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STORAGE BATTERIES



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STORAGE BATTERIES

THE CHEMISTRY AND PHYSICS OF THE
LEAD ACCUMULATOR

BY

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New York

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STORAGE BATTERIES

CHAPTER I

INTRODUCTORY AND HISTORICAL

1. Into our present age of power, where we reckon by thousands and tens of thousands of kilowatts, there has come down from a previous era one single form of the galvanic cell which retains sufficient commercial importance to be worth consideration in connection with modern power plants and modern power operation. This is the lead-sulphuric acid accumulator. It was invented and perfected in the heyday of galvanic cells—at a time before the dynamo and the electric motor had any technical importance. In our own laboratory, hidden away in the attic where cast-off things are stored, lie the remains of the big Bunsen cells which were once the source of our heaviest currents and with which the remarkable phenomena of current electricity were shown to classes and in public lectures in those days. These same cells were used to charge small storage cells of the original Planté type — mere strips

of lead, separated by soft rubber insulators and rolled into spiral form; then formed with the aid of the primary cells, by a series of reversals, until the plates attained a certain capacity. One of these cells is shown in Figure 1. With these storage cells, which have low resistance and high current-giving capacity even in comparison with the large Bunsen cells, the

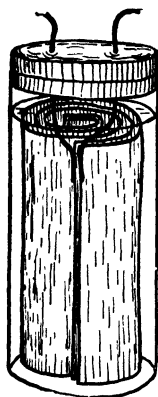


FIG. 1. — Original type of Planté accumulator. (About $\frac{1}{3}$ full size.)

most wonderful experiments could be performed — experiments which are to us now so commonplace and so much a part of our everyday life that their description brings a smile from the high-school boy who has studied physics and chemistry. These cells would run an arc light for several minutes; heat small platinum wires to the melting point; provide current for electromagnets of power enormous for that

time. It was the duty of the laboratory assistants to set up the battery of Bunsen cells. Huge zincs in dilute sulphuric acid and great blocks of carbon were arranged in glass jars with porous cups, and from this fuming source the storage cells were charged all day, to be used the day following in demonstrations of the power of the electric current. After the charge was finished the big Bunsens were taken apart and cleaned up, then stored away until

the time for the next lecture on electric currents approached.

These early Planté batteries were so arranged that they could be easily thrown into parallel connection, and in this way they could be charged from the Bunsen battery of a few large cells. We still use one of these batteries of 20 cells, dating from the early eighties or earlier. After charge was complete the simple mechanism permitted all the cells of the set to be connected in series by simply turning the handle through 90°, and clips were provided to show the melting of wires of various metals by the current.

The current which could be drawn from these small sets of storage cells reached its maximum at forty or fifty amperes—an enormous value then, a mere bagatelle now, for we have electrolytic cells and electric furnaces which require tens of thousands of amperes for their operation. Since then lead cells have grown in size along with everything else electrical, and I have seen large batteries which can furnish thirty or forty thousand amperes for a short time and ten thousand for several minutes of discharge.

2. No one of the very numerous **primary** cells which have been devised and patented has ever reached commercial importance for the heavier work of the present period, though a few have survived to

do the lighter tasks. The Leclanché and numerous similar types are used in large numbers for bell-ringing installations and similar open-circuit applications. And the dry cell has a very large and distinct place of its own in sparking batteries for motor cars and boats and everywhere that internal combustion engines are used. Certainly well over ten million of these little primary cells are made and used each year in the United States.

From the beginning of the nineteenth century until the early eighties was the era of the primary cell. Then came the dynamo and the motor, accompanied by improvements in our main prime source of power, — the steam engine, — and the storage cell has grown along with all of these in a somewhat subordinate place. It is a mere assistant, to be called on for temporary aid in time of need, either to help over an ugly peak in the load on the prime source, or as insurance to be called in when the main source is disabled for a short time, and its aid is often quite invaluable under these conditions. As a real factor in the problem of prime power sources it has of course no place at all.

There is not much value in prophecies about scientific or technical things and no particular credit is due the prophet who utters them. Nevertheless, I feel impelled to say that I believe the day of the primary cell will come again. From every funda-

mental and theoretic point of view we must admit that it **should** be possible to make a primary galvanic cell which should be more efficient than a steam engine can possibly be; more flexible as a primary source of power; a better appliance in every way.

3. At first glance a lead-sulphuric acid storage cell seems a very simple and uninteresting sort of machine. It is only a plate of lead and a plate covered with lead peroxide, dipping into rather concentrated sulphuric acid. But for those who make them and those who care for them in service they become much more complex and puzzling, and worth careful consideration. As an integral and essential part of many power arrangements they are of interest to the engineer and as a complex of puzzles and problems they demand attention from the electrochemist and the physicist. Many books have been written about them, some purely scientific and others nearly purely technical. As far as the fundamental chemical reaction is concerned we seem to be on pretty firm ground, and there is every reason to believe that we know how the cell works. But there is still plenty of room for speculation and research on the more minute physical changes and a good many questions on such important matters as formation, cementing of pastes, sulphation, and life under various conditions cannot even now be answered very clearly.

A very large number of combinations have been suggested for storage battery purposes since Planté began to study his cell in the late fifties, but until within the last few years no one of them has seemed able to meet the rather difficult and peculiar requirements. Now comes the Iron-Nickel Oxide-Alkali combination as applied by Edison in this country and Jungner on the continent of Europe, and this type seems destined to find a place of its own in light traction work. But by far the greater part of all storage battery plates now made are descendants of the original Planté type—hardly recognizable with their highly developed, ribbed, or corrugated surfaces, and formed in the factory by rapid methods, but still “Planté” plates. We have in active use in our own laboratory a unique battery which harks back to the earliest form. It has twenty thousand cells, made of test tubes, and the plates are merely corrugated strips of lead. It is used to give the small currents necessary for vacuum tube and spark work, and it was formed by the old method of reversals (see page 179) until it reached the needed capacity.

4. Faure was the inventor of the “paste” plate, and this seemed at first so great an improvement that prophets were not wanting to predict that the older type, with its greater weight, comparatively small capacity, and higher cost, would be completely

ousted by the new invention. These prophecies have not been fulfilled. The paste plate has been gradually relegated to traction work and to duty where weight is the important factor, and the plates which are direct descendants of the Planté originals do the really hard work. It took much experience and expense to reach the decision that the Faure plates could not compete in the more strenuous positions, but now we seem to appreciate fairly well the limitations of both types.

5. As the storage battery developed to a point where it could handle real power loads, there came a time when its powers were somewhat overestimated. It was suggested for many positions where it would have been quite unfit for the work—for farm purposes, for motor cycles, and even for airships. For long-continued discharge, where it must take the place of the prime source of power over considerable periods of time, the storage battery is often a cumbersome and expensive substitute for the source itself. But for many kinds of work, and especially where a very large amount of power is needed suddenly or for short periods, the battery is the ideal machine. In many modern plants the load fluctuations are very great—a thousand per cent or more, and this within a fraction of a minute. No mechanical arrangement can absorb this and regulate the load on the power source in a satisfactory way. But a storage battery

can, for there is hardly a limit to the rate at which large-surface Planté plates can be discharged or charged without injury.

In certain classes of work—in submarines, as a source of under-water power, for example—the battery is an absolute necessity. In the regulation of irregular loads it is of the utmost importance, and in emergency or “stand-by” work as well. Car and train lighting systems demand its use. It has proven itself economical and efficient in traction work, especially for electric road vehicles.

Study of the storage battery calls for attention to two rather distinct viewpoints—one chemical, the other physical; and these will be found of nearly equal importance. The questions about the fundamental reactions, and many others as well, are purely chemical. Questions about the life of the cell, and its behavior in service, are nearly purely physical. In manufacture or operation the chemical side must be kept in mind, but the anatomy and physiology (and sometimes the pathology, too) of the individual plate are matters of prime importance. Underlying all, we will need as a foundation for study the fundamental ideas and laws of general electrochemistry.

The following chapters are based on lectures which have been given for the last few years at Harvard University. In the course the work on storage cells is preceded by study of the general theory of gal-

vanic cells, and the simplest of this theory has been included in this book. No attempt has been made to give any of the detail of storage battery engineering, but only to introduce the reader to the peculiarities of the cell itself.

