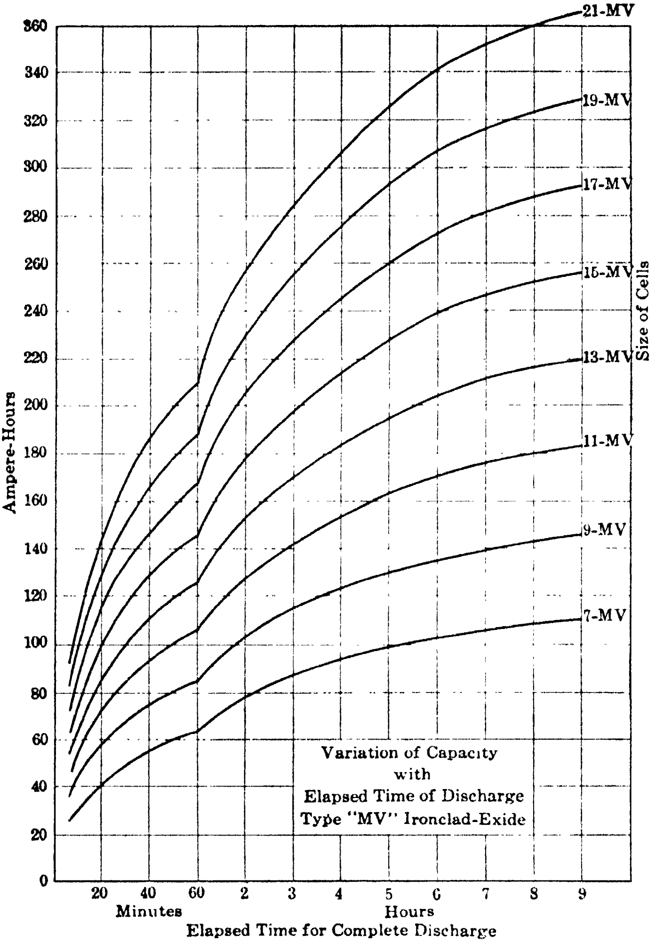


FIG. 149. Variation of capacity with rate of discharge and size of cell.

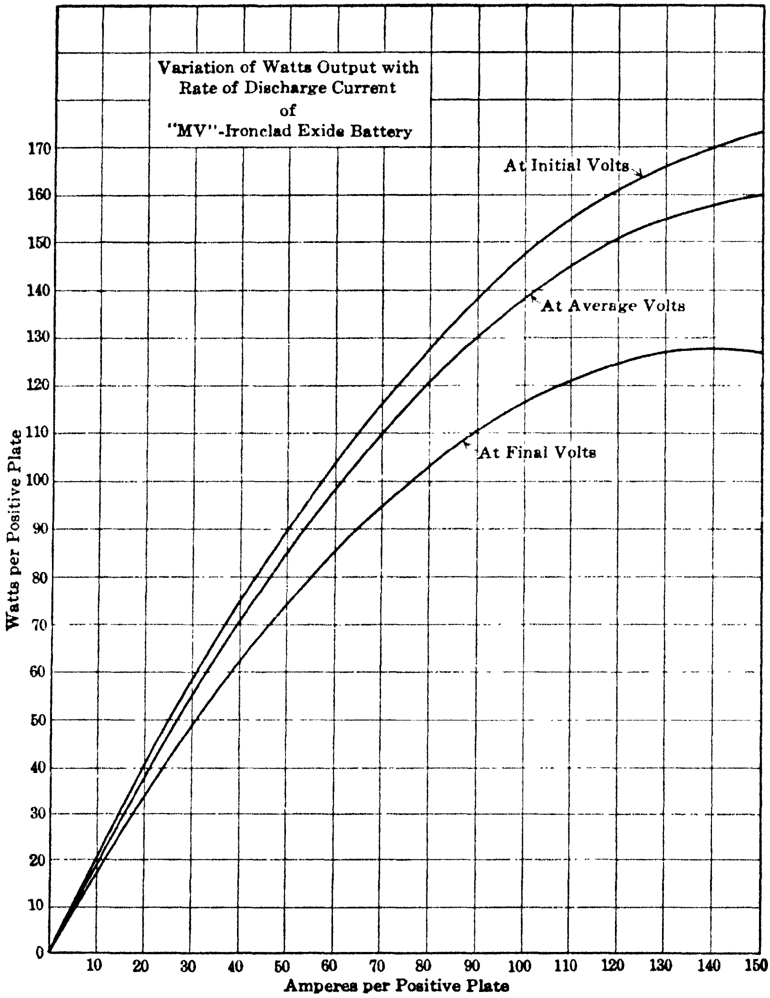
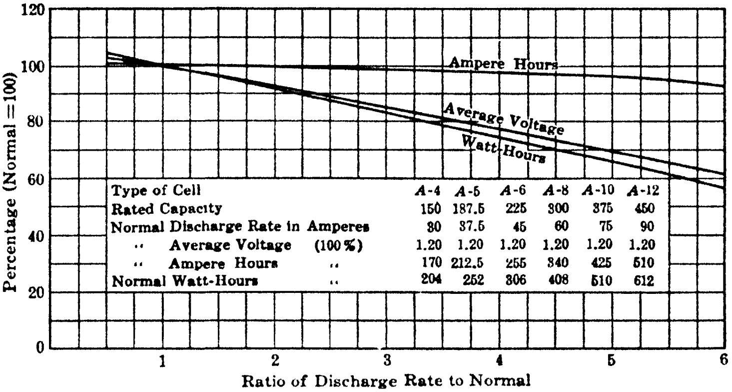


FIG. 150. Variation of power output with rate of the discharge.

d. The Service Which the Battery Has to Perform

The electric vehicle differs from the gasoline truck in the matter of starting torque. The torque of the motor on the electric truck increases as the speed of the truck decreases, that is to say, the torque is a maximum when the truck is beginning to move. The gasoline engine, on the other hand, delivers its maximum torque at high speeds. The performance of an electric truck as compared with a gasoline truck at *low speed* is therefore in favor of the former.

The tractive effort of the truck is the force required to overcome the resistance of the vehicle and its load to motion. Drawbar-pull is a term applying to the trailing load and is usually expressed as pounds per ton of the total weight of the load. The drawbar-pull varies with the surface over which the vehicle moves, the grades which it encounters, and the speed of the vehicle. Figure 152 shows the relation of the drawbar-pull to the amperes which the battery discharges. From this it is evident that the drawbar-pull increases as the current increases. The speed of the vehicle decreases because of the diminished voltage of the battery and the characteristic of the series motor. In Fig. 152 the relation of the current to the voltage and to the speed is shown for a tractor.



Type of Cell	*A*-4	*A*-5	*A*-6	*A*-8	*A*-10	*A*-12
Rated Capacity	150	187.5	225	300	375	450
Normal Discharge Rate in Amperes	30	37.5	45	60	75	90
" Average Voltage (100%)	1.20	1.20	1.20	1.20	1.20	1.20
" Ampere Hours "	170	212.5	255	340	425	510
Normal Watt-Hours "	204	252	306	408	510	612

FIG. 151. Variation of capacity and power output of Edison cells with the rate of discharge.

The variation of the drawbar-pull with the surface over which the vehicle passes is shown in Table LV, which has been taken from an article by Pace.[2]

Pace states that the drawbar-pull is increased 20 pounds per ton of load for each 1 per cent of up-grade. When the vehicle is going on a down-grade, however, an allowance of 20 pounds per ton may be made for each per cent of down-grade. From the data which are given it is possible to compute the drawbar-pull required for any given load conditions.

The service which a vehicle or tractor performs is measured in terms of ton-miles per hour of the "pay load," the ton-mile being a unit which corresponds to the transportation of one ton through a distance of one

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[2] *Electrical World*, 74, p. 795. 1919.

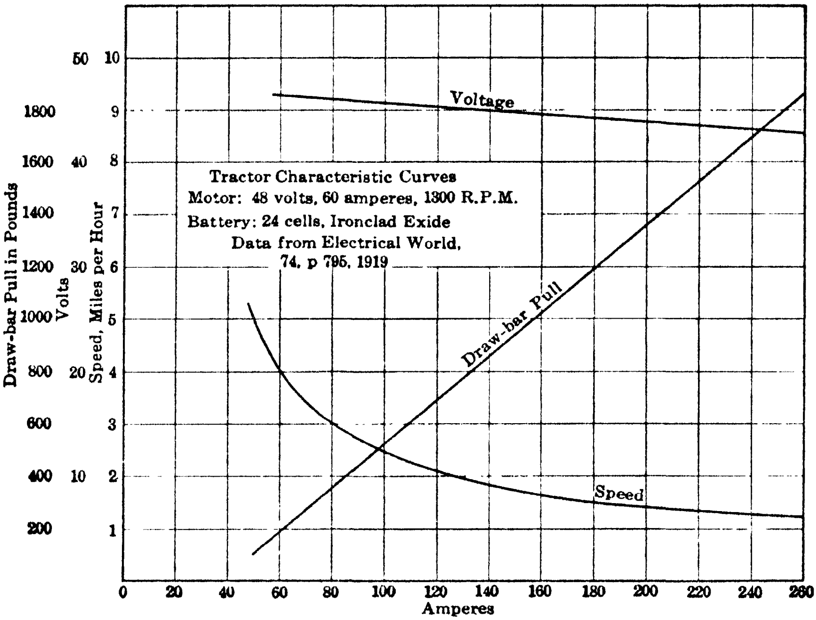

Fig. 152. Operating curves of a tractor.

TABLE LV

Road Resistances Encountered with Trailers

Type of Road Surface: Resistance (Pounds per Ton)		Type of Road Surface: Resistance (Pounds per Ton)	
Asphalt, hard	28	Snow, soft	66
Brick, smooth or cement floor	40	Gravel road	75
Brick, poor	57	Poor, macadam	75
Brick, glazed	47	Clay	200
Macadam	47	Sand road	275
Tarvia	47	Loose sand, 3 inches deep	330
Granite blocks	56	Concrete road	36
Wood blocks	40	Poor concrete	53
Snow, hard	50	Wood planking	43
Ice and Snow	40	Wood, planking, sticky surface	57

mile. The quantity "ton-miles per hour" is therefore a measure of the transportation service which the truck or tractor can render. This varies with the amount of the load and the grade along which it passes.

It depends also on the size, the design, and the construction of the vehicle. The maximum number of ton-miles per hour is not, however, a sufficient guide in choosing a truck, tractor, or vehicle, unless it is considered in connection with the requirements of the work to be performed. For example, a given tractor may have a large transportation capacity because it can haul a very heavy load at a low speed, but this would not be suitable for use where small or medium loads must be transported rapidly. Or again, two tractors may be capable of drawing equal loads, but one of these may exceed the other in ton-miles per hour because of greater speed. In some cases the high speed may be objectionable, as where frequent curves occur or obstacles are to be avoided. If the high-speed tractor cannot be operated efficiently at low speed in such places, the tractor of lower transportation capacity may prove to be better adapted to the service. The question of the ton-miles per charge of the battery is also an important item to consider.

6. CENTRAL-STATION BATTERIES

It has been stated by competent authorities that years of experience in the operation of electrical switching and protective apparatus has led to the conclusion that the storage battery is the most dependable source of power where direct current is required for operating such equipment in manual and automatic stations.

The character of the service required of central-station batteries has changed during recent years, and this has brought about a change in the type of battery and the method of its operation. In the early days of electrical engineering, central stations were confronted with heavy loads at certain times of the day and light loads at other times. The load factor was low and efforts were made to improve the efficiency of operation by the use of batteries. The storage battery is particularly well suited to equalize an uneven load because of its ability to receive energy at one time and deliver it at another. The first central-station battery in this country is said to have been installed in 1885, and in the years that followed many battery installations were made. The primary purpose of these batteries was to assist in carrying the heavy, or "peak," loads, the battery receiving its store of energy at such times as the generating equipment could carry the external load and charge the battery too. In some installations, when the minimum load was too light for efficient operation of the generators, the battery was used to carry the entire load for part of the time. The batteries were charged and discharged daily and it was necessary, therefore, that they should be provided with rugged plates of long life. Planté plates were commonly employed, and the output of the cells for the space which they occupied was relatively small.

Within recent years, advances have been made in both the power and reliability of steam and electrical generating equipment, and the load factor has greatly improved. It is possible now to operate boilers under forced draft when necessary, and the modern generators can carry overloads for sufficiently long times to pass the peak. The necessity for the storage battery in central stations, as it existed some years ago, has practically vanished, but at the same time a new demand for central-station batteries, particularly in the downtown districts of the large cities, has arisen because of the increased importance of continuity of service. One argument in favor of direct-current distribution systems in thickly populated districts has been the possibility of insuring continuous service by the use of batteries held in reserve. The necessity for maintaining lights on business thoroughfares and in places of public assembly, and for the uninterrupted operation of telephones, elevators, underground railroads, etc., can hardly be overestimated. The storage battery is peculiarly well adapted to insure continuous operation, because it has no moving parts and because, when an emergency arises, it can pour its store of energy into the line at enormously high rates of discharge, without delay.

The central-station batteries of today are primarily for stand-by and control service. Their capacities are specified at a very short time rate, such as six minutes or less. It has been stated that the emergency discharge rate of the numerous stand-by batteries of the light and power companies in New York City in 1923, for a period of six minutes, was 2,125,000 amperes at 125 volts.