CHAPTER II

SOME ELECTROCHEMICAL FUNDAMENTALS

6. Theoretically any chemical reaction whatever which takes place of its own accord can be so coupled and arranged that it will work as the source of energy for a galvanic cell. Practically there are difficulties which exclude a large percentage of the known reactions of chemistry from such service. It is also true that a great many of the combinations which have practical value as primary cells can be considered theoretically reversible enough to be used as storage cells. As a matter of fact, only a very few of the cells which have been used or thought of are chemically and mechanically reversible enough to fit them for actual use as storage cells. In some cases the fault is in the reaction itself, and the cell is not chemically reversible. In others, the reaction reverses smoothly enough, but the materials of the cell do not go into and out of solution well. Here the fault is a mechanical one. As far as the general theory is concerned, we must choose fundamentals which fit all the cases, even those which cannot be realized practically.

7. Faraday's Law. — We have one general fundamental electrochemical law, which apparently fits every case, and which brings order of the simplest kind out of what at first appeared to be a most chaotic mass of unrelated material. This is Faraday's law, and it states the relation between the quantity of material used up in a galvanic cell and the quantity of electricity which can be obtained from it.

This law says : —

The amount of each substance which takes part in an electrochemical reaction is proportional to the quantity of electricity which passes through the circuit.

And when various substances enter an electrochemical reaction, their amounts are proportional to their chemical equivalent weights.

Numerically, and in terms of a unit later to be defined : —

96,540 coulombs pass through the cell and the external circuit with each gram-equivalent of each substance involved in the reaction.

8. Faraday's Definitions. — This law applies to **electrolytes**. Faraday himself felt the necessity of a careful set of definitions for the new ideas involved in this law and its application, and no one has since given better ones, so we shall use them wherever it is possible to do so.

To quote Faraday ("Experimental Researches," Series VII, 1834): —

“ . . . In place of the term pole, I propose using that of **Electrode**, and I mean thereby that substance, or rather surface, whether of air, water, metal, or any other body, which bounds the extent of the decomposing matter in the direction of the electric current. . . . The **anode** is therefore that surface at which the electric current, according to our present expression, enters. It . . . is where oxygen, chlorine, acids, etc., are evolved; and is against or opposite the positive electrode. The **cathode** is that surface at which the current leaves the decomposing body, and is its positive extremity; the combustible bodies, metals, alkalies, and bases, are evolved there, and it is in contact with the negative electrode.

“ . . . Many bodies are decomposed directly by the electric current, their elements being set free; these I propose to call **electrolytes**. . . .

“ Finally, I require a term to express those bodies which can pass to the electrodes. . . . I propose to distinguish such bodies by calling those **anions** which go to the anode of the decomposing body, and those passing to the cathode, **cations**, and when I have occasion to speak of them together, I shall call them **ions**. Thus, the chloride of lead is an **electrolyte**, and when **electrolyzed** evolves the two **ions**, chlorine and lead, the former an **anion**, and the latter a **cation**. . . .”

Figure 2 shows the different parts of a cell as Faraday defined them.

These definitions of Faraday's were made with the greatest care, but since they were formulated, rather careless use has sometimes been made of them. Note the term **anode**. It is the **surface** where the current enters the cell, and Faraday meant just exactly this whenever he used the word. The plates of a cell are not anode or cathode in this sense, but the surface between plate and cell solution is. There will often be occasion to retain this strict meaning of the word.

Again, an electrolyte is the body which carries the current and which

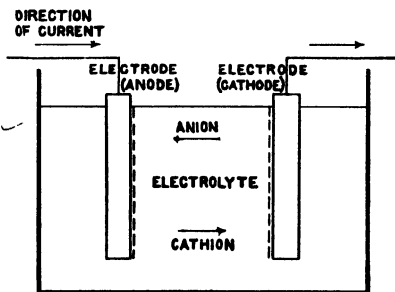


FIG. 2. — The parts of an electrolytic cell.

is at the same time decomposed by it. In this sense a dry salt is not an electrolyte, but a solution of a metallic salt, or a molten salt, belongs in this class.

9. Electrical Units. — Before we can apply this law of Faraday's we should review a few more electrical definitions. In what is called the practical system, we use as unit of quantity of electricity one **coulomb**. This is derived from the unit of current, the **ampere**, and one coulomb is the quantity of electricity which passes through a circuit altogether, when a current of one ampere has been flowing constantly for one

second. These units have been fixed with reference to the magnetic effect of a current and not specially with reference to Faraday's law. It is, however, an easy calculation to state them in terms of units which bear directly on electrochemical effects. Suppose we have in the circuit an amperemeter which measures the current in amperes. We keep the current constant and note the entire time during which it flows through an electrolytic cell in which silver is being deposited from silver nitrate solution. We will find that one ampere flowing for one second deposits 0.00111775 gm. of silver. The equivalent weight of silver is in this case the same number of grams as its atomic weight, and has the value

$$107.88 \text{ gm.}$$

The number of coulombs required to deposit this weight of silver is then

$$\frac{107.88}{0.0011175} = 96,540 \text{ coulombs.}$$

This same number of coulombs will deposit the equivalent weight of any other metal which can be electroplated in the same way, and it is the electrochemist's unit of quantity of electricity.

If the silver were to be used in a galvanic cell as a source of power, exactly the same relation holds between the weight of silver and the quantity of electricity—107.88 gm. of silver always travels

through an electrolyte and dissolves or precipitates at the electrode in company with 96,540 coulombs.

Silver ion is univalent, and the equivalent weight is the same as the atomic weight. In most of its reactions, chemical and electrochemical, copper forms a bivalent ion. This means that in company

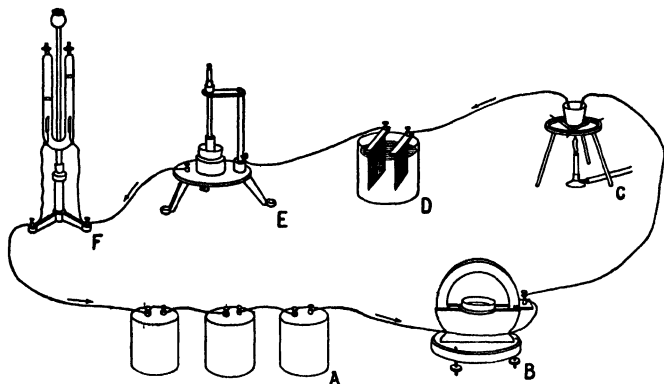


FIG. 3.—Diagram of apparatus to show Faraday's law.

with the atomic weight of copper (63.6 gm.) twice 96,540 coulombs pass through the circuit; so the equivalent weight of copper is 31.8 gm., and this is the electrochemist's **unit weight of copper**.

10. Experimental Arrangement for Faraday's Law. — Figure 3 gives diagrammatic representation of an experiment to illustrate Faraday's law. Current is supplied by the battery *A* and passes first through the tangent galvanometer *B*, which measures it, and then on through the various cells in which electro-

chemical reactions take place. In *C*, a molten salt, silver chloride, for example, is decomposed. *D* might represent a copper coulometer, in which copper is dissolved at one electrode and precipitated at the other. The same arrangement might be used for many other metals. *E* is one form of silver coulometer, and here the current enters at a silver anode, which goes into solution, and leaves the cell at the surface of a platinum crucible (cathode) on which silver is deposited. The electrolyte is a strong solution of silver nitrate. Last in the row is a gas coulometer *F*, containing dilute acid or alkali as electrolyte and having platinum electrodes. Oxygen gas is formed at the anode, the electrode where the current enters the apparatus, and hydrogen gas is evolved at the other electrode.

Suppose we have sent a constant current of one ampere through the circuit for 96,540 sec. We have weighed the electrodes before and after the passage of this current, and we have measured the volumes of the two gases produced. We should find: —

1. At *C*, 107.88 gm. of silver dissolved from the wire at which the current enters the cell and the same weight of silver deposited on the other wire. The electrolyte remains unchanged.

2. At *D*, 31.8 gm. of copper dissolved at one plate and precipitated at the other. No change in the electrolyte.

3. At *E*, the same amounts of silver dissolved and precipitated as in *C*.

4. At *F*, 8 gm. of oxygen formed, or 5.6 l. if measured at 0° C. and 760 mm. pressure, and at the other electrode, 1 gm. of hydrogen, having a volume of 11.2 l.

5. Inside the cells at *A*, there will have been exactly equivalent effects, and they will be the same in each cell. Whatever the materials of the anode and cathode, equivalent weights of each will have entered into reaction, for as far as the application of Faraday's law is concerned, it makes no difference whether work is performed as the result of a reaction, or must be performed from without in order to make the reaction take place. The law describes every electrochemical reaction, and has been shown to be as exact as any law we have.

11. Practical Application. — Let us examine some applications of this law. A great deal of copper is purified in this country by an electrolytic process. It is interesting to calculate the quantity of electricity needed to deposit a pound of copper in this way.

$$1 \text{ lb.} = 453 \text{ gm.}$$

$$96,540 \text{ coulombs deposit } 31.8 \text{ gm.}$$

We therefore need

$$\frac{453}{31.8} \times 96,540 = 1,376,000 \text{ coulombs per pound.}$$

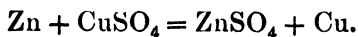
Since an ampere is 1 coulomb per second, it will require

$$\frac{1,376,000}{3600} = 382 \text{ ampere-hours}$$

to deposit a pound of copper in a single cell. 382 amperes deposit 1 lb. of copper per hour in a single cell, and if we wish to obtain a ton of copper per hour in such a cell, it would take a current of nearly 760,000 amperes to give the desired result. As a matter of fact cells of this size are never used. It is better to arrange a number of cells in series, so that the current flows through one after the other and produces the same effect in each. The yield of copper is then to be found by multiplying the yield per cell by the number of cells.

The atomic weight of lead is about 207, and it is formed from a bivalent ion, so the equivalent weight of lead is 103.5. Rather more than three times as much lead as copper is deposited by the same quantity of electricity. The calculation is $\frac{453}{103.5} \times 96,540 = 422,000$ coulombs per pound of lead.

12. Electrolysis in the Daniell Cell. — In the Daniell type of primary cell the chemical reaction is a very simple one: Copper is deposited as metal from copper sulphate solution; zinc (metal) passes into solution as zinc sulphate.



The reaction is indicated in the diagram of Figure 4.

How many ampere-hours can we get from a Daniell cell per pound of zinc?

The atomic weight of zinc is 65.4, and it acts as a bivalent ion, so we will get 96,540 coulombs from

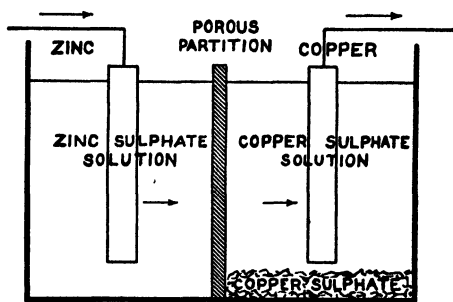


FIG. 4. — Diagram of the reaction in a Daniell cell.

$$\frac{65.4}{2} = 32.7 \text{ gm. of the metal. A pound is 453 gm.}$$

Per pound of zinc we can therefore obtain

$$\frac{453}{32.7} \times 96,540 = 1,337,000 \text{ coulombs,}$$

and since an ampere-hour is 3600 coulombs, one pound of zinc will give 372 ampere-hours.

We can get this same number of ampere-hours per pound of zinc in any galvanic arrangement whatever, and it requires the same number to deposit a pound of zinc electrolytically from its solution.

How much copper sulphate must we supply during this time to keep the copper side of the Daniell cell active ?

Its formula is $\text{CuSO}_4 + 5 \text{H}_2\text{O}$, and the total weight equivalent to 65.4 gm. of zinc is therefore 249 gm. Copper ion passes through a bivalent step in its deposition as metallic copper, so it requires $\frac{249}{2} = 124.5$ gm. of "blue vitriol" to give 96,540 coulombs. To furnish 1,337,000 coulombs we must use

$$\frac{1,337,000}{96,540} \times 124.5 = 1725 \text{ gm., or } 3.8 \text{ lb.}$$

Since all our electrochemical reactions are really only chemical ones arranged in such a way that they furnish or require a current of electricity, we could calculate the amount of copper sulphate needed for our run with the Daniell cell directly from the preceding figure for the deposition of metallic copper in the purification process.

$$\text{A pound of blue vitriol contains } \frac{63.6}{249} = 0.255 \text{ lb.}$$

of copper, and we found that it required 382 ampere-hours to deposit a pound of copper. The same quantity of electricity will pass through the Daniell cell with a pound of copper, and to get 1,337,000 coulombs from the cell we must deposit

$$\frac{1,337,000}{382 \times 3600} = 0.972 \text{ lb. of copper.}$$

This amount of copper is contained in 3.8 lb. of blue vitriol.

13. Electrochemical Units.—It is evident that the 96,540 coulomb unit which the electrochemist is obliged to use is a rather cumbersome one and leads to large numbers. If we had the choosing of our own unit we would of course make 96,540 coulombs = 1 electrochemical unit of quantity of electricity, and then the calculation for copper would look like this:—

$$\begin{aligned} 63.6 \text{ g. Cu} &\sim 2 \text{ units,} \\ 1 \text{ lb. copper} &\sim 14.24 \text{ units,} \end{aligned}$$

and for zinc it would be equally simple. But electrochemistry is not a big enough branch of science to be able to dictate units to the dynamos which furnish the current, and we must be content to accept the electrical engineer's unit.

In every case it is necessary to know the complete and exact chemical reaction with which we are dealing before we can apply our law, for it very often happens that metals carry different multiples of the unit quantity of electricity with them in different chemical reactions, and they sometimes complicate things still further by changing the number of units carried as the concentration of the solution from which they are deposited is changed. But if we arrange to have the conditions in the cell constant

and have once found the correct chemical reaction, the law can always be applied without fear of error.

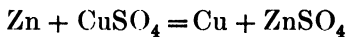
14. Electromotive Force. — Faraday's law gives a complete statement of the quantity of electricity which accompanies the reaction of gram-equivalent weights of various substances in any galvanic combination or electrolytic cell. But it can tell us no more than this. It says nothing about the amount of work we can do with this amount of electricity, nor about the amount of work we must do to cause the separation of a gram-equivalent of a metal from solution. The driving force of the chemical reaction and the corresponding electromotive force of the cell are specific for each reaction and cannot be calculated by any inclusive general law. The driving force is called the **chemical potential** of the reaction, and it can be very conveniently and accurately measured by coupling the reaction into the form of a galvanic cell and measuring the **electromotive force**.

Very early in the development of galvanic electricity Volta found that the various metals could be arranged in a series, such that the most favorable combinations for producing current were to be made by choosing metals as far apart as possible in the series. Better results were obtained from cells using zinc and copper than from those using iron and copper, or zinc and tin. We know now that not only the metal, but the whole reaction must be taken into ac-

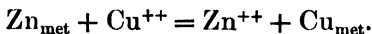
count, but the "Voltaic series of the metals," as it is called, gives an approximate view of the matter.

It was found very early that more work could be obtained from a pound of zinc in a cell where copper is deposited at the cathode, than from a cell where iron is used in the same way. The same quantity of zinc is used up in each case, and since we get different results in the various combinations, there must be some other factor of importance and some other law besides Faraday's to be considered.

Suppose we have a very large Daniell cell, where the reaction



is taking place. We choose a big cell in order that we may send 96,540 coulombs through it without any danger of changing the concentrations in the different parts of the cell. When this quantity of electricity has passed through the cell, 32.7 gm. of zinc have gone into solution at the anode and have become zinc ion. During this same time 31.8 gm. of copper ion have changed into metallic copper. The SO_4 part of the reaction has not been affected at all. Electrochemically we could write the reaction



15. Ions. — The small sign + indicates that the substance carrying them is an ion and that it moves toward the cathode—it is a **cation**. Two of them

indicate that this particular ion carries with it per gram-atom twice the unit quantity of electricity ($2 \times 96,540$ coulombs). The SO_4 ion (SO_4^{--}), which remains unchanged in this particular case, carries two times the unit quantity also, but toward the anode. It is an **anion**. And in chemical parlance both of these are **divalent ions**.