Because the battery is seldom used, and then at high rates of discharge for which the maximum obtainable capacity is desirable, the batteries with Planté plates are now being superseded by batteries with relatively thin pasted plates. These batteries are less durable than those with massive Planté plates, and they would not be well adapted for daily discharges as in the case of peak load batteries, but for stand-by service they have proved satisfactory. The greater rate of depreciation on the pasted-type batteries as compared with the others is compensated by the saving in initial cost and decreased bulk. The pasted-plate batteries give about 2¼ times the capacity at emergency rates that the older types of cell could give. The decreased bulk is an important item when these batteries must be installed near the center of congested districts where land values are high.

Large batteries (Fig. 153) ordinarily consist of 150 cells, one-half of which are on each side of the neutral of a three-wire line. The cells vary in size from those of 29 plates per cell to the very large cells containing 169 plates per cell. Cells containing 141 plates are the ordinary maximum. The dimensions of the plates have now been standardized as follows: width, $15\frac{5}{16}$ inches; height, $30\frac{3}{4}$ inches; thickness, positives $\frac{7}{32}$ inch, negatives $\frac{3}{16}$ inch. In places where floor space is not too valuable and relatively small capacity is required, plates of one-half the height of these are used, because the shorter path for the current gives a slightly better voltage characteristic. The separators are of wood and the standard spacing of the plates is $\frac{9}{16}$ inch between plate centers. The specific gravity of the acid used is about 1.210 when the battery is fully charged. The cells are contained in lead-lined wooden tanks which are necessary for the larger sizes of cells because of their great weight.

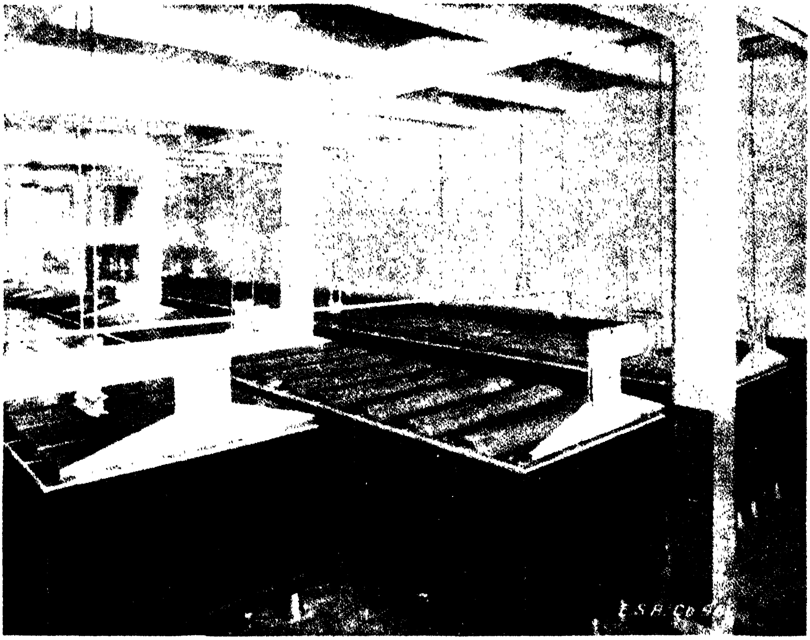

FIG. 153. Central-station battery.

The insulation of the cells is of particular importance where the distribution system is grounded to avoid corrosion of the tanks. Insulators used to support the cells are usually glass bodies with an annular trough filled with oil and protected by a lead-alloy cap hanging free of the sides to keep dirt and moisture out of the oil.

The design of the conductors to lead the current out of the cells requires care, because it is necessary to work the plates equally and provide sufficient conductivity for the large currents required at times of emergency. The bus bars on the sides of the cells, at ends of rows, and on the regulating cells are often reinforced by copper bars embedded in the lead. By this means the conductivity can be increased and uniform current distribution to the various plates provided. The conductors leading from the cells are ordinarily copper bars with bolted joints, supported from the ceiling. The attractions and repulsions between these conductors are strong when they are carrying heavy currents and, therefore, a rigid construction is necessary. Less protection is required now than formerly from the corrosion produced by acid spray, for the reason that the batteries are kept floating on the line with very little gassing. In places where the gassing is strong, the copper is covered with a lead sheathing, but a high-melting-point grease or acid-resisting paint may be sufficient.

Regulation is obtained by the use of end-cell switches in an outside room adjacent to the battery. In emergencies it is usually necessary to cut in all the end cells very rapidly, and therefore groups of two or more cells may be connected to the successive points of the switches. The current required of the battery may be 40,000 amperes or more in emergencies, and the voltages across the successive points are higher than formerly. The newer switches have contact points consisting of copper, and adjacent carbon and graphite contacts also, to provide necessary resistance in the circuit as the switch passes from one group of cells to the next. The switches are motor-driven by semi-automatic control, except that the motor may stop only when the switch is upon a copper contact point.

The main cells of a stand-by battery are normally floated on the line continuously and they are, therefore, fully charged at all times and ready for emergencies. The end cells, however, are usually on open circuit, and they, rather than the main cells, often determine the necessity for equalizing charges. It is the practice of some central stations which maintain large stand-by batteries to remove the batteries for the duration of an equalizing charge from any bus on which load is being carried. The charging current may then be taken from a charging bus through a booster or a motor-generator set, designed to provide the necessary higher voltage through a bus to which no other load is connected. When the booster arrangement is used, it is usually possible to charge end cells separately, but the motor-generator requires that the main battery be included when charging end cells. In some installations end cells are floated separately by a source of current independent of the main supply.

The life of these batteries is dependent very largely on the life of the positive plates. Ten years' service and upwards may reasonably be expected from one set of plates. This will depend somewhat on the amount of service required. The maintenance cost for stand-by batteries is stated to be about 3 per cent per year of the initial cost of installation.

Besides the large batteries for stand-by service in central stations, there are other batteries for important uses. Exciter batteries are provided in large central stations to guard against the damage that would result from failure in the field circuits of the generators. Exciter batteries are therefore one type of stand-by batteries designed for use in the power station itself at times of emergency. Exciter batteries are generally calculated to carry the maximum load for excitation for a period of one or two hours. Another battery is usually provided for the operation of remote-control switches and signal lamps.

Smaller stationary storage batteries, usually in glass jars, find use in power stations for emergency lighting circuits and for the operation of switches and control devices. The earlier installations of this character carried the entire control bus load, except when the batteries were removed from the bus for charging. With the introduction of the floating method of battery operation, the size of such batteries was reduced and their life in service extended. Current for the control bus, which is separate from the main station bus, is usually furnished by a small motor-generator set which supplies the steady station load for indicating lights and control equipment and for maintaining the battery in a fully charged state. The generator must have a drooping voltage characteristic to protect it against overloads when heavy demands are made for current to operate oil circuit breakers, etc. At such times the battery must carry the greater part of the increased load. The battery does little work under normal conditions, but it should be always fully charged and available for emergency service.

Maintenance of the proper floating condition is important, because the life of the battery depends on it. The floating voltage for a lead battery having electrolyte of a specific gravity of 1.215 to 1.220 is usually specified as an average of 2.15 volts per cell or 129 volts per battery of 60 cells. This should be maintained within limits of 2.10 to 2.20 volts per cell. When these batteries are installed at an unattended location, this condition is often difficult to attain.

While the batteries are normally in a charged condition, it is necessary to specify the limit for a discharged battery. This is 1.75 volts per cell or 105 volts for the battery, if the circuit contains equipment requiring 90 volts as a minimum. The difference allows a margin of safety for the line drop in voltage. Some apparatus is designed to operate at 70 volts and in this case a battery voltage of 90 volts (1.5 volts per cell) is permissible, the rate of discharge being high. These batteries are rated at the 1-minute rate to either 1.75 or 1.50 volts per cell. There is a material gain in carrying the discharge to the lower end point as the available ampere-hour capacity is nearly doubled.

To charge a discharged battery, the voltage need not exceed 140 volts. This figure is fixed more or less by the needs of the battery and the fact that the continuous rating for indicating lamps and holding coils permits 140 volts to be used.

In estimating the size of battery required in any particular case, the engineer is at once confronted by the widely different services that these batteries perform. Current needed for the various low-rate services may be estimated and the proper number of positive plates of a specified size decided upon. Then the heavy current demands are added. Normally a switching operation requires a large current for one second or less, but the number of probable simultaneous switching operations must also be considered in estimating the current demand. The number of positive plates to deliver the required number of amperes at the 1-minute rate is determined and the total number required for the battery is the sum of the two estimates.

In previous parts of this book, the fact has been emphasized that the ampere-hour capacity of a battery is proportional to the number of positive plates at a specified time rate of discharge. At extremely high rates, however, the voltage drop in these cells caused by the internal resistance of the cells becomes appreciable and the proportionality no longer exists. The current-carrying parts of the cell might be made heavier, but this is not always desirable or economical. The ampere ratings, like the ampere-hour capacities, are not strictly proportional. For example, a flat-plate cell, having 3 positive plates of the E size, has a discharge rate in amperes at the 1-minute rate of 288 amperes, but a similar cell, having twice as many positive plates, has a rating of 554 amperes, or less than twice as much.

Planté batteries, including cells with Manchester positives and box negatives (Fig. 22) are used for this purpose, but many pasted-plate batteries are used also. The service life is normally greater in full-float service than in cycle service, but continuous floating on the line tends to form (peroxidize) the grids of pasted-plate batteries. This ultimately results in terminating the service life of the cells, and the effect is greater if the average floating voltage exceeds that specified. To meet this situation, manufacturers have developed various types of batteries. (1) In certain small types of Exide batteries the cells contain a greatly increased ratio of positive active material to negative active material. This is accomplished by using two positive plates and one negative plate in three-plate cells. This provides low current density at the positive plates; grid formation is retarded. The higher current density at the negative plates is beneficial in keeping them fully charged and active. (2) Batteries containing reinforced grids (see Fig. 5) have been developed for floating service under the trade names of Floté (Philco) (Fig. 20) and Tytex (Exide) (Fig. 21). The grids have heavy members interspersed among those of more nearly the conventional size. The mass of metal is embedded in the active material. (3) Planté plates, which are well adapted to floating service, are combined with pasted negatives under the name Planté-paste (Gould), (see Fig. 26). The negatives are not subjected to the corroding action which affects the positives.

All of these are batteries of the glass-jar type. They have covers which effectively close them and the vents are designed to trap the spray and return it to the electrolyte within the cell. These batteries may be installed in the same room with other apparatus, as shown in Fig. 154.

The general rules for operating these batteries include attention to such matters as cleanliness, insulation, ventilation, addition of water, and proper charging. No further comments need be made on these points, but two others should be emphasized. (1) At yearly intervals, all the bolted connections should be tightened. Lead tends to flow under pressure and loose contacts result. These faulty connections impair the ability of the battery to deliver the large currents needed for switching operations. (2) Equalizing charges should be given at monthly intervals, notwithstanding the fact that the batteries in floating service are normally fully charged. The length of time needed for the equalizing charge will depend upon the available voltage of the charging line. This is usually the bus for which the limit may be 140 volts (2.33 volts per cell). In any case the equalizing charge should be continued until all cells are gassing freely and the low cells have been fully charged. Measurements of voltage of all cells are desirable. It will often be found that most of the low cells are in the warmest location, that is, near stacks or heating equipment.

The sizes, varieties, and ratings of cells are too numerous to list here. Catalogs should be consulted for these. Unlike some other types, the cells are generally rated according to the amperes which can be discharged for a specified time, as 72, 24, 8, 3, 1 hours and 1 minute. These numerous ratings reflect the diversified service that the batteries perform. In size, lead-acid batteries vary from 1-ampere rating at the 8-hour rate or 20 amperes at the 1-minute rate to 133 amperes at the 8-hour rate or 2640 amperes for 1 minute. These current ratings are usually specified for a temperature of 25° C. (77° F.) but should be reduced by 0.9 per cent at the 1-minute rate or 0.6 per cent at the 8-hour rate for each degree Fahrenheit below 77° F.

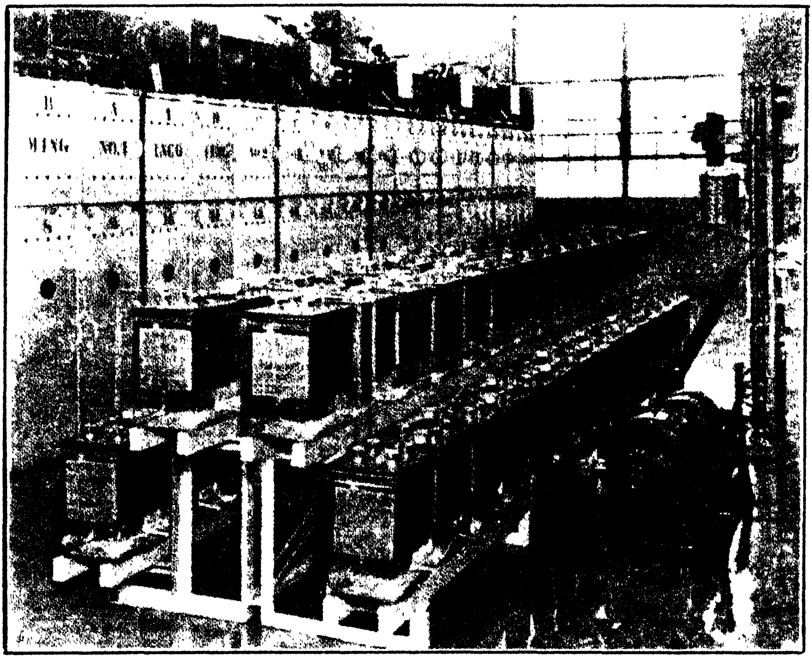

FIG. 154. Control bus battery of 60 cells, installed in room with other equipment.