Now suppose we connect the cell with an external source of current and send 96,540 coulombs through it in the opposite direction. 32.7 gm. of zinc will deposit on the zinc plate,—now the cathode,—and 31.8 gm. of copper will go into solution at the copper plate,—now the anode. By the time we have sent our unit quantity through the cell it has been completely restored to its original condition. The case of the Daniell cell is theoretical rather than practical, for zinc does not behave very well when it is forced out of solution. It grows in sponge and trees and often reaches across to the other plate and short-circuits the cell. But we have chosen our cell so large that this does not bother us, and the Daniell cell can be considered completely reversible in its reactions. It might therefore be used as an accumulator.

16. Other Electrical Units.—Besides the coulomb, we have been supplied with two other units, and these fortunately fit electrochemical needs pretty well without requiring so many figures. One of these is the

volt, the unit of difference of potential, and the other is the **ohm**, the unit of **resistance**.

The following terms and relations are important:—

Coulomb	(<i>q</i>)	Quantity of electricity.
Ampere	(<i>i</i>)	Current.
Volt	(<i>e</i>)	Difference of potential.
Joule	(<i>j</i>)	Energy.

$$1 \text{ volt-coulomb} = 1 \text{ joule.}$$

$$\text{watt} = \text{rate of furnishing energy.}$$

$$1 \text{ volt-ampere} = 1 \text{ watt.}$$

$$1 \text{ joule per second} = 1 \text{ watt.}$$

$$3600 \text{ coulombs} = 1 \text{ ampere-hour.}$$

$$1000 \text{ watts} = 1 \text{ kilowatt, KW.}$$

$$746 \text{ watts} = 1 \text{ horse power, H.P.}$$

$$746 \times 3600 \text{ joules} = 1 \text{ horse-power hour, H.P.H.}$$

Beside our units we can also get instruments for measuring them from the electromagnetic branch of electrical science. If we borrow a voltmeter from our neighbor, the electrical engineer, and apply its terminals to our Daniell cell, we measure what is called its electromotive force in volts. The voltmeter reads about 1.1 volts.

17. Electrical Energy. — We can now calculate the electrical energy obtainable from this cell. By expending 32.7 gm. of zinc and 31.8 gm. of copper ion we can expect to get $1.1 \times 96,540$ volt-coulombs (joules) with which to do useful work outside the

cell. If we are sending current through the cell in the opposite direction, we can reverse the reaction and return the cell to its original condition by an expenditure of the same amount of work.

We can now calculate both work and power. How many horse-power hours can be obtained from a Daniell cell per pound of zinc?

32.7 gm. of zinc give

$$1.1 \times 96,540 = 106,300 \text{ joules.}$$

1 H.P.H. is

$$746 \times 3600 = 2,683,000 \text{ joules.}$$

1 lb. of zinc will give

$$\frac{453}{32.7} \times 106,300 = 1,472,000 \text{ joules.}$$

1 lb. of zinc will therefore give

$$\frac{1,472,000}{2,683,000} = 0.55 \text{ H.P.H.}$$

Or, we must use a little less than 2 lb. of zinc per horse-power hour.

Other forms of zinc-consuming cells were formerly much in use, and some of these had electromotive forces as high as 2 volts. One of these would require only

$$\frac{1.1}{2} \text{ lb. of zinc to produce } 0.55 \text{ H.P.H.,}$$

and we would need only 1.07 lb. of zinc per horse-power hour in the case of one of these cells.

Resistance. — The unit of resistance has an interesting and simple relation to the units of current and voltage. What is called Ohm's law states

$$\text{current in amperes} = \frac{\text{electromotive force in volts}}{\text{resistance in ohms}}.$$

Or, an electromotive force of 1 volt will send a current of 1 ampere through a circuit having a resistance of 1 ohm.

A column of mercury 106.3 cm. long and one square millimeter in cross-section has a resistance of 1 ohm. A good-sized copper wire has a resistance of an ohm for a length of a thousand feet or so.

18. If it is desired to furnish 0.5 H.P. from a single Daniell cell, at what rate must zinc dissolve?

0.5 H.P. is 373 watts (volt-amperes) (volt-coulombs per second). Our cell gives 1.1 volts and must therefore give a current of 349 amperes (349 coulombs per second).

32.7 gm. of zinc furnish 96,540 coulombs.

We must therefore furnish $\frac{349}{96,540} \times 32.7$ gm. of zinc per second; 0.118 gm. of zinc per second or 425 gm. per hour will give 0.5 H.P.

If we set up a whole row of Daniell cells as a battery, and draw our 0.5 H.P. from this, we will be much nearer the practical truth, for it would take an enormous cell to give 350 amperes, owing to the

rather high internal resistance caused by the porous cup.

19. Cells in Series and Parallel. — Suppose we have 100 cells in our battery, each with an electromotive

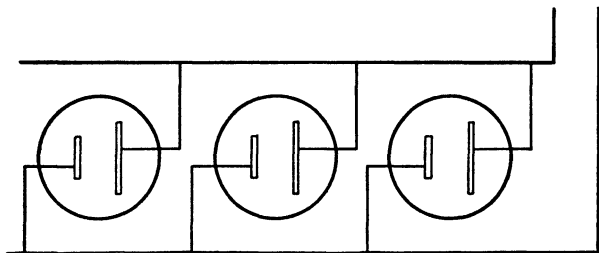


FIG. 5. — Cells connected in parallel. The effect is the same as though all the plates were placed in one large cell.

force of 1.1 volts. If they are connected so that the zinc of each cell is fastened to the copper of the next

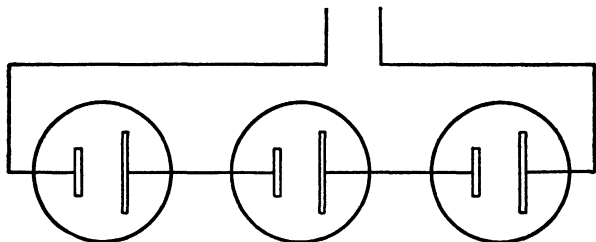


FIG. 6. — Cells connected in series.

one as shown in Figure 6, their electromotive forces will add, and our whole battery will have an electromotive force of 110 volts. To get 373 watts or 0.5 H.P. we need to draw only $\frac{373}{110} = 3.4$ amperes from

our battery, and this would not be an unreasonable current for large Daniell cells. You will notice that the total weight of zinc dissolved and copper deposited is exactly the same as though it had taken place in one huge cell, though now it is distributed over 100 cells.

In our very first problem, on page 17, where we calculated the current required to deposit a ton of copper per hour by electrolysis, we obtained a value for a single huge cell. Practically copper would never be purified in that way, for the voltage necessary to deposit copper is not more than 0.3 volt, and it is not feasible to build a generator to work at that voltage. Besides, it is not necessary, as it is just as well to work a number of electrolytic cells in series like a battery. In many copper refineries 200 such cells are used and a current of perhaps 4000 amperes is sent through the whole series. This requires a generator capable of giving this number of amperes at about 60 volts, and the power required is therefore 240 KW. The copper deposited has the same weight as though 800,000 amperes were sent through a single cell, and is therefore a little over a ton per hour.

CHAPTER III

ABOUT IONS

20. All electrochemical processes follow Faraday's law absolutely as far as any one can find out, and they therefore invariably depend on **ions** in the simple sense in which Faraday himself used this term (page 12). There is, nowadays, a whole field of science which has to do with the study of the ions of gases, and some of the most interesting and suggestive of all modern developments are being made in this field. These hypotheses and theories, now just being cleared of their mysteries and made a part of general science, will no doubt some day become a safe and useful basis for the study of electrochemistry. But for the present, at least, we will be safer if we stick close to Faraday, and call our ions ". . . those bodies which can pass to the electrodes." We shall meet with rather strange ones when we come to the lead storage cell itself, and some general knowledge of the simpler sorts will be found a useful introduction.

21. Conductance by Ions. — In the first place, the ions are **already there** in a solution of a metallic salt

or in a molten electrolyte. They are not produced by the action of the current. And they are able to begin carrying electricity toward the electrodes as soon as the circuit is closed. It is also certain that they do all the work of carrying the current through the cell. These last two statements are merely another way of stating the extreme accuracy of Faraday's law. No current seems to pass through an electrolyte unaccompanied by the movement of an exactly equivalent amount of each of two ions—an anion and a cation.

Water itself is a conductor of the electrolytic kind. It has a high resistance, to be sure, but it does contain small concentration of the ions H^+ and OH^- . It is chiefly remarkable for the aid it gives to other substances in the process of ionization. Metallic salts, and acids and bases as well, are famous carriers of current when they are in solution in water, and they always follow Faraday's law. Many of them are also good conductors in the molten state, and their ions pass to the electrodes under these circumstances just as well as they do in water.

22. Chemical Facts connected with Ions. — Since Faraday offered his suggestion about the names to be used in describing the process of electrolysis, and gave to the ions their simple definition, much of chemistry has been restated. The general facts about solutions, and especially those which have to

do with ions, even apart from their power of carrying a current, have been brought together into one of the most united and easy branches of the science of chemistry. Let us consider a few of the simpler generalizations. All acids in water solution contain hydrogen ion, H^+ , and their acid properties are dependent on its presence and are measured by its concentration. All bases in solution contain OH^- (**hydroxyl** ion). Solutions of metallic salts usually contain an ion produced from the metal, like Cu^{++} , Zn^{++} , Ag^+ , K^+ , Al^{+++} , Pb^{++} , and an ion formed from the other part of the salt — Cl^- , Br^- , NO_3^- , ClO_4^- , SO_4^{--} , CrO_4^{--} . We quickly get into the habit of thinking about the particular ion we want for any special set of properties it may have, and I have often heard a student just beginning chemistry — one who had not the slightest idea of Faraday's law or of any electrochemical theory — say to his neighbor, "Pass the copper bottle," when he meant copper sulphate or nitrate or any other soluble copper salt. He needed copper ion for his experiment, and in the same way a more advanced student will ask, "Have you some acid?" when he wants hydrogen ion. In neither of these cases does the other ion, which is sure to be present, interest the chemist, provided it has not some special peculiarity of its own. But if the other ion can form a difficultly soluble salt with one of those in his test tube, he will be more ex-

plicit in stating the kind of copper salt solution or the kind of acid solution he needs. If you will think over your own experiences with solutions of acids, bases, and metallic salts, you will see that the chemistry of aqueous solutions can all be brought into the easiest form by a classification of the properties of ions. Besides this, one only needs knowledge of the solubilities of salts to have a pretty full command of the facts about aqueous solutions.

This same statement is almost equally true of electrochemistry. A current only passes through a solution when two ions carry it. These ions pass back and forth at the electrodes and send their quota of electricity out through the wires of the circuit as a current. Each ion travels through the electrolyte with its own special velocity and carries a fraction of all the current flowing which is proportional to this velocity. If we had space for a really complete theory of galvanic cells, we would need careful study of the changes which take place at various parts of such a cell as the result of differences in ionic migration velocity. We should at the same time find some very simple and interesting generalizations about the part played by the individual ions in electrolytic conductivity.

23. The Ionic Theory. — In some of our explanations we shall feel the need of a much more minute and detailed picture of what happens than can be ob-

tained by adhering closely to Faraday's careful definition of an ion. We shall need to bring in occasionally a more hypothetical, or rather theoretical, ion than Faraday's. This does no harm, for more and more proof of the general usefulness and truth of the general theory of ions is being accumulated every day. The step from Faraday to the theoretical picture is not a great one.

Ions are, in this picture, parts of molecules, each one connected with a definite and constant quantity of electricity, either positive or negative. If we collect enough of these little carriers to make a gram-equivalent, and send them along to discharge against an electrode, 96,540 coulombs will pass this surface and flow out through the wires of the external circuit. At the same time enough of the ions of opposite sign to carry the same quantity of electricity will have been discharged at the other electrode. Faraday's ion was singular, and we shall refer to an ion as *it* when we need no further statement than that involved in Faraday's law. When we want to describe the more complicated changes about the electrodes, we shall make use of the other picture and refer to **the ions** of copper or silver, using the plural and picturing an electrolyte filled with them, each carrying its unit quantity of electricity, and all swarming toward the electrodes when current passes.

The electrolyte which is used in a storage cell is

a rather concentrated solution of sulphuric acid in water. It contains considerable concentrations of the ions H^+ and SO_4^{--} , and these do the carrying of the current across the space between the electrodes. During the passage of current in either direction, H^+ , the cation, moves toward the cathode, whichever plate this may happen to be, and at the same time SO_4^{--} , the anion, moves toward the anode. The direction of flow of the current is reversed when the cell passes from charge to discharge and the direction of the motion of the ions changes also.

24. Migration Velocities. — If both the ions moved through the electrolyte with the same velocity, there would never be any difference in ionic concentrations in any part of the cell. It was found a long time ago that considerable differences are set up during electrolysis, and from measurements of these concentration differences it was found possible to calculate the relative migration velocities of all the ions. Later the actual velocity with which an ion passed through the solution was measured, and, of course, as soon as the real velocity of motion of one single ion was found, all the other velocities could be calculated from the relative numbers found by means of the concentration differences.

H^+ ion moves through the solution about five times as fast as SO_4^{--} . Figures 7 and 8 show the condition of things in the cell (7) before any current has

passed, and (8) after 6 SO_4^{--} ions have separated at the anode.

We must remember that the number of + and - ions must always be the same at any point in the cell.

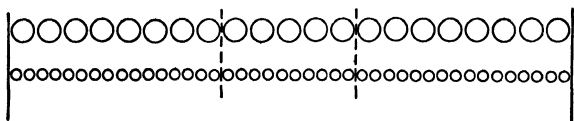


FIG. 7. — Diagram of ion concentrations in an electrolyte before current begins to flow.

The attraction of the + and - charges on these very small bodies is so great that we can never hope to get more than the most minute concentration of any one kind of ion off by itself, and we have very good evidence that our solutions are everywhere electrically

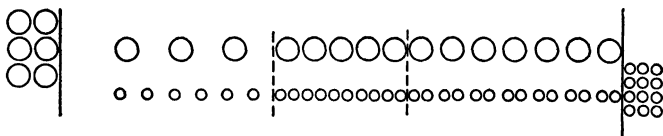


FIG. 8. — The cell of Figure 7 after six SO_4^{--} ions have left the electrolyte at the anode.

neutral, which means that the concentration of + and - ions is everywhere the same.

This statement suggests the question : How can a slow-moving ion get to its electrode fast enough to keep up the supply there ?

And the answer is that it cannot keep the concentration at its original value. During electrolysis the

electrolyte about the place where the slow-moving ion is going out of solution is depleted. Its concentration becomes less and less, until diffusion finally stops the dilution. In the meantime the fast-moving ion has become heaped up about its electrode. The diagrams in Figures 7 and 8 will make this clear.

When the current begins to flow, the H^+ ions move toward the right, and are removed at the cathode (either as gas or by some secondary reaction), and at the same time the SO_4^{--} ions move toward the left, and are removed at the anode. The H^+ ion moves five times as fast as the SO_4^{--} ion. By the time six SO_4^{--} ions have passed through the electrode, 12 hydrogen ions have gone out of solution. 10 H^+ ions have in this period of time entered the region about the cathode, and one SO_4^{--} ion has entered the region about the anode. The region in the center of the cell has not changed in concentration, but the parts of the cell on both sides of it have changed, and the relative change has been a large one.

It will be seen at once that the relative migration velocities are inversely as the **losses about the electrodes**. The cathode has lost one, the anode has lost five, and the migration velocities are as five (cation) to one (anion). This means, too, that five sixths of all the electricity that has passed through the cell has been carried through by the cation, and only one sixth by the anion.

25. Ionic Reaction.—In cells of the Daniell type the ionic changes are very simple. A single cation carries the current toward the cathode, and leaves the electrolyte at that electrode, while a single anion attends to all the cell activities at the anode. The concentration changes which result from taking away material from the electrolyte at the cathode and from adding it at the anode are indicated in Figure 9.

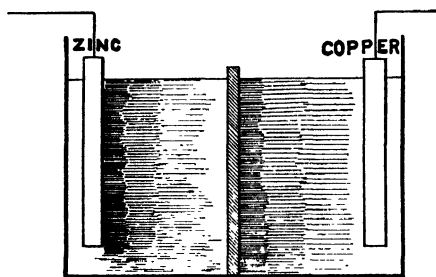


FIG. 9.—Concentration changes in the Daniell cell.