Edison batteries are used also for circuit-breaker control and emergency-lighting service as required by central-station or substation operation. They find their widest acceptance on low-voltage tripping circuits where 19-cell batteries are recommended for nominal 24-volt systems, 38 cells for nominal 48-volt systems, and 88 cells for 120-volt systems. These batteries are so applied that they are trickle-charged from normal power sources within the maximum voltage ranges of circuit-breaker equipment. For 120-volt systems, the maximum is 140 volts and for other systems values correspondingly above the nominal-system voltage. The formula for computing the proper trickle charge for Edison batteries is given in Chapter VI. Discharge voltage data on cells of the A type are given in Table LVI.

TABLE LVI

CELL VOLTAGE AFTER 15 SECONDS DISCHARGE AT INDICATED MULTIPLES OF NORMAL RATE. TYPE-A CELL

Condition of Cell	Multiples of the Normal Rate					
	1	2	3	4	5	6
Fully charged	1.38	1.29	1.20	1.11	1.02	0.93
50% rated capacity out	1.21	1.12	1.04	0.97	0.87	0.79
100% rated capacity out	1.08	0.97	0.85	0.74	0.63	0.52

Cells of type G will average about 0.05 volt higher at 6 times normal.

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7. EMERGENCY-LIGHTING BATTERIES

Increasing use is being made of storage batteries as a source of power for emergency lighting in buildings. Compact, self-contained units, including batteries and provision for automatically charging them, have been developed to meet increasing needs of this service. Notwithstanding the present high standard of reliability of central-station power, occasional interruptions of service occur as a result of storms, fires, floods, traffic crashes, short circuits and other causes, some of which may be classed as "freaks." Failures are generally localized and beyond the control of the central station, but the public of today is less tolerant of interruptions and the effects may be serious. Continuous light lessens the liability to accidents, loss of life, panic, theft, property damage, and law suits. Such a list suggests the places where emergency lighting is particularly applicable: places of public assembly, banks, hospitals, large stores, power and industrial plants, schools, hotels, and ships.

Only in the most congested areas of large cities is provision made for carrying all, or nearly all the normal load on an emergency system. Huge batteries are necessary for such a purpose in an area of direct-current distribution, but on a smaller scale batteries are equally applicable to emergency service where the current supply is normally alternating. This became possible with the development of efficient rectifiers and automatic control.

Individual emergency-lighting systems, which may be installed anywhere that power is normally available, do not necessarily provide for the full lighting load, but rather for lights in particular locations where dangerous conditions could arise suddenly and without warning in the event of power failure. All parts of a building or ship are not equally affected by the lights being out. The danger zones are typically assembly halls, exits, operating rooms, bank vaults, etc.

Selection of the danger zones is the first step in planning an emergency-lighting installation. The proper locations for lights and the amount of light required at each place then become problems for the illuminating engineer, but it is obvious that conditions are widely different. Sufficient light to enable people to move in an orderly manner to exits is wholly unrelated to the needs of a physician at the operating table where an illumination of 1000 foot-candles is wanted with the added stipulation that it must be free from shadows.

Having selected the places requiring emergency-lighting protection, the next step is to determine the total watts required for a given floor area. Two hundred watts may provide sufficient light to enable a person to read ordinary newsprint anywhere in a floor area of 2000 square feet, but the same number of watts expended over a floor area of 4000 square feet would limit him to reading coarse print; and if the floor space were doubled again, that is, to 8000 square feet the average illumination would be approximately equivalent to moonlight. In any case, the particular problem is to determine the requirements to provide minimum necessary illumination. Several rooms may be involved or the service needs may include general illumination, localized illumination, or a combination with exit lights. The watts necessary to provide this is the first factor in estimating the size of battery.

The next step is to estimate the protection period required. That is, the time factor, which will depend in part on the reliability of the power supply and in part on the time which is needed to complete a course of events such as clearing an auditorium, completing a surgical operation, or repairing broken machinery. Protection periods are usually estimated at about 1½ hours with 3 to 5 hours as the upper limit.

Selection of the battery equipment depends on the watt-hours required, that is, on the product of the power necessary by the protection period.

If the estimated watt-hours required are not too great, a low-voltage system of 12 volts operating lights on an independent circuit may be entirely sufficient, but it should be noted that the wiring in such cases must be heavier than that for the normal 115-volt circuit. This is because of the larger currents required for any given number of watts. The line-voltage drop increases as the current increases, and the heating increases as the square of the current. To avoid long lines, the battery and its control equipment should be located as near the center of the load as possible. The line-voltage drop to the farthest lamp should not exceed one volt. Special 10½-volt high-efficiency lamps are available in sizes of 15 to 100 watts for such a system. The significance of rating these at 10½ volts lies in the fact that some line drop in voltage must necessarily occur between the lamps and the battery, which begins its discharge with a terminal voltage of slightly less than 12 volts and reaches the limit of its capacity with a terminal voltage of 1.75 volts per cell or 10½ volts for the whole battery if it is the lead-acid type. The lamps are operated, therefore, at the rated voltage and the light is not materially dimmed as the battery completes its discharge.

The smaller units of 240 watts at 12 volts are usually provided in ventilated metal cabinets which house the battery, switching equipment, relays, and rectifiers. This cabinet may be mounted on a wall of the room where it is to be used, as the cells are of the sealed glass-jar type with vents which effectively prevent the escape of spray. Under normal conditions the battery is maintained in a fully charged condition by a trickle current from a copper oxide rectifier which is connected to the alternating-current circuit through a transformer. After an emergency discharge, however, the battery is recharged quickly at a higher rate. When the battery becomes charged or nearly so, the voltage control relay returns the battery to the trickle-charge circuit. Test circuits are provided to check the operation of the emergency lamps. A pilot light is furnished to indicate when the battery is delivering current. Some models are provided with an additional alternating-current circuit of 12 volts for "exit" lights. These are normally supplied with alternating current, but they are transferred to the battery circuit in the event of a power failure, along with the emergency lamps of 10½ volts for general illumination. In the diagram of Fig. 155 the lights marked "normally on" are the exit or other special lamps, while those marked "normally off" are the emergency lamps which are used only at the time of a power failure. The circuit shown is for fully automatic operation. A few models require manual adjustments for an accelerated charge after a discharge. Inspection is recommended at frequent intervals, such as once a week. The test switch should be operated and the cells having pilot balls inspected to determine whether both balls are "up," indicating that the battery is charged. Water should be added as needed, and occasionally the specific gravity of electrolyte in each cell should be measured; this should be about 1.210 when the battery is fully charged.

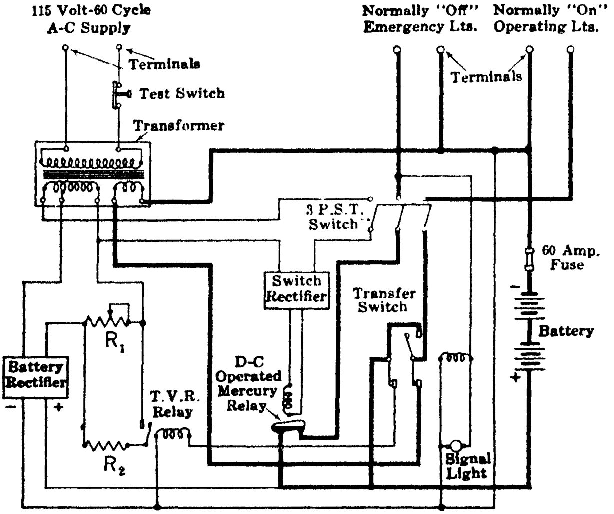

FIG. 155. Connections for a fully automatic emergency lighting unit, 115 volts alternating current to 12 volts direct current.

If the floor space to be illuminated exceeds 10,000 square feet, larger units of 115 volts, having 60 cells of the lead-acid type, are usually recommended. These operate on much the same principles as the smaller units, but they furnish current to lamps on the same wiring as that which carries the normal alternating-current load. The circuit, however, is usually divided so that only selected lamps are lighted by the battery current in emergencies. Simplified diagrams of the circuits for two- and three-wire systems are shown in Figs. 156 and 157. The latter shows how a three-wire circuit is operated as a two-wire circuit when battery current is furnished. It is necessary that the neutral wire have sufficient current-carrying capacity. Operation of the switches is automatic and practically instantaneous.

In these larger emergency equipments, the control unit only is contained in the metal cabinet. The battery of 60 cells is mounted on a suitable acidproofed rack. The capacity required varies with the lighting requirements and the protection period which is needed. The high-rate charging is provided by a bulb-type charger until a voltage relay with compensation for temperature transfers the battery to a trickle-charge circuit having a copper rectifier. Since a two-wire 115-volt circuit would be insufficient to charge a battery of 120 volts through these rectifiers, the battery is divided into two parts which are charged in parallel. The change from parallel to series connection is accomplished automatically when the battery is required to discharge.

Meters to indicate the output of the trickle charger and the voltage of the battery are provided, together with test circuits and signal lights to indicate when the battery is discharging and when the battery is being charged at a high rate.

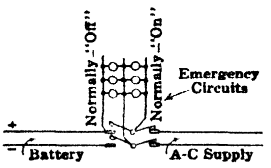

FIG. 156. Two-wire system.

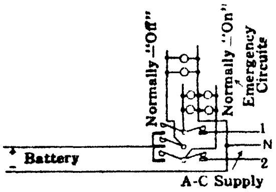

FIG. 157. Three-wire system.

Emergency-lighting systems on shipboard operate on much the same principles. Both lead-acid and nickel-alkaline batteries are used. These are of much larger sizes than for the smaller units described above. Ship circuits are frequently direct current so that rectifiers are not required for charging the batteries. They are either floated across the line of the generator or charged in parallel halves.

Edison batteries in a variety of sizes are available for 32, 110, 115, and 120-volt systems. Cells of the smaller types, N, L, and B, are employed for the smaller systems. Larger cells of the types G, A, and C find use on 32-volt systems above 1500 watts and the type A on 110- and 115-volt systems above 7000 watts. The number of cells varies somewhat, but for a specified watt output at the 1½-hour rate of discharge on 32-volt systems they are calculated to deliver approximately 27.8 volts at the end of the discharge. For the higher voltage systems, 85 to 110 cells are used, depending on the watts required at the 1½-hour rate to supply a final voltage not less than 87 per cent of the nominal lamp voltages, for 110-, 115-, and 120-volt systems, respectively. Recharge is specified to be in 12 hours.

An emergency power and lighting system recently designed for use with Edison batteries on a 115-volt system for marine use, but applicable to other direct-current circuits, has the following cycle of operation. If the supply voltage of the line falls below a predetermined value, lockout relays operate to (1) transfer the load to the battery of 100 cells and (2) to start a Diesel-driven generator After the voltage of this has attained a suitable value, another relay transfers the load to this generator. When normal line voltage is restored, the load is transferred again to the normal source of supply. The panel provides for charging the battery in parallel halves at the normal rate and thereafter maintaining a trickle charge. Provision is also made for a regulated bus voltage not exceeding 5 per cent above normal. This is done by a carbon pile which is short-circuited when the emergency bus voltage falls below a predetermined value.

8. AUTOMOTIVE STARTING AND LIGHTING BATTERIES

a. Development of Starting and Lighting Systems

The application of storage batteries to starting and lighting service on passenger cars, trucks, and motorcoaches has been one of the notable developments in the battery industry. Starter systems for internal-combustion engines were first suggested about 1902, but the practical application of electric starters began about 1911. Before the electric systems were adequately developed, various other systems employing compressed air, acetylene, and mechanical devices were in use. All these have been superseded by the electric systems, employing batteries, motors, and generators. Aside from the fact that many of the earlier systems were not convenient to use or satisfactory in other respects, the demand for electric lights was an important factor in establishing the supremacy of electric starting. Between 1912 and 1914 development was rapid, and electric starting became the commonly accepted method. At that time systems were classified as "single-unit" or "two-unit" systems. The former employed a combined motor and generator. During the cranking period, this operated as a relatively low-speed motor, but after the engine started it functioned as a generator. Two-unit systems comprised separate motors and generators. These were smaller than the single unit starters and they operated at higher speeds. Occasionally reference is made to three-unit systems, the third unit being a magneto for ignition. Two-unit systems have superseded the others and are now practically universal.

b. Principal Parts of Starting and Lighting Systems

Any internal-combustion engine must be set in motion before it can operate on its own power. Each car must have, therefore, its individual source of energy for starting the engine. This is a battery of 6 volts on passenger cars and trucks or 12 volts on large motorcoaches. Electricity supplied by the battery operates a small electric motor which is automatically connected to the engine through a reduction gear when the starter switch is closed and automatically disconnected when the engine begins to operate under its own power. The battery also supplies current for lights and other services when the engine is not running. Current furnished by a generator, driven by the engine, maintains the battery in a charged state. The fact that a battery may need to be removed from the car at some time for extra charging is merely evidence of a maladjustment of operating conditions, in the absence of any obvious defect. At such a time 125 to 150 ampere-hours may be supplied, but this is small compared with 2000 to 5000 ampere-hours supplied yearly by the generator on the car. Besides charging the battery, the generator supplies most, if not all, of the current requirements of the car when the engine is running.