In our storage cell we have a much more complicated system. H^+ and SO_4^{--} do not pass in and out at the electrodes, and the really fundamental cell

activities are cared for by other ions. The ions which are active at the electrodes do not travel a measurable distance into the main body of the electrolyte. We must therefore expect two sets of ionic reactions in a storage cell—those between the conducting ions and the active electrode ions and those between the active ions and the substances of the electrodes. We shall examine some possible and plausible theories in Chapter VIII.

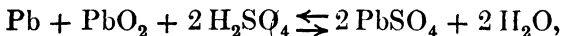
CHAPTER IV

THE FUNDAMENTAL CELL REACTION

26. An active storage cell contains two quite different kinds of plates immersed in a rather strong solution of sulphuric acid. In storage battery parlance one of the plates is called the "negative" and the other the "positive." In spite of the fact that the cell reaction is completely reversed each time the cell is charged and discharged, so that each plate is really positive half the time and negative the other half, these terms are about as good as any that can be found. Anode and cathode are no more definite. Lead plate and peroxide plate could very well be used, and by "the positive plate" is meant the one which has lead peroxide as its chief constituent. The "negative" is the one which has as its chief constituent spongy, finely divided metallic lead.

In order to apply the laws which we have developed for galvanic cells in general to the case of the lead accumulator we must first of all know exactly what chemical reaction takes place when current flows through the cell.

27. The Lead Cell Reaction.—The complete reaction of a lead accumulator, working under ordinary conditions of service, is



and the sign $\rightleftharpoons$ indicates that it is perfectly reversible. During discharge the reaction goes from left to right. It takes place of its own accord and the cell furnishes electrical energy which can be utilized for work outside the cell. Under these circumstances the sponge lead plate is the anode,—lead goes into solution as lead ion, Pb^{++} , here,—and the peroxide plate is the cathode—lead peroxide is reduced to lead ion there. Everywhere in the cell the lead ion which is produced finds SO_4^{--} handy, and since lead sulphate is a difficultly soluble substance, the two ions unite to form non-ionic lead sulphate, which soon saturates the solution and precipitates in solid form.

28. Effect of High Current Density.—It has been said that the reaction is completely reversible as long as the currents sent through the cell are anywhere near the limits of practical operation. If a very large current is sent through a cell with very small electrodes, secondary effects appear in measurable amount. Persulphates are formed and some other complex ions make their appearance.

Ordinary Currents.—In ordinary practice all these effects can be wholly neglected. If we are working

with a comparatively large cell, we can take out the electrochemical unit of quantity of electricity without greatly changing the distribution of materials in the cell, and by the time 96,540 coulombs have been sent through, $2\frac{0}{2}$ gm. of lead have been changed to lead ion at the anode (the lead plate) and $2\frac{3}{2}$ gm. of lead peroxide have become lead ion at the cathode (the peroxide plate). At each plate these amounts of lead ion have found sulphate ion waiting for them and equivalent amounts of lead sulphate have been precipitated — $3\frac{0}{2}$ gm. at each plate. Nothing has yet been said about the nature of the ion which travels back and forth at the peroxide plate. Whatever this ion may be, it is evident that its decomposition into Pb^{++} leaves 2 O behind, and from the reaction it can be seen that the sulphuric acid which reacts with the lead ions furnishes enough hydrogen to produce 2 H_2O at the positive plate.

29. Reaction during Charge. — If now we charge the cell, after a period of discharge, we merely reverse everything that happens during discharge. The peroxide plate is now the anode. Here lead ion goes out of solution — leaves the ionic state — and with the aid of the water in the electrolyte becomes lead peroxide. At the lead plate, which is now the cathode, lead ion changes into metallic lead, just as at any other simple metal-ion electrode. At both plates it is the lead sulphate which furnishes the

constantly renewed supply of lead ion for the reaction. This seems a little difficult at first glance, for is not lead sulphate an insoluble substance? If it were really insoluble, of course our cell could not work in this way, but it is not. It has a perfectly definite and well-known solubility, and while the concentration of lead ion in the solution is very small indeed, it must be remembered that the reservoir of lead sulphate is very near at hand, so that the supply of lead ion has only "molecular" distances to travel to the point where it is to be used.

30. Proof of the Formula. — This fundamental reaction has been tested with the greatest care by many investigators. There are evidently several things to be proven and there are several ways of proving some of them.

What we must know is this. When we pass 96,540 coulombs through the cell in the discharging direction, is the result the formation of $\frac{302}{2}$ gm. of lead sulphate and $\frac{36}{2}$ gm. of water? During this same period has the lead plate lost $\frac{207}{2}$ gm. of metallic lead and has the peroxide plate lost $\frac{232}{2}$ gm. of lead peroxide? And during the same period has the electrolyte decreased its acid content by $\frac{196}{2}$ gm. of H_2SO_4 ?

These points must be proven for the discharge reaction. We must also prove that the reaction is perfectly reversible and that during charge exactly the

same amounts of exactly the same materials react, and **no others**, the reaction being now from right to left.

The change in the content of lead, lead peroxide, and lead sulphate in the plates must be found by

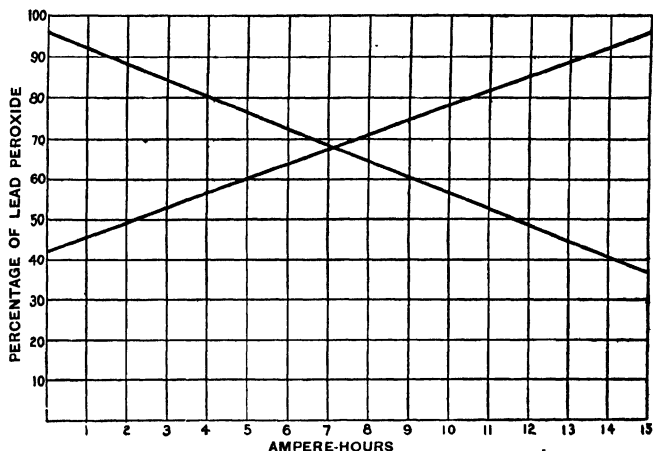


FIG. 10. — Change in the PbO_2 content of the peroxide plate during charge and discharge.

careful chemical analysis of plates after various times of charge and discharge.

Figure 10 shows the results obtained by analyzing the active material of the positive plate after various times of charge and discharge. It will be seen that the content of the plate in peroxide is accurately proportional to the amount of electricity which has passed through the cell, just as required by our fun-

damental reaction. Similar analyses of the active material of the negative plate show similar curves for the lead content, and the lead sulphate content has been found to be an equally good indication of the condition of the cell as to charge or discharge.

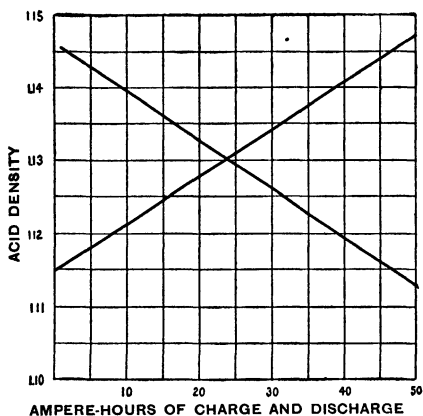


FIG. 11.—Change in acid density during charge and discharge.

The easiest of all the changes to follow is that in the electrolyte. Here we can follow the change of concentration by merely measuring the density of the acid from time to time.

This is shown in Figure 11. Evidently there will

be a lag of density behind the value properly belonging to any given time after charge or discharge has begun. For the acid is being formed or used up **inside** the plate, and must diffuse in or out as the reaction goes on. This is a comparatively slow process, and we must therefore expect that just at the beginning of either charge or discharge the acid density will remain constant, even though some current has passed. The curves of Figure 12 are for the very

beginning of charge and discharge, and they show this lag effect very clearly. These are really pieces which belong at the beginning of the curves of Figure 11, but they would not show if plotted in the time units of that figure. In their own diagram the time axis is greatly drawn out to show the effect more clearly.

When we have once decided that this fundamental reaction really represents what happens in a lead accumulator during its practical operation, we have made a great step, and with the aid of the general theory developed in earlier chapters we can go a long way toward explaining the effect of various factors on the cell.