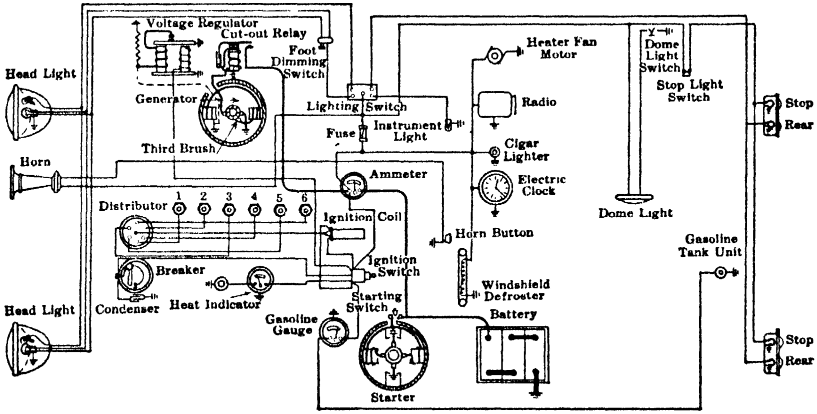

Fig. 158. Electrical circuit of an automobile.

The load on the electrical system of automobiles has increased very greatly. In addition to the requirements of former years for starting, lighting, and ignition, modern cars have more and brighter lights, cigar lighters, multiple horns, defrosters, fans, heaters, marker lights, panel indicators, and radios. During the past ten or twelve years the electrical load of passenger cars has increased from about 7 amperes to 25 amperes and to even more for trucks and motorcoaches. Battery sizes have not been increased in proportion, but the output of generators has been materially increased.

In the early days, batteries of 6, 12, 18, and 24 volts were used on passenger cars. These are now universally 6 volts. Factors which brought about standardization of 6-volt systems undoubtedly included the previous development of 6-volt ignition systems, operated by four dry cells, and the fact that 6-volt tungsten lamps were successfully produced with short, rugged filaments which could withstand the mechanical shocks and vibration of automotive service. Electric lights were in favor because they were convenient, because the beam of light could be focused, and because electrical equipment for automobiles was a part of a fast developing electrical age. From relatively simple circuits on the earlier cars, we have passed to the circuit of a modern car shown in Fig. 158.

c. Starting and Lighting Batteries

These batteries (sometimes called SLI batteries, meaning starting, lighting, and ignition batteries) for passenger cars and trucks consist of three cells of the lead-acid type in a unit case of hard rubber or bituminous composition. The size and arrangement of the cells and the location of parts are all specified in detail in the standards of the Society of Automotive Engineers (S.A.E.). Changes in this standard must be made at fairly frequent intervals to keep pace with advances in the automotive industry. In past editions of this book the standard has been quoted, but within a few years it became obsolete. It is better, therefore, to refer to current issues of the S.A.E. standard. The tendency in recent years has been to employ batteries with thinner plates and higher capacity. Many of the batteries now are less in height because of decreased clearance for the batteries on low-slung cars. The present standard list includes 16 sizes for passenger cars, 5 sizes for trucks, and 6 for motorcoaches. The shapes and general type of assembly are shown in Fig. 159.

Capacity requirements vary from about 90 ampere-hours at the 20-hour rate for the smallest passenger car batteries to 200 ampere-hours at the same rate. Many small trucks use passenger-car batteries, but those specifically designated as truck batteries are usually found on larger and heavier vehicles. The latter range from 118 to 236 ampere-hours. Motorcoach batteries include both 3- and 6-cell batteries. Maximum capacity of the 12-volt batteries is 117 ampere-hours at the 4-hour rate.

The S.A.E. list of batteries includes the smaller sizes of the lead-acid type in general use on motorboats, tractors, and other automotive industrial applications as well as on motor vehicles. Actually, three or four sizes are more commonly used, and these are sufficient to supply a vast majority of automotive installations.

On small vehicles, having only a normal lighting and accessory load, the size of battery is determined by the cranking load. For motorcoaches, on the other hand, the lighting load is extremely heavy and the size of battery is determined by the lighting load in relation to the output of the generator. The greater the margin of generator output over the actual load, the smaller the battery can be, provided that it is not less than would be adequate for cranking the engine. Motorcoaches with Diesel engines require special batteries which are described in another section.

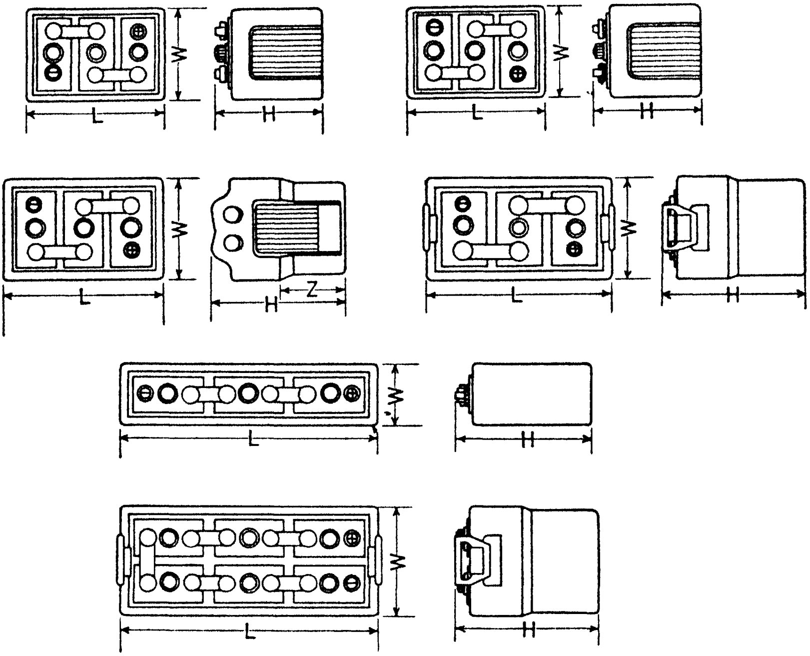

FIG. 159. Types of starting and lighting batteries for passenger cars, trucks, and motorcoaches.

Batteries for combined starting and lighting service have a dual rating. The first is an indication of lighting ability and is the capacity in ampere-hours of the battery when it is discharged continuously at 80° F. to an average final voltage of 1.75 volts per cell at the 20-hour rate, or 4-hour rate in the case of motorcoach batteries. New batteries must equal or exceed their rated capacities on or before the third discharge. The second rating, applying only to passenger-car and motor-truck batteries, is an indication of the cranking ability under adverse conditions of low temperature. It is expressed as the number of minutes, when the battery is discharged continuously at 300 amperes to a final terminal voltage of 1.0 volt per cell, the temperature of the battery at the beginning of such discharge being 0° F. As a part of the same low-temperature test, the terminal voltage of the battery is recorded at the end of the first 5 seconds. Minimum requirements for time and voltage of each size and type of battery are part of the standard of the Society of Automotive Engineers. These batteries are required also to meet certain minimum specifications for life tests, ranging from 234 cycles to over 500, depending on the size and type. These tests are described also in Chapter IX.

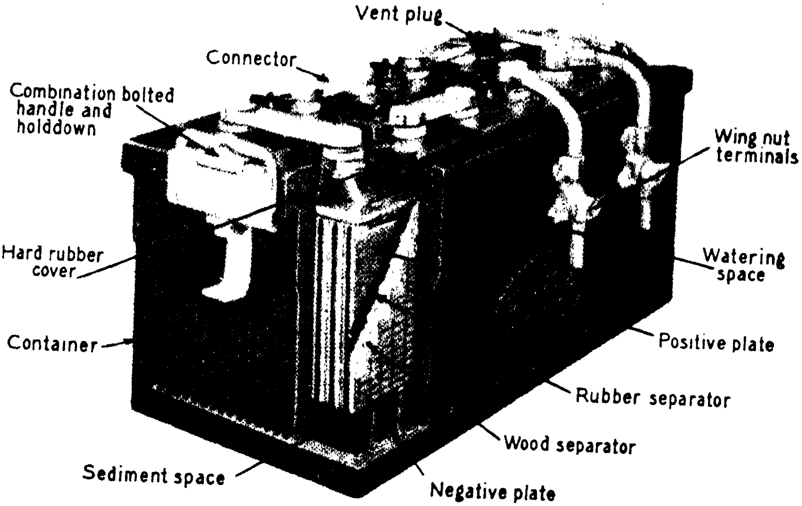

FIG. 160. Starting and lighting battery for use on motorcoaches, 12 volts. For the passenger-car type, see Fig. 19.

Most of the automotive batteries are provided with single insulation, that is, wood or porous rubber separators between plates of opposite polarity. Some of them, however, have double insulation which is defined for purposes of the specifications as the use of a retaining sheet of porous or perforated material between the positive plates and the customary single separator (Fig. 160). The effect of double insulation on the operating characteristics of the batteries is recognized in the S.A.E. standard. Additional insulation increases the internal resistance of the battery and a reduction of 10 per cent is allowed from the specified time and voltage requirements. The requirement for life cycles, however, is increased 15 per cent. Truck and motorcoach batteries normally are provided with double insulation and must meet the requirements specified for such batteries.

The terminals are ordinarily taper posts of different diameters to prevent wrong connections from being made. The standard for such terminals is specified by the Society of Automotive Engineers as follows:

	Inch
Small diameter, negative post	$\frac{5}{8}$
Small diameter, positive post	$\frac{11}{16}$
Taper per foot	$1\frac{1}{3}$
Minimum length of taper	$\frac{5}{8}$

The polarity of the terminals should be indicated by letters or by plus (+) and negative (−) signs.

Connections are made to these terminal posts by clamp connectors, of which there is considerable variety. These must fit well to avoid appreciable contact resistance which would limit the amount of current delivered by the battery when cranking the engine. It is possible for the battery to supply current for the lights and other services and yet be limited by resistance at the contacts sufficiently to make starting difficult or impossible. Corrosion at the contacts requires that they be cleaned: First, all products of corrosion should be removed; second, acid on the surface and in recesses should be neutralized with dilute ammonia or soda; third, the terminals should be washed, dried, and greased; fourth, the clamp connections should be restored and tightened. Vaseline is satisfactory for the purpose, but other neutral greases may be used. Occasionally, some greases are found that promote corrosion. The number of patents which have been issued for various battery terminals and means of preventing corrosion is surprisingly large.

Structure. The cells for starting and lighting batteries contain plates of the pasted variety, which are burned to the connecting straps to form the plate groups. Ordinarily there are not less than 13 plates, including 6 positives and 7 negatives, in any cell. The largest sizes of cells may contain as many as 25 plates. The dimensions of the plates vary, but the ordinary sizes are about $5\frac{5}{8}$ inches in width, 5 inches in height, and $\frac{3}{32}$ inch or less in thickness. The separators for these batteries are commonly made of wood, or wood separators are combined with perforated or slotted rubber separators; but in some cases the wood separator has been superseded entirely by separators made of other materials, as for example porous rubber separators.

The electrolyte consists of a solution of sulphuric acid of a specific gravity 1.270 to 1.300 when the battery is fully charged. The specific gravity decreases to about 1.140 when the battery is fully discharged. A high degree of purity of the electrolyte is desirable, but perhaps not as necessary for automobile batteries as in the case of stationary or signal batteries, since the automobile batteries are charged and discharged at very frequent intervals. The temperature of the electrolyte, which also represents the temperature of the cell as a whole, should not exceed 110° F., because of the increased local action within the cell and the charring of the separators. The temperature of starting and lighting batteries will rarely rise to this figure if the charging currents are not excessive, provided they do not receive too much heat from the engine.

Cases for starting and lighting batteries are of hard rubber or bituminous compounds, molded to provide compartments for the individual cells. They are made in a variety of shapes and sizes, such as that illustrated in Fig. 14, in Chapter II. In general, cases of hard rubber or bituminous materials are much the same in appearance, but the former are usually marked to indicate that they are hard rubber. These are preferred, because their life in service is generally longer and because they are less subject to deleterious effects of the electrolyte. Figure 15 shows a cover.

The covers for cells of the starting and lighting type are ordinarily of molded rubber. The cover is provided with several openings, through two of which the terminal posts of the cell project, the middle opening being used as a vent for the escape of gas when the cell is being charged. The cell may be filled with water or electrolyte by removing the vent plug. Since batteries of this type are ordinarily subjected to severe vibration, it is necessary that the vent plugs be provided with baffle plates to prevent the escape of the electrolyte, which would otherwise flood the top of the battery. On many of the cheaper batteries, however, vent plugs without baffle plates are used.

The size and shape of the connectors and terminals for starting and lighting batteries are of importance, since the batteries are required to give very large currents during the period of cranking the engine. For this reason the connectors between cells are much heavier than on ordinary types of portable storage batteries. Solid connectors of lead or of lead-antimony alloy are used almost exclusively on batteries for service on passenger cars, but flexible copper connectors, heavily lead-coated, are used on some types of batteries for truck service. The voltage drop in the intercell connectors should not exceed 10 millivolts per inch of distance between post centers when the battery is discharging at the 20-minute rate. The resistance of the connectors will vary from 0.00005 to 0.0002 ohm per inch of distance between the centers of the terminal posts of adjacent cells, according to the capacity of the battery. It is obvious that if the resistance is more than a few thousandths of an ohm, the loss in voltage during the cranking period due to the *I R* drop in the connectors will be an appreciable part of the total voltage of the battery.

Starting and lighting batteries may be obtained in the condition best suited to the needs of the purchaser. The conditions for shipment have been specified as follows:

a. **Filled and Charged.** Batteries intended for immediate use or for wet storage where suitable facilities are available shall be filled with electrolyte and fully charged.

Such batteries may be put in service after a brief inspection to determine whether the electrolyte stands at the proper height in each cell and whether the specific gravity of the electrolyte is normal. If electrolyte has been spilled, it should be replaced by electrolyte of corresponding specific gravity. If the battery is to be tested for capacity or if the specific gravity of the electrolyte is low as a result of considerable time elapsing since the last charge, the battery should be given a freshening charge. This is done at the finishing rate until the specific gravity ceases to rise, measurements being made on each cell.

b. **Charged and Dry.** Batteries intended for storage in the charged condition within the time limit specified by the manufacturer shall contain dry charged plates and dry porous rubber separators or double insulation. The vents of each cell shall be sealed at time of assembly and remain so until the battery is prepared for service.

These batteries are made ready for service by filling them with electrolyte in accordance with directions furnished by the manufacturer. In the absence of specific instructions, the following procedure may be used: Fill the battery with electrolyte of 1.280 sp. gr. (temperature not exceeding 80° F.) to about one inch above the plates and allow the battery to stand one hour. At the end of this time the battery may be put in service after adjusting the electrolyte to the proper height in each cell. Such batteries will give about one-half to two-thirds of their rated capacity on the initial discharge. If the battery is not put in service within 12 hours it should be charged.

c. **Uncharged.** Batteries intended for storage in the uncharged condition within the time limit specified by the manufacturer shall contain dry plates and separators. The vent of each cell shall be sealed at the time of assembly and remain so until the battery is prepared for charging.

When the batteries are filled, electrolyte of the specific gravity recommended by the manufacturer should be employed. The specific gravity will depend on the amount of sulphate in the plates and on the final specific gravity to be reached when the cells are fully charged, but it is usually within the range 1.250 to 1.280. The temperature of the electrolyte should not exceed 80° F. at the time it is poured into the cells, but a rise in temperature will be observed caused by the formation of lead sulphate. Twelve hours is usually required for the electrolyte to diffuse into the pores of the plates and for the battery to cool. After this and before 24 hours has elapsed, the battery should be placed on charge. The rate of charge suitable for this purpose is sometimes specified as the finishing rate, but a better guide is to calculate the 20-hour rate from the rated capacity of the battery and continue charging at this rate for at least 48 hours. At the conclusion of the charge the electrolyte may be adjusted to the proper value.

d. Charging System

A generator driven by the engine is the source of electricity on each car. The connection between the generator and the engine is usually a belt, although gears and couplings are sometimes employed. Small generators running at high speed can deliver as large an output as larger and more expensive generators operating at lower speed, but the latter are likely to last longer in service. Notwithstanding the greatly increased loads of the modern automobile, the size of generators has not materially increased. The larger output now required has been obtained by refinements in design and by providing ventilation. The generator capacity should equal the total load with some reserve to keep the battery charged. The generator must provide sufficient voltage for the lamps over a wide range of car speeds and a variation of about 20 amperes between light and full-load conditions. Satisfactory operation depends in part on the selection of the best drive ratio and on the regulation of the generator's output.

The third-brush generator without other means of regulation has been in almost universal use until recently. Its characteristic of maximum output at a definite car speed was suitable for average driving conditions. It carried the load through a speed range of about 14 to 40 miles per hour and the charging current was not excessive.

Enlarging the battery would take care of increased charging currents of the present day but would offer no solution for increased voltages which came with the increased speeds and heavier loads of the modern car. Third-brush generators of higher output can carry the maximum load, but, if the load is light, the battery is likely to be seriously overcharged. On the other hand, when the battery becomes fully charged and the load is light, voltages are likely to be excessive during severely cold weather. This causes arcing at the ignition contacts, shortens the life of lamp bulbs, and affects radio tubes adversely. The result has been the introduction of current or voltage regulators, or both, as a means of limiting the current and voltage supplied by the generator which may be a shunt or compound type. Voltage regulators are essentially electromagnets whose windings are energized so that the magnetic pull on the armature is approximately proportional to the impressed voltage. At a specified value the armature opens contacts and thereby inserts a resistance in the generator field circuit. This reduces the generator voltage and, consequently, the charging current to the battery. The armature is released, subsequently completing the cycle which is repeated often enough to maintain the voltage at the desired value. This is set for about 7.5 volts which is necessary for the battery, but temperature compensation is needed to meet the varying conditions of summer and winter driving. Another method of regulation has been to insert a resistance in the field circuit of the generator when the lights are off and to remove it when they are on. This resistance is controlled by the light switch.

Burning the headlights to decrease the charging rate on the battery is of little use on modern cars. The voltage relay automatically reduces the charging rate when the battery voltage rises to a predetermined value which is characteristic of a fully charged battery. At lower voltages than this the battery can safely absorb larger charging currents.

In addition there is a cutout relay which disconnects the battery from the generator circuit when the generator voltage is too low to charge it. This relay closes at about 7 volts corresponding to a car speed of about 8 to 12 miles per hour. The cutout relay normally remains open when the engine is stopped.

e. The Service That Starting and Lighting Batteries Must Perform

During the period of cranking an automobile engine, the battery is called upon to supply a large current which fluctuates rapidly because of the compression of gas in the cylinders of the engine. It has been possible to study the demands made upon starting and lighting batteries in the operation of various types of automobiles by using an oscillograph. Photographic records of the instantaneous values of current and voltage were obtained at the Bureau of Standards.[3] In addition

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[3] Vinal and Snyder, *Technologic Paper* 186, Bureau of Standards. See also, "Some Oscillograph Tests on Electric Starters for Motor Cars," by Smith-Rose and Spillsbury, *J. Inst. Elec. Eng.*, 67, p. 133, 1929.

to the data relative to the battery requirements, the interpretation of these records has brought out interesting facts with relation to the study of lubrication and engine problems.

The instantaneous values of current and voltage were obtained by means of a three-element moving-coil type oscillograph. In order to obtain records for periods of sufficiently long duration, the ordinary film drum of the oscillograph was replaced by a camera of special construction in which photographic paper in rolls of 100 feet could be used. When making a record the sensitized paper was wound upon a drum in the lower end of the camera after having passed the oscillograph slit, through which the recording images were projected. One of the elements was used to record the voltage at the terminals of the battery, another to record the current through the battery circuit, and the third to make the time record, which consisted of the half-second ticks of a chronometer. The general character of the curves is shown in Fig. 161. This oscillogram begins at the right and is to be read from right to left. The time intervals are recorded at the top of the record. The curve next below the time record represents the fluctuations of the voltage at the terminals of the battery when the starter is in operation. The last curve represents the current and shows the fluctuations due to compression in the successive cylinders. The zero value of this current is shown by the horizontal line in the lower corners. This car had a two-unit system operating on 6 volts. During the first half-second after closing the starting switch, the current fluctuated rapidly through a range of more than 100 amperes, the maximum value being about 250 amperes. In this figure it can be clearly seen that the minimum values of voltage correspond to the maximum values of current.

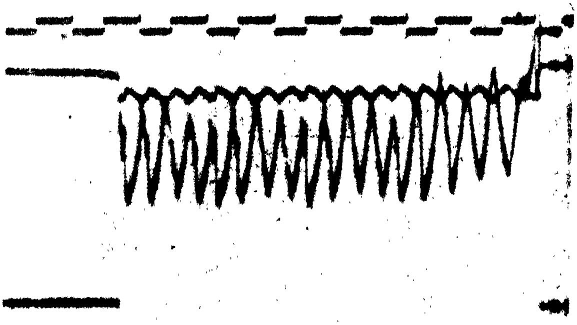

FIG. 161. Record of the current and voltage in the battery circuit of a 4-cylinder car when the starter was cranking the engine, 2-unit system.

Temperature plays a very important role in determining the successful operation of an electric starter system. Automobiles are subjected to extremely low temperatures in winter. In some states of the United States the average temperature during the three winter months may be as low as 0° to 10° F. The low temperatures increase the viscosity of the oils, decrease the terminal voltage and capacity of the battery, and increase the difficulty in producing combustion of the gasoline vapor in the cylinders of the engine. The effect of the increased viscosity of the oil on the work which the battery has to do

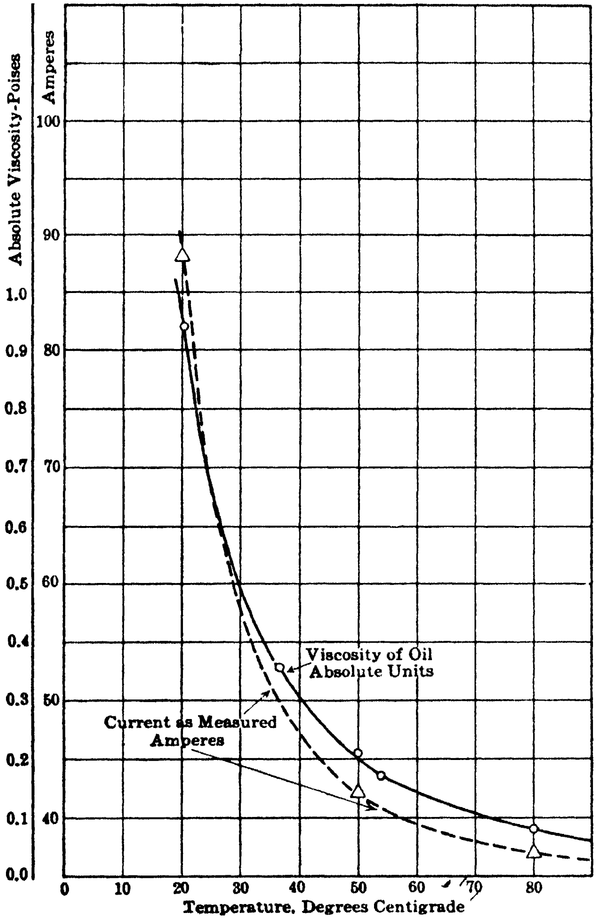

FIG. 162. Relation of current in the starter system to the viscosity of the oil in the engine.

is shown in Fig. 162.[4] This figure shows the relation of the current in the electric circuit to the viscosity of the oil used in the engine. The current which the battery delivers to the starting motor is proportional to the torque which the motor is able to exert in cranking the engine. The torque required to start any engine is obviously dependent on the friction, and therefore dependent on the viscosity of the oil which the engine contains. The data for Fig. 162 were obtained by determining the currents required to operate the engine when all compression was relieved by removing the spark plugs, measurements being made at three different temperatures. The relation of the electric current furnished by the battery to the temperature of the engine is given by the dotted curve in the figure. The viscosity of the oil, expressed in absolute units, is given by the curve which is almost superposed upon the dotted curve.

Both temperature and rate of discharge affect the available capacity of the battery. These matters have been discussed in preceding sections, but it is appropriate here to indicate some of the facts about starting and lighting batteries that may seem rather surprising. Take, for example, a battery which normally has a capacity of 100 ampere-hours at the 20-hour rate at 80° F. This same battery has a capacity of about 16 ampere-hours at a discharge rate of 300 amperes at 0° F. which is an assumed condition for starting a car, according to the S.A.E. standard. This seems very small, but to find whether it is adequate, comparison must be made with the capacity needed for actually starting a car. Assume for the moment that an average current of 300 amperes is needed for cranking the engine and that the time is unusually long, 10 seconds. The battery output is 3000 ampere-seconds or 0.83 ampere-hour, which is about one-twentieth of the battery's capacity.

The effective or terminal voltage is reduced also by low temperatures. This should not be attributed to the temperature coefficient of electromotive force which is discussed in Chapter IV, because this effect is very small in comparison with the differences actually observed. The *IR* drop through the cell when discharging large currents is considerable at ordinary temperatures, and this is materially increased by the greater resistivity of the electrolyte at low temperatures. The resistivity of the electrolyte increases threefold as the temperature is decreased from 25° C. (77° F.) to −20° C. (−4° F.).

The storage battery ordinarily furnishes the electrical energy for the ignition of the engine also. This is an intermittent service, the

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[4] *Technologic Paper* 186, Bureau of Standards.

current being made or broken by the distributor at the required time in the cycle of each cylinder.

f. Care of Starting and Lighting Batteries

Although starting and lighting batteries are often subjected to severe charging conditions, they will give satisfactory service provided they receive ordinary care and maintenance. This includes the proper adjustment of the charging system as well as the care of the battery itself.

The most convenient means of estimating the state of charge of the battery is by the hydrometer readings. When the battery is fully charged the specific gravity will range from 1.270 to 1.300. When the battery is discharged the specific gravity will range from 1.140 to 1.160. These are the specific gravities when measurements are made at ordinary temperatures. Intermediate states of charge of a battery may be estimated by interpolating between the limits for the charged and discharged conditions.

Batteries which are used for automobile service in the tropics, require considerably lower specific gravities owing to the increase in chemical activity due to the higher temperature. It is customary to adjust the electrolyte for these batteries to a maximum value of 1.220, and this may decrease to 1.080 when the battery is completely discharged.