It has taken a long time to gather the evidence which proves the correctness of our fundamental cell reaction, and there are probably a good many storage battery experts who still feel doubtful as to its completeness. Many of them have wished to introduce intermediate steps, such as the formation of lead persulphate or persulphuric acid at the peroxide plate during charge. It is evident that as long as the processes assumed are reversible and lead to the same final formula as the one we are using, any

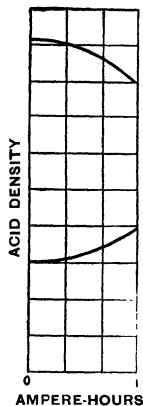


FIG. 12. — First part of curves of Fig. 11. Enlarged scale.

number of intermediate reactions could be assumed without affecting the validity of our reaction in the least. But even this opportunity for introducing hypotheses and analogies is removed when we examine the electromotive force equations for the cell, which we shall take up in a future chapter. When all the evidence is taken into consideration, our fundamental reaction seems to be proven.

CHAPTER V

THE ACTIVE IONS

31. It does not take any training in theoretical science to make it quite clear that the actual carrying of current through the storage cell is done by the sulphuric acid, and we can be very sure that it is done by the ions H^+ and SO_4^{--} . Both lead and lead peroxide are so very slightly soluble in sulphuric acid that their presence in the electrolyte can hardly be shown by analytical means. The concentration of the ions which pass back and forth at the electrodes must always be exceedingly minute, and this small amount of ion cannot have the least relation to the huge current that can be sent through a large storage cell.

In this respect the storage cell differs from most galvanic cells. And it is precisely in this very point that the remarkable properties of the lead cell as an accumulator are all bound up. If the ion of the electrodes reached any large concentration, we would have all the difficulties in the way of trees and short circuits which appear in most cells when we try to reverse them and use them as accumulators. The

active material would soften and move all about the cell, growing at the favored points and not at the others. In the lead cell material produced during either charge or discharge is deposited "right in its tracks," to use a homely expression, and the plates preserve their condition.

32. What Ions carry Current? — But if the current is all carried by ions which do not pass back and forth at the electrodes, there must somewhere in the cell be a loading and unloading of electricity from ion to ion, and the complete expression for the cell reaction should show this transfer. As a matter of fact it cannot be shown by any purely chemical means, nor is it at all necessary to try. The reaction we have adopted is the necessary and complete expression for everything that takes place in the cell, from a merely chemical point of view. We can get some theories which fit the facts pretty well, and it will be seen a little later that these theories are subject to rather severe tests of a quantitative sort. At any rate, it is always interesting to develop the possible theories for such a chemically unattackable problem, and so we will examine one of the most plausible.

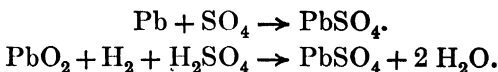
33. At the Negative Plate. — Let us start with the negative plate. During discharge this is the anode of the cell. The acid is doing the carrying of current through the cell, and SO_4^{--} ion is therefore moving

toward the anode. The electrode is probably reversible with respect to Pb^{++} ion, and lead goes into solution as Pb^{++} in proportion to the amount of current which passes through the electrode. It never gets far, for the SO_4^{--} is moving toward it, even if there were not enough in the electrolyte, and lead sulphate is precipitated in the very spot where the lead ion was formed from the metal. The only thing that is left over after this reaction has been completed is hydrogen ion, H^+ , and this is doing the carrying of current through the electrolyte toward the cathode,—in this case the peroxide plate. If we can take this extra H^+ into our reaction at the cathode, we will be able to reach a balance, and our theory will at least be a possible one.

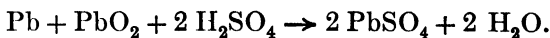
Leaving aside for the moment the matter of the ions, we can say with certainty :—

Sulphuric acid carries the current across the space from plate to plate. The acid is separated during this time into 2 H and SO_4 .

For discharge

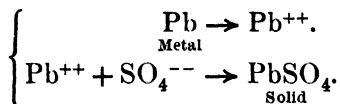


In sum

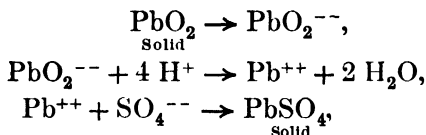


34. At the Peroxide Plate.—It does not require a very vivid scientific imagination to discover a simple

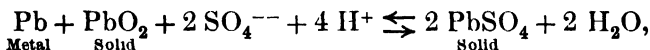
and reversible reaction which takes in the ionic change at the lead plate.



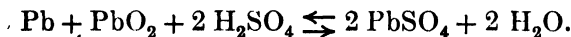
For the peroxide plate we need a more complicated set of changes, and Liebenow has suggested an ion which fits the facts very well indeed. Suppose the peroxide plate to be reversible with respect to the PbO_2^{--} ion. We then have at this plate during discharge



and if we add the reactions at the lead and lead peroxide plates, we get



which is our fundamental reaction

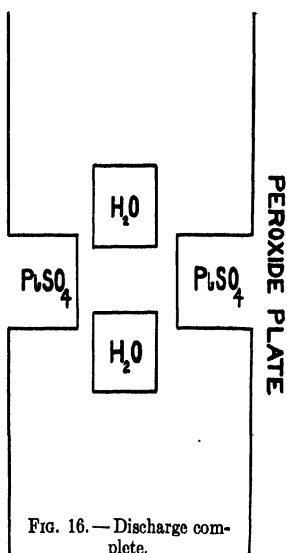
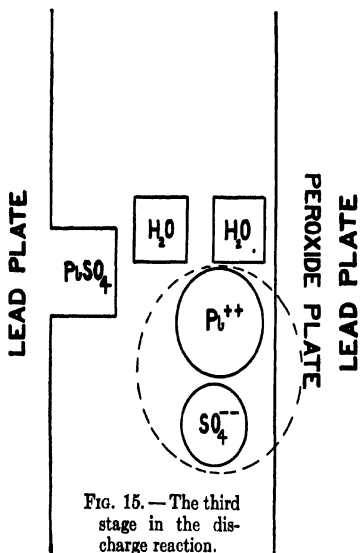
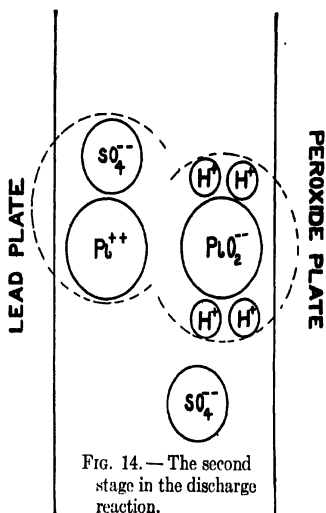
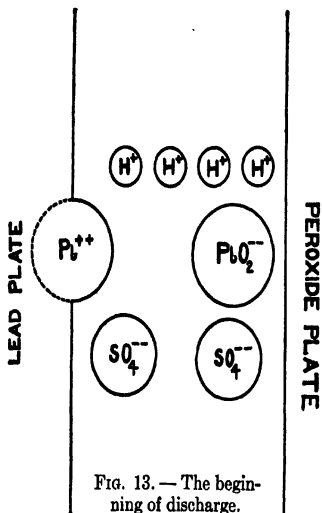


This is completely reversible, and it will also be found that our separate ionic reactions represent completely reversible changes.

35. Diagrams of Charge and Discharge.—The accompanying diagrams may make all this still clearer. The cell is discharging—it is furnishing current

for use in the external circuit. The current is flowing into the cell at the lead plate, which is therefore the anode. Here metallic lead passes through the electrode (Fig. 13) and changes into lead ion, Pb^{++} , carrying 96,540 coulombs with it for each $\frac{207}{2}$ gm. of lead that go into solution. The lead ion has hardly passed the electrode before it meets with SO_4^{--} in the electrolyte (Fig. 14). Lead sulphate being so slightly soluble, it requires only a very small concentration of lead ion and sulphate ion in solution to reach the limit of solubility of lead sulphate. This substance is therefore formed from the two ions as a solid, and removed from the electrolyte as fast as it is produced.

36. Discharge. — On discharge (see Figure 14) the lead peroxide plate is the cathode. It is certainly reversible with respect to **some** ion, and PbO_2^{--} seems to fit the necessary conditions. This PbO_2^{--} is constantly formed from the solid PbO_2 of the plate, just as Pb^{++} is formed from the solid lead of the anode. It starts toward the anode, being an anion, as its two — signs indicate. Before it has more than passed the electrode it meets with H^+ , of which there is always plenty about in a concentrated sulphuric solution, even if it were not moving toward the cathode carrying the current. It reacts with this H^+ , forming Pb^{++} and water (Fig. 15), and the Pb^{++} , finding SO_4^{--} in plenty, soon saturates the



solution with lead sulphate, which is precipitated very nearly in the spot from which the peroxide started (Fig. 16).