The second essential in the ordinary care of the batteries is the addition of pure water as necessary to keep the plates well covered. The water is added to replace the so-called evaporation. By the term "evaporation" is meant not only the evaporation which takes place in the ordinary sense, but also loss of water due to gassing when the cells are on charge. The water should always be added after the hydrometer readings are completed. This is because the water, being less dense than the electrolyte, tends to remain on the top and give a false indication of the specific gravity. The water gradually mixes with the acid, and the electrolyte comes to a uniform density as a result of the gassing which takes place when the cells are on charge. This also suggests the necessity of making additions of water to cells in extremely cold weather before running the car, rather than after, to avoid the danger of freezing. Distilled water is much to be preferred but is not always available. As substitutes, artificial ice which has been melted in a porcelain receptacle, or in some cases rain water, may be used. Rain water collected on metallic roofs is not satisfactory, and it often happens that rain water collected in the neighborhood of large cities contains considerable amounts of impurities which have been taken up by the drops of water in their passage through the air. The natural water supply can be used in some cases, but it is not to be recommended in general. When only natural water is available it is better to use it than to allow the battery to go dry.

Within recent years a number of testing devices have been developed to determine quickly the condition of starting and lighting batteries. They depend for the most part on the interpretation of voltage data when the cells are discharging at a high rate comparable with conditions for starting the engine. Some of these are simple prongs applied to the terminals of the individual cells, causing a current of several hundred amperes to flow while the terminal voltage is read on a meter. Others which are more elaborate provide a variety of meters for the different tests and these may be adjusted for the size and type of battery to be tested and the number of plates which it contains. The objectives sought in making these tests are, first, to determine whether the battery is in serviceable condition without the necessity of opening it; and, second, to convince the customer of the battery's condition by a demonstration.

As a preliminary, the specific gravity of each cell is read. If all cells are uniform in this respect and if the value of specific gravity in each cell is above 1.225, the battery is presumed to be in reasonably good condition. Below this figure, charging is recommended. Considerable variations in specific gravity readings (50 points or more) usually indicate sources of trouble such as short circuits through separators; leakage of electrolyte through partitions between cells; worn-out plates in one or more cells or badly contaminated electrolyte. The emphasis is placed on uniformity. Electrical tests which show voltage variations between the individual cells amounting to 0.15 volt or more when the cells are being discharged at a rate of 25 or more amperes per positive plate are usually interpreted to mean that a short circuit is present in the low cell or cells.

In the absence of evidence that short circuits exist in the battery, charging is usually recommended. This is conveniently done by using one of the various types of rectifiers designed for the purpose. As charging proceeds, the cells, if in good condition, should "come up" uniformly and finally reach a constant specific gravity of about 1.280. Voltage measurements made at this time should be uniform, but no definite figure can be set because the charging voltage varies with the current and temperature. Ten or twelve hours after charging has been completed and the battery disconnected from the charging circuit, equilibrium between the plates and electrolyte should be reached. There is then a definite relation between the state of charge and the terminal voltage of the individual cells. The high-rate discharge test may be repeated and continued long enough (30 seconds or more) to determine (1) whether the terminal voltages are uniform and (2) whether they are equal to, or greater than, some specified value. If below this value, the indication is that the plates are deficient in capacity and the battery should be replaced.

Loss of charge on standing for a few days may be determined by noting the decrease of specific gravity readings on successive days. If excessive, this is an indication of an internal short circuit, leakage between adjacent cells, excessive impurities in the electrolyte, or, in the case of old batteries, the local action produced by antimony deposited on the negative plates.

Another essential for the satisfactory operation of a starting and lighting battery is cleanliness. Water or electrolyte which has been spilled on the top of the battery should be wiped off. A rag moistened with dilute ammonia (approximately 1 to 10) or a solution of baking soda may be used to neutralize the acid on the top of the battery.

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9. AIRCRAFT BATTERIES

Storage batteries are often subjected to extreme conditions. This is particularly true of the batteries used on airplanes, where they may be exposed to low temperatures when high rates of discharge are required. These batteries are subject to further limitations of space and weight. The batteries which have been designed for airplane service contain unusually thin plates and they are equipped with non-spill devices and other features which make them especially suited to military airplane service.

The performance of these thin-plate batteries cannot be predicted safely by extending the curves for the performance of other types, such, for example, as those used on automobiles. The capacity of the negative plates is often the limiting factor when the battery is discharging at high rates and at low temperatures. In an effort to meet the space and weight limitations for the batteries the amount of electrolyte has, in some cases, been too small. The amount required is fixed by Faraday's law (see Table XVI). There are uncommon limitations that fix the allowable upper limit as well as the lower limit of the specific gravity. If the specific gravity is too high the capacity of the negative plates will be much reduced at high rates of discharge. Too great a range in specific gravity from the charged to the discharged condition cannot be permitted, since this will also limit the capacity and may result in freezing. The concentration of the electrolyte is therefore something of a compromise and calls for more thought on the part of the manufacturer designing the battery than it sometimes receives. Results of tests on batteries are given in Table LVII, showing the effect of rate of discharge, temperature, and concentration of electrolyte.

TABLE LVII

RELATIVE CAPACITY OF AERONAUTICAL BATTERIES AT VARIOUS TEMPERATURES AND RATES OF DISCHARGE, AND FOR VARIOUS CONCENTRATIONS OF ELECTROLYTE

(The rates of discharge are based on capacity at normal temperatures and electrolyte of 1.300 specific gravity.)

Discharge Rate	Temperature		Relative Capacity (Per Cent)		
	° C.	° F.	1.300 sp. gr.	1.260 sp. gr.	1.235 sp. gr.
5-hour	27	80	100	90	81
5-min	27	80	38	34	31
5-hour	−7	20	74	69	63
5-min	−7	20	17	22	21
5-hour	−23	−9	46	40	33
5-min	−23	−9	9	12	12

The temperature coefficient of capacity has been determined for the positive and negative plates separately by Vinal and Snyder,[5] who

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[5] *Trans. Am. Electrochem. Soc.*, 53, p. 240, 1928.

have found that the coefficient of the negative plate is nearly twice that of the positive plate at a specific gravity of 1.315. This means that a normal performance of the battery at ordinary temperatures is no guarantee that the same performance will be found at low temperatures, even allowing for the diminished capacity in accordance with some curve such as Fig. 62. The capacity may be much less, depending on the behavior of the negative plates. At low temperatures the viscosity of the electrolyte is greater than at high temperatures. Apparently this has much to do with the performance of the battery. A definite relationship was found to exist between the increased viscosity and the decreased capacity of a battery at 0° C. (32° F.) as compared with its performance at 25° C. (77° F.) or 50° C. (122° F.).

Localized freezing of the electrolyte doubtless occurs sometimes without being observed, and it may be very destructive to the positive plates. As a battery discharges, the electrolyte becomes more dilute. This is particularly true at the positive, where, in addition to the removal of the sulphate radical, water is formed. The electrolyte in the pores of the positive plates is more dilute during discharge than the main body of the electrolyte and, therefore, will freeze at a higher temperature. High-rate discharges must be made at a temperature somewhat above the freezing point of the electrolyte as a whole, otherwise the electrolyte in the pores of the plates may freeze without the main body of electrolyte showing any signs of freezing. From the standpoint of the aviation battery this imposes an interesting limitation on the lower range of specific gravity which can be permitted.

The airplane batteries contain plates that are seldom thicker than $\frac{1}{16}$ inch. The life of such plates is less than for the plates of an automobile battery, but more than 100 cycles may reasonably be expected. Life of these batteries can well be sacrificed somewhat to make them as light as possible.

Because airplanes fly upside down and do other "stunts" for which there is need in military combat, great emphasis has been placed on making the batteries non-spillable. This is accomplished by the use of the so-called double chamber with stand-pipe vent-plug. Above the plates is a compartment (Fig. 163) into which the electrolyte can flow from the plates if the battery is inverted. The vent-plug is elongated and is vented at the lower tip which is so placed as to be always out of the electrolyte, whatever the position of the battery may be. This requires that the electrolyte shall be adjusted to the proper height when the battery is made ready for service. The use of the double chamber necessitates a considerable superstructure which adds to the weight of the battery and the space that it takes up in the plane. This offsets to some extent the increased capacity which is gained by the use of very thin plates.

Aircraft batteries in hard-rubber containers commonly consist of 6 cells of the double-chamber type, as shown in Fig. 163. There is a distinct tendency at the present time, however, to use higher voltages, and it is probable that 24-volt batteries will supersede many of the 12-volt installations. One reason for this is the reduced current for the same wattage and the consequent reduction in the weight of copper conductor which is required.

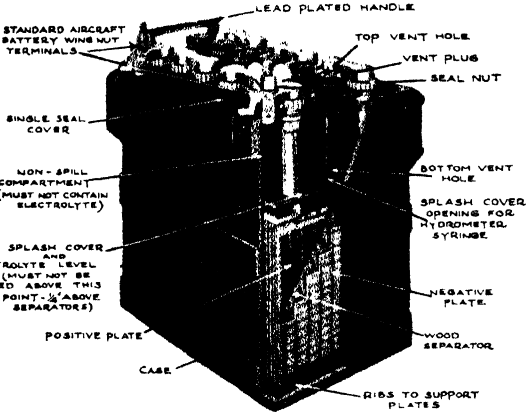

FIG. 163. Aircraft battery with double chamber.

The individual cells of the 12-volt batteries contain 7 to 25 plates, according to the service for which they are intended. Aircraft batteries supply current for engine cranking, radio, ignition, navigation instruments, landing gear, cabin lights, and power apparatus. The batteries do not carry the whole load, however, as they are usually floated on a bus supplied by a generator. The batteries weigh from 17 to 70 pounds. The weight of the 24-volt batteries is not greatly different from that of the 12-volt batteries of equivalent watt-hour capacity.

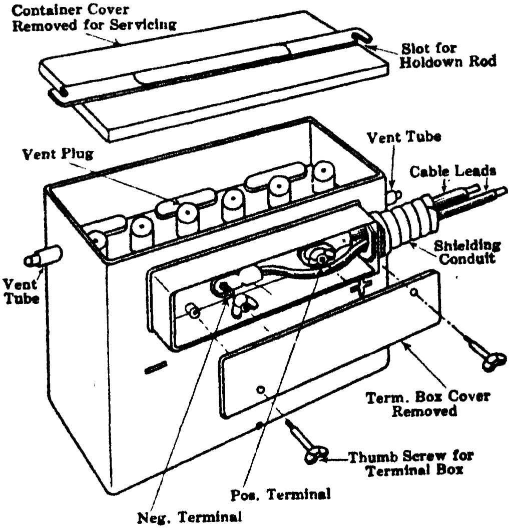

FIG. 164. Shielded aircraft battery.

To avoid radio interference, metallic shielding is finding increasing use. The containers for such batteries (Fig. 164) are made of sheet aluminum, protected on the outside by an acid-resisting lacquer and on the inside by a lining of soft rubber. The metal container extends considerably above the top of the cells and is closed by a cover of aluminum and fastened by hold-down bolts. The cable connections are in shielded conduit. These are brought to a covered terminal box on the side of the battery. All metallic shielding is electrically connected. Vents passing through the side of the box serve to equalize the pressure inside the container with that of the outside atmosphere.

Wiring of the plane consists of insulated copper conductors varying in size from No. 20 wire to No. 00 A.W.G., enclosed in a thin-wall rigid or flexible aluminum conduit, which with junction boxes and all fittings forms a complete metal-enclosed system.

Charging may be done either by manual control of the batteries when off the plane or by connecting them in parallel with direct-current generators on the plane. In the latter case the generator must have drooping characteristics to make the battery carry the excess loads, but the generator carries the normal load at other times and charges the battery. Voltage regulation is necessarily installed, because of both the battery and the lamp loads. Usually the bus is set for about 14.2 volts (6-cell battery), but this can be varied slightly to give the best conditions for any particular case. The performance of the battery is sometimes judged by the amount of water which it requires. If the amount exceeds that specified by the manufacturer, the indications are that the charging rate is too high and the bus voltage must be lowered accordingly. If batteries are located in different parts of the plane and connected to the same bus, the voltage at the terminals of each battery should be maintained at the same figure. This is not always easily done, unless precautions are taken, because of the *IR* drop in the line and the effect of numerous branch circuits. The method of charging the batteries on the plane is essentially constant-potential charging with some limitation of the maximum current that the batteries can receive. This method has been found satisfactory on all but the largest planes, some of which have 110-volt alternating-current lighting systems.

Electric starters for airplane engines are not used as universally as in the case of automobiles. A recent handbook [6] lists eight different methods of starting airplane engines. The first of these is swinging the propeller. Obviously this method applies only to low-powered

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[6] Swann's *Handbook of Aeronautics*, 2, p. 422, 1938.

engines. Starters on mobile trucks are used for this purpose to some extent in Europe. The second method involves a hand-turning gear built into the engine. A gas-air mixture provides the third method. This is fired by a hand magneto. Compressed-air starters, the fourth method, supply carburized vapor under sufficient pressure to turn the motor. The fifth method consists of firing cartridges which generate sufficient expanding gases to turn the engine. Electrical methods, which are of particular interest here, are in use in this country on some of the larger planes. The best-known is the inertia starter which stores energy in a rapidly rotating flywheel. Engagement between starter and engine is made by advancing a pinion to engage a gear on the engine. The flywheel can be energized by hand, but the more common method is by an electric motor, using power supplied by a battery. Another electrical method is direct cranking of the engine by a small motor which is connected through a high gear ratio. On very large ships an auxiliary engine coupled to the main engine is sometimes used. This is essentially an electrical method since the auxiliary engine is electrically started. The list of mechanical, gas and electric starters is reminiscent of starter systems for automobiles of thirty years ago, but the problem of starting airplane engines of great horsepower is vastly more difficult.