It will do no harm to go over the changes in the reverse direction, just to fix the whole reaction more firmly in our minds.

Charge.—The cell is charging (see Figure 17). The peroxide plate is now the anode, and contains a considerable proportion of finely divided lead sulphate from the previous discharge. Pb^{++} and SO_4^{--} are formed as fast as they are needed from this reservoir in the plate, and the Pb^{++} reacts with the water of the electrolyte, forming H^+ and PbO_2^{--} (Fig. 18). The PbO_2^{--} passes through the electrode (Fig. 19) and is deposited as solid PbO_2 very close to the point where lead sulphate went into solution. H^+ and SO_4^{--} are left in the electrolyte in proportion to the amount of current which has passed (Fig. 20).

The lead plate is cathode during charge. Here also there is a reservoir of fine lead sulphate from the previous discharge. This furnishes a constant supply of Pb^{++} and SO_4^{--} , and the electrode is reversible with respect to Pb^{++} . So Pb^{++} passes out and changes to metallic lead, sending a corresponding quantity of electricity along through the external circuit, while the SO_4^{--} finds itself moving toward the anode. It will find its equivalent of H^+ in the solution, and our equations show that

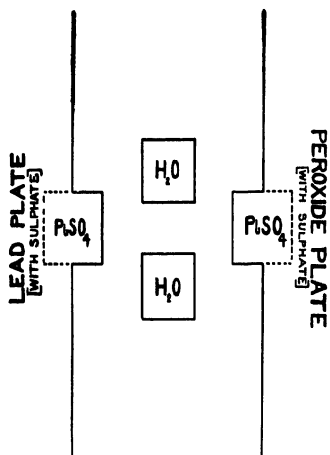


FIG. 17. — The beginning of charge.

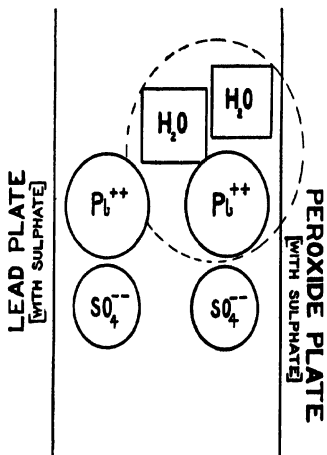


FIG. 18. — Second stage of the charge reaction.

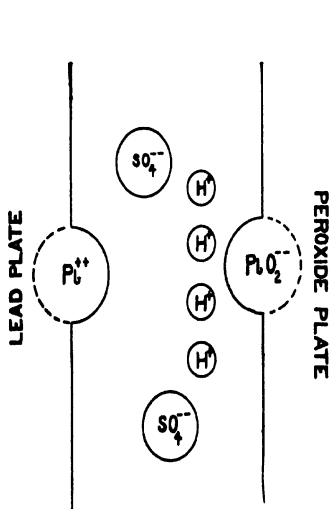


FIG. 19. — Third stage in charge reaction.

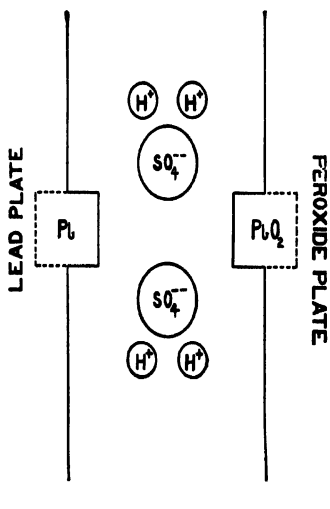


FIG. 20. — Charge complete.

acid is produced during charge in proportion to the amount of material reacting, and that it is used up in the same proportion during discharge. It also expresses everything else that is contained in our fundamental reaction, and gives us at least a possible picture of what takes place at the electrodes as well. We have shown that it is quite possible to have all the current carried through the cell from plate to plate by the ions of the acid, provided these two ions react near the electrodes to produce ions like the ones we have assumed. Our electrode reactions are perfectly reasonable ones, and are, as matter of fact, supported by a great deal more evidence than we can yet call to their support. We shall return to them in a later chapter.

CHAPTER VI

SOME PERTINENT PHYSICAL QUERIES

37. A host of questions arises even at this early point in the discussion of the lead storage cell. Even if we suppose that we have satisfactorily disposed of the chemical changes, and found a pair of ions that might do the work at the electrodes, how can we explain a good many things about the peculiar nature of the materials of the cell?

Premises. — These questions can best be discussed if the reader will keep in mind : —

(I) The ions which pass back and forth at the electrodes have only molecular distances to travel.

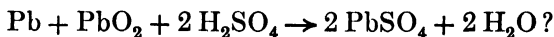
(II) The particles of active material are very small indeed.

(III) The active materials: — lead, lead peroxide, and lead sulphate are all very slightly soluble in concentrated sulphuric acid.

38. Queries and their Answers. — **QUERY 1.** How can storage plates keep their shape? How does it happen that a battery can be sent through thousands of charges and discharges without much growth of trees or sponge?

Just because all the solid substances concerned are so very slightly soluble in the electrolyte. The ion which passes back and forth at the electrode has no chance to wander far enough to deposit at even a measurable distance from its point of origin. SO_4^{--} is everywhere waiting for the Pb^{++} , and insoluble PbSO_4 is precipitated almost instantly. This is one of the prime secrets of the success of the lead cell, and the main reason why its plates preserve their mechanical structure as well as they do. In another sense it is a disadvantage, for it means that the particles of active material will be exceeding fine and small, and that there will not be much intergrowth and interlocking between neighboring particles. In the ideal cell both extreme insolubility and intergrowth of particles might occur simultaneously, but not in practice.

QUERY 2. The lead peroxide of the positive plate is in contact with a lead support. Why does not the plate discharge of its own accord? Does it not contain all the necessary substances for the reaction



It does; and self-discharge always takes place when a peroxide plate is standing fully charged. But before it has gone far all the finely divided rough lead on the surface of the lead support has reacted and then the plate is protected by its dense

layer of lead sulphate, just as a lead plate protects itself in sulphuric acid.

If the surface of the lead support is roughened or increased, the action will be stronger, and Planté plates were originally formed for service by means of this very action. Our modern plates have a very much greater proportion of active material to surface of lead support, and therefore the loss of energy due to this "local action" is a comparatively small one. (See page 182.)

QUERY 3. How does it happen that a lead accumulator with a difference of potential of two volts between its plates can stand on open circuit without immediately discharging itself? Under proper conditions water (made acid with sulphuric acid) can be completely decomposed into hydrogen and oxygen at 1.5 or 1.6 volts. Why does not our cell begin to decompose its electrolyte and keep on forming gas until the plates are quite discharged?

Because the plates of our cell are made of lead and lead peroxide. There is a great difference in the amount of work required to form bubbles of hydrogen rapidly on surfaces of various metals. It takes 2.5 or 2.6 volts to cause gas to form rapidly in a lead accumulator, and at 1.6 volts—the electromotive force at which gas forms on platinum electrodes—hydrogen forms bubbles so slowly on a lead surface that losses due to this cause are quite negligible.

Even at 2 volts the evolution of hydrogen is so slow as to be unmeasurable. (See page 217 for the effect of impurities.)

QUERY 4. How can it be that lead sulphate is formed during the discharge of our cell, and how can this substance change back so readily to lead and lead peroxide? Is not "sulphation" the most dangerous disease that can come upon a battery?

The explanation is a matter of **surface**, like so many others in this subject. The lead sulphate which forms in the plate during a healthy discharge differs greatly in size of grain from the same substance taken from the bottle on the laboratory shelf, and just as much from the material which causes what is called in battery parlance "sulphation." If ordinary commercial lead sulphate be made into a paste and filled into a lead support, it does not change to lead at the cathode and lead peroxide at the anode easily. It can be subjected to the action of the current for a very long time without being completely transformed, and it never does make a good coherent plate. When a cell is allowed to stand discharged for many weeks the fine grains of sulphate which are formed during normal discharge