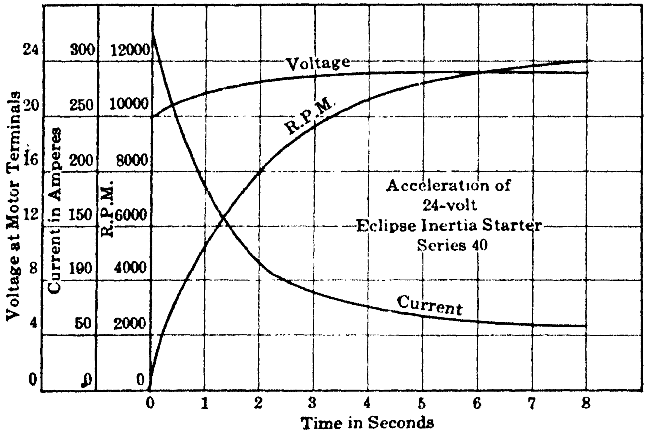

FIG. 165. Operating characteristics of an inertia starter.

An inertia starter of 24 volts requires about 8 seconds to reach top speed of 12,000 revolutions per minute. The current drawn from the battery is about 320 amperes at the breakaway, but this drops rapidly as the counter electromotive force of the motor rises, reaching a constant value of about 60 amperes. The voltage of the battery at this time is about 23 volts, depending on the current. Operating characteristics are shown in Fig. 165.

For proper maintenance the batteries should be seated evenly and held firmly in place, but they should be readily accessible for inspection. Connecting cables must be flexible and sufficiently long to prevent pull on the battery case. Considerable care in the addition of water should be taken to prevent flooding. The high level is usually stated to be at the splash cover in double-chamber cells, or $\frac{3}{8}$ inch above the top of the protective plate over the separators in other cells. Water should be added with due regard for freezing temperatures. Use helps to equalize the water with electrolyte and the current provides a slight heating effect, but on no account should a freshly watered battery be allowed to stand in freezing temperatures immediately after the addition of water.

Airplane batteries are rated for several time intervals corresponding to the various services that they perform. The ratings and cutoff voltages are usually those given in the Table LVIII below.

TABLE LVIII

TIME RATES AND CUTOFF VOLTAGES FOR AIRPLANE BATTERIES

Time Rate of Discharge	Cutoff Voltages
40 hours	1.80 volts per cell
5 hours	1.75 volts per cell
20 minutes	1.50 volts per cell
5 minutes	1.20 volts per cell

In addition a "safe rate" is specified in amperes for one minute. This exceeds the 5-minute rating. The purpose is to assure the safe current-carrying capacity of the intercell connectors and other parts of the cell.

The terminals of airplane batteries are of the wing-nut type fastened to the battery box in such a manner that vibrations from the external leads will be absorbed by the battery box and not transmitted to the terminal posts (Fig. 164). It is standard practice that both terminals shall be on the same side of the battery with the positive to the right when looking at the terminal side of the battery. The terminals have a standard thread of $\frac{5}{16}$ − 18 with a tolerance providing for a class 2 fit. The battery terminals are to be lead covered.

10. ISOLATED LIGHTING-PLANT BATTERIES

The lighting of houses and the operation of small motors and other appliances by electricity, in communities not served by central-station power, has been made possible by the development of the so-called isolated electric lighting plants. These miniature power plants possess the essential parts of the larger systems. First there must be a "prime mover" or engine of some sort. This is generally a gasoline or kerosene engine with an automatic speed regulator. The next unit is the generator, which is driven by the engine. It may appear as a separate unit connected to the engine by a belt, or it may be directly connected to the engine and appear to be a part of it. The third element of the system is the storage battery, which serves as a reservoir to supply electrical energy whenever it is needed. The battery receives its energy from the generator at intervals, but these miniature generators, unlike those of central stations, are in operation only part of the time. There is also a control panel, although it may be very simple, which provides the necessary switches to connect the generator, the battery, and the distribution system. Ordinarily an ammeter and a voltmeter are provided on this board, and perhaps a regulating resistance to control the charging current. Finally, there is the distribution system.

a. The Wiring

Low voltages have become standard for the isolated electric lighting system. This makes an economical battery possible. The customary discharge voltage is 32 volts, except in the largest plants, some of which are 110 volts. Since the lower voltage requires an increase in current to provide any specified amount of power, the problem of wiring is somewhat different from that presented by the 110-220-volt systems which are found in urban districts. Low-voltage lamps and appliances are required. Metal-filament lamps of both the vacuum and and the gas-filled types are obtainable at voltages of 28-32 volts. The voltage at the fixture is slightly lower than the maximum at the battery terminals. The various appliances are also rated for the same voltage. The wiring must be larger than for the higher voltage systems, in order to carry the current without undue voltage loss and without excessive heating. The current of the 32-volt system is 3.5 times as great as the current of a 110-volt system through a lamp or appliance of the same watt capacity. The voltage drop through a given wire is therefore 3.5 times as great, and the heating effect, which is proportional to the square of the current, is twelve times as great. The size of wire to be used will be governed by the maximum load and the distance between the power plant and the place of utilization. A diagram showing the required size of wire to meet any ordinary conditions has been published by the Engineering Department of the National Lamp Works.[7] The economical solution of the wiring problem requires that the lighting plant be centrally located with respect to the houses and barns and other buildings in which lights or appliances are to be placed.

Although the voltage is low, the insulation standards for 110-volt systems should be followed, because it is then possible to connect to a 110-volt power-distribution line that may be put through the locality in the future, without changing anything but the lamps or accessories. The reverse is not true, however, since the smaller wire of the 110-volt systems is not adequate for the low-voltage system.

b. The Battery

The battery usually consists of 16 cells of the lead-acid type, but Edison batteries have been used for this purpose. The former type has pasted plates about $5\frac{5}{8}$ inches wide by 5 inches high. When larger capacities are required, however, plates $7\frac{3}{4}$ by $7\frac{3}{4}$ inches are used. The number of plates in the small,cells ranges from 5 to 23. The approximate capacities for a few of these are given in Table LIX.

TABLE LIX

CAPACITY OF ISOLATED PLANT BATTERIES

Number of Plates per Cell	Capacity in Ampere-Hours	
	At 8 Hours	At 72 Hours
7	60	90
9	80	120
11	100	150
13	120	180
15	140	210
17	160	240

The positive plates are somewhat thicker than the plates of starting and lighting batteries. The separators are of wood and perforated rubber, the latter being placed between the positive plate and the wood separator. Cells of the Ironclad construction are used also.

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[7] *Bulletin* 34, p. 7, 1918.

Some means are usually provided to lock the element in place to prevent possible buckling of the plates.

Whenever possible, it is preferable to use the larger cells, particularly if heating devices and motors for power purposes are to be operated. For example, a motor of one horsepower requires 746 watts or 5968 watt-hours during a discharge period of 8 hours. This exceeds the capacity of all but the largest batteries in Table LIX. It is possible to minimize the load on the battery by running the charging apparatus during the periods when the power consumption is high. Current can be taken from the battery and generator together.

Lead batteries of this type are usually contained in glass jars through which the element is clearly visible, but when they are installed on yachts or required for portable service rubber jars are preferable.

c. Installation and Operation

The cells are usually furnished assembled, filled, and charged so that they are ready for immediate use after they have been unpacked and properly connected. If the crates are carefully opened, they may be used to make a suitable rack for mounting the cells permanently. Figure 166 shows 16 cells mounted on a rack constructed from the packing cases. If a jar has been cracked, the element, consisting of the plates and separators with cover attached, should be removed and placed in an upright position in a wooden pail or porcelain crock filled with pure water until a new jar and electrolyte can be obtained. Before the cells are connected, the ends of the soft-lead connecting straps should be scraped to insure good contact, and the cells should be placed on the racks so that the covers are at least $\frac{1}{4}$ inch apart; more space is desirable. The cells are then connected by the flexible lead straps. To avoid corrosion, the cell terminals should be wiped clean and dry, and a thin layer of vaseline smeared on each bolted contact. Poor contact can be detected after several hours, when the battery is in operation, by a rise in temperature at the defective connection.

d. Windmill-Battery Systems

A windmill is essentially a stream motor which extracts energy of the stream (atmosphere in motion) by retarding or diverting the flow of the stream. No stream motor can attain 100 per cent of theoretical efficiency. Usually the efficiency is less than 50 per cent. Windmill electric plants were suggested and tried many years ago, but standardized commercial types are a development of recent years.

Winds vary widely in direction and intensity. The wind stream provides a source of kinetic energy which must be intercepted, if mechanical power is to be developed from it. The average annual wind velocity for the entire country is about 10 miles per hour, but this varies with the elevation and the locality. Wind velocities increase with elevation above the surface of the earth.

The essential parts of a windmill-battery system include (1) the air wheel with its tower, turntable, vane, and governor; (2) a gear drive; (3) an electric generator of the proper voltage characteristics and an automatic switch to cut it into, or out of, the circuit, according as its voltage is above or below the battery voltage; (4) a storage battery to receive electrical energy when there is sufficient wind and to deliver energy when needed for lights or appliances. The battery stores the surplus energy of the wind and provides a reservoir for use at times of little wind.

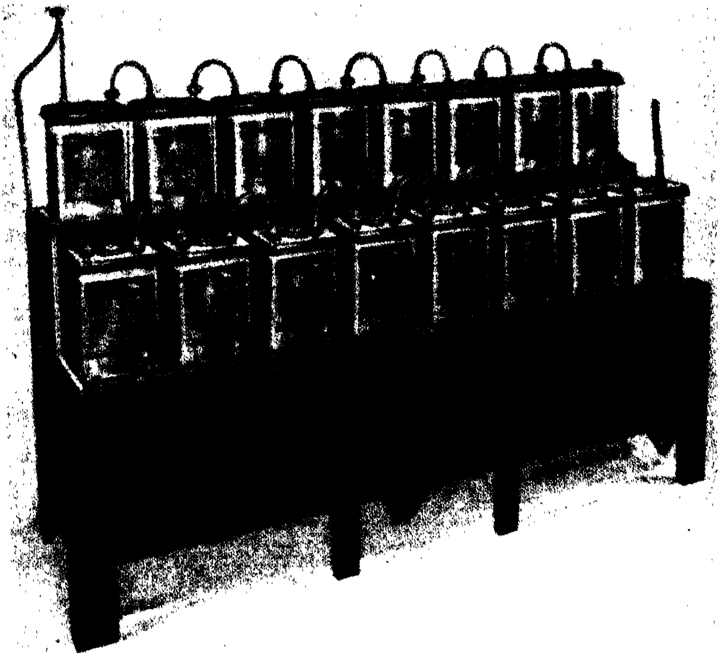

FIG. 166. Isolated lighting-plant battery. The rack for supporting the cells has been made from the crates in which the cells were shipped.

The storage batteries vary in capacity from 175 to 300 ampere-hours at the 8-hour rate. The size of the battery depends partly on the load and partly on the probable time that the generator will be unable to charge the battery. The cut-in switch operates at voltages corresponding to wind velocities of about 7 to 10 miles per hour. Sometimes an auxiliary engine is provided for use in prolonged periods of light winds. In such cases the size of the battery can be reduced.

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11. RADIO AND HIGH-VOLTAGE BATTERIES

The operation of direct-current electron tubes for radio receiving requires at least two batteries. One of these (the A battery) furnishes the current to heat the filament of the tube to incandescence and thereby cause it to emit electrons. The other battery (the B battery) is used to maintain the plate at a positive potential with respect to the filament, which causes the negatively charged electrons emitted by the hot filament to flow to the plate. Between the filament and the plate is interposed a grid whose fluctuating potential controls the flow of electrons and therefore the flow of electric current through the tube.

For receiving sets, A batteries (Fig. 167) supply 2 to 6 volts and a current ranging from a fraction of an ampere to several amperes, depending on the number and type of the tubes. Storage batteries are well adapted to this purpose, but their use for this purpose declined with the development of alternating-current radio receivers. Radio batteries are not intended to deliver large currents and can, therefore, be made with thick and durable plates, and with small terminals. They should contain electrolyte of relatively low specific gravity, such as 1.250, to decrease the local action taking place within the cells.

The A batteries are rated on the basis of a continuous discharge for 100 hours to a cutoff voltage of 1.75 volts per cell, the initial temperature being 80° F. For test purposes the current is determined by dividing the manufacturer's announced capacity by 100. The smaller B batteries are similarly rated at 200 hours. Any battery which fails to give its rated capacity on the third repeated cycle of charge and discharge is considered to be misrated.

High-Voltage Batteries. The B battery units of 12 or 24 cells are particularly well adapted to building up of high-potential batteries.

Such batteries find use in the laboratory, the broadcasting station and in other fields quite apart from radio. In case the cells of the B batteries are of too small capacity, small A batteries may be used. The capacity of the small B batteries is from 5000 to 6000 milliampere-hours. The smallest sizes of A batteries are 12 to 15 ampere-hours.

In the construction of any high-potential battery of storage cells provision must be made for (1) insulation, (2) ventilation, (3) periodic inspection and maintenance, (4) charging.

The cells are easily damaged by small leakage currents that would be entirely negligible for cells of larger size. Insulators of oil or paraffin for each unit of cells are generally necessary, but in planning the installation it is usually possible to arrange the cells so that the potential differences between adjacent cells are small.

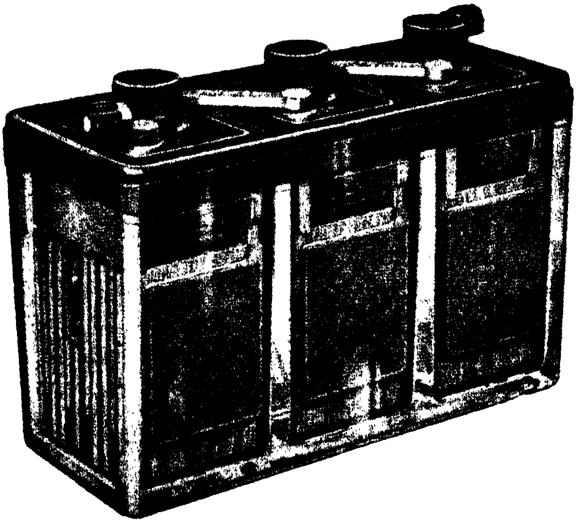

FIG. 167. Radio A battery, having sprayproof funnel vents and a built-in charge indicator.

If B batteries are used, each group of twelve or twenty-four cells should be treated as a unit. The group is insulated from the other similar units and should be so placed that it can be removed from the battery at any time that repairs may be required. The failure of a single cell can be easily detected and repairs made if the unit system is adhered to in making the original installation.

When the cells are to be charged, it is convenient to parallel the units. A charging circuit of 120 volts will provide for two units of 48 volts each in series and these are paralleled with similar groups of cells. Charging may be done at relatively low rates. This has the advantage of avoiding hard gassing, which would throw acid spray into the air and impair the insulation.

The specific gravity of the electrolyte should be low to avoid local action; 1.210 to 1.225 should be sufficient. Some high potential batteries have been constructed in the past from sheets of lead, being in reality Planté cells. The local action of such cells is likely to exceed that of the small pasted plates.

The successful operation of a high-voltage battery depends very largely on the maintenance. Frequent inspection, regular charging and the addition of distilled water as needed are essential.

Switches for parallel and series connections may be planned so that the closing of any one would be mechanically impossible if another inconsistent connection were already made. Protective fuses should also be installed and proper means taken to isolate the battery. Although the battery may be intended for potential purposes only, even the smallest sizes will have sufficient capacity to be dangerous if not properly handled.

12. APPLICATIONS TO PORTABLE ELECTRIC LAMPS FOR USE IN MINES

Safe and adequate illumination for miners has been the subject of experiment and development for more than a hundred years. The early safety lamps of Clanny (1811), and Stevenson (1815) and the better known invention of Sir Humphrey Davy (1816) contributed greatly to safety in gaseous mines. The success of Davy's safety lamp was immediate; within a year its use in Northern England became general. With modifications in structure and improvements in illuminants, the principle of the Davy lamp has continued to the present time. The first mention of portable electric lamps for use in mines appears to have been about 1901, but they were not used in considerable quantity until more than ten years later. In 1918, 48,000 electric lamps were reported to be in use in Pennsylvania.

Nearly all of the half million or more portable lamps now used underground in the American hemisphere are the cap-lamp type, but a small proportion of hand lamps are used for inspection and signaling. In Europe, however, hand lamps outnumber cap lamps.

The electric cap lamp was first developed to replace the flame safety lamps employed in gaseous mines. Open-flame carbide lamps continue to be used, however, in many non-gaseous mines. The early electric cap lamps could not compete from an illumination standpoint. This condition continued for some years, but great improvements have been made recently in the electric cap lamps and these are now finding use in many non-gaseous coal and metal mines.

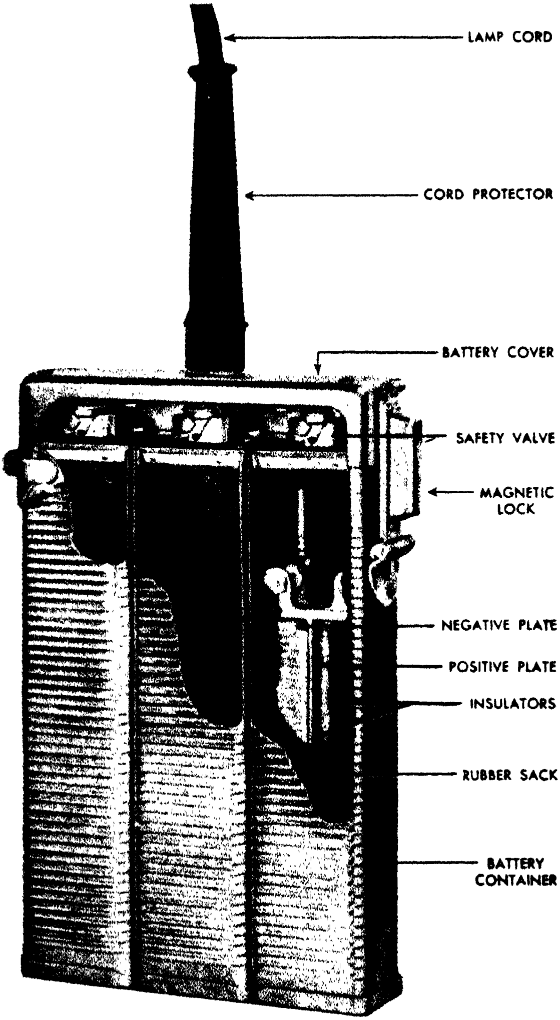

FIG. 168. Edison mine-lamp battery, usually worn on the miner's belt.

The effective illumination provided by cap lamps is many times greater than that available from the first electric cap lamp. This improvement has resulted from (1) increased battery capacity, (2) increased lamp efficiency, (3) improved headpieces, and (4) improved distribution of the light. A notable advance in efficiency of the lamp bulb, amounting to about 20 per cent, was made by substituting krypton gas for argon. Krypton has a lower heat conductivity than either argon or nitrogen, which are commonly used in incandescent lamps. Krypton is a very rare gas whose atomic weight is 83.7. Its use is limited at present to those small lamps for which the highest efficiency is desired. If Xenon, another inert gas, which is even more rare than krypton should become available, it is possible that a still greater gain in efficiency might be made. Its atomic weight is 131.3.

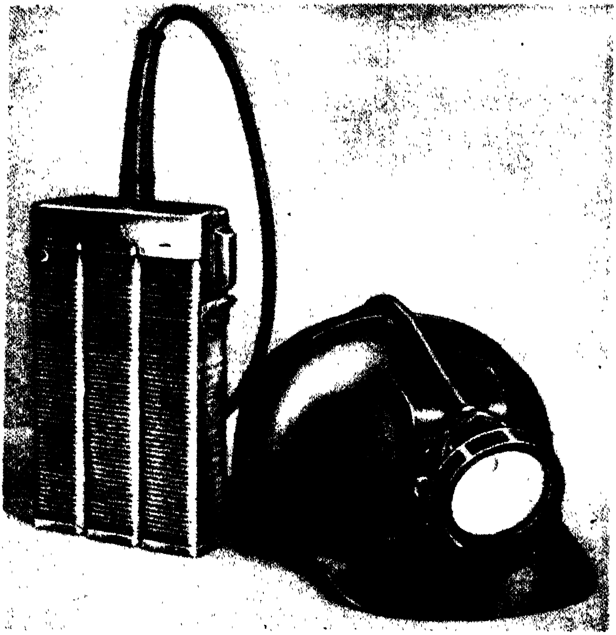

FIG. 169. Miner's cap lamp and battery. The lamp bulb is krypton filled. The battery is Edison nickel-iron-alkaline type, model P.

Service underground is considered the most severe for portable batteries. The battery may be in almost any position when used and it may suffer from mechanical shocks, abuse, and neglect. To prevent spillage of electrolyte, various special vent tubes, spring-actuated valves, absorbents, and jelly electrolytes have been employed. Jelly electrolytes are usually the sulphuric acid-sodium silicate type.

Tests to determine the suitability of these batteries and lamps for service in mines are specified by the Bureau of Mines. These tests cover the character of the light beam, the capacity of the battery, and safety features of lamp-mounting to avoid the possibility of igniting explosive gases, if the lamp bulb should be broken.

Many types and kinds of miner's lights have been used. Some of these employ alkaline storage batteries and others the lead-acid type. Only a few of them can be described here.

The first Edison electric cap lamp was brought out in 1914. The mechanical construction of the Edison battery together with its ability to withstand overcharge, or to remain in a discharged condition for an indefinite period of time without serious injury, makes it well adapted to this service. These batteries, although smaller than the industrial sizes, are made in the same manner and use the same sizes of tubes and pockets in the positive and negative plates, respectively. Figure 168 shows the construction of the battery, and Fig. 169 shows the complete unit, battery, cord, headpiece, and lamp of the latest Model P cap lamp. There are three cells, provided with automatic safety valves. The battery is in a nickel-plated steel container which is fastened by a magnetic lock to prevent unauthorized opening. The headpiece is molded bakelite. The lamp is equipped with a krypton gas-filled, parallel filament bulb.

Table LX shows the increase in capacity and weight efficiency of the Edison cap-lamp batteries from the beginning to the present time (1940).

TABLE LX

EDISON CAP-LAMP BATTERIES

Model	Date	Type of Cell	Number of Cells	Volts	Amperes	Amp-Hr. Capacity	Watt-Hr. Capacity	Weight in Ounces	Watt-Hr. per Ounce
C	1914	M8	2	2.50	0.37	5.5	13.8	44	0.312
E	1923	M14	2	2 40	1.10	15.0	36.0	68	0.530
H	1928	M14	2	2.40	1.20	15.0	36.0	68	0.530
J	1931	F2	2	2.40	1.00	13.0	31.2	48	0.650
K	1931	F3	3	3.70	1.00	13.0	48.1	71	0.677
P	1939	F2R	3	3.65	1.15	13.0	47.5	66	0.719

The Wheat mine lamp, Model GW, employs a battery of the lead-acid type. It is contained in a hard-rubber case and consists of two cells, giving 4 volts. The positive plates are of the Exide-Ironclad type of small size as shown in Fig. 5 of Chapter II. The individual pencils in these plates, however, have the same diameter as others used in motive-power batteries. The negative plates are of the flat-pasted type. Between the positive and negative is a relatively thick spongewood separator. A battery of this type is shown in Fig. 170. The lamp is equipped with a krypton gas-filled bulb at the center of the reflector. A second bulb is provided as a "stand-by" bulb which can provide sufficient illumination for working purposes. The nearly flat voltage characteristic of these cells on discharge is advantageous, as the lamps are quite sensitive to changes in voltage. Charging is accomplished through safety contacts on the headpiece. The charging current is conducted to the battery through the cord, and it is not necessary to open or disconnect any part of the equipment in order to charge the battery. As in the case of other electric cap lamps, the battery is worn on the belt of the miner.

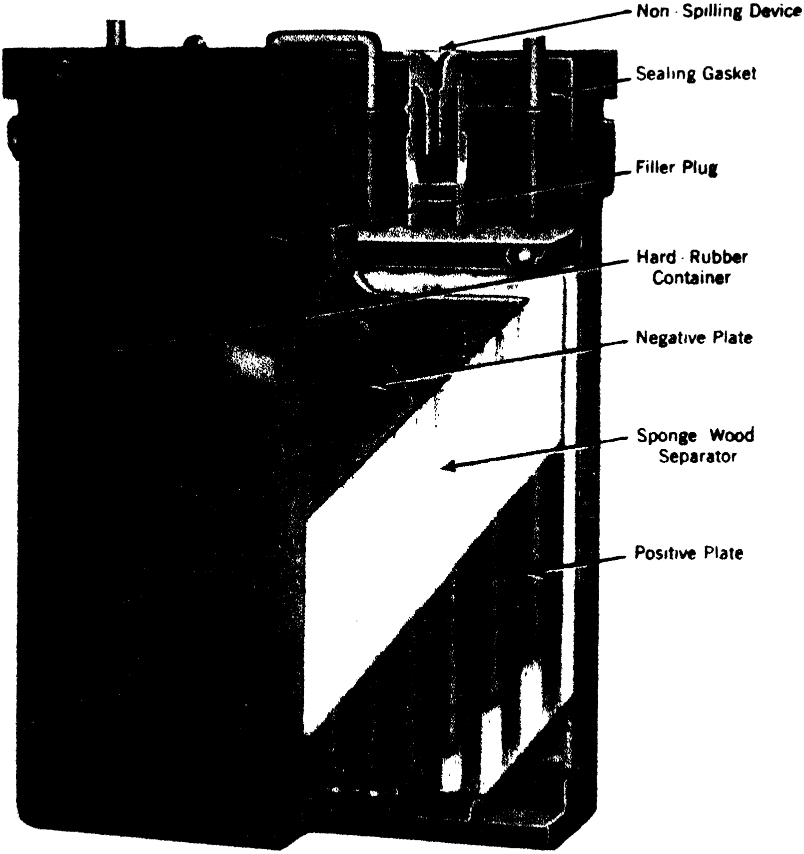

FIG. 170. Wheat mine-lamp battery of the lead-acid type.

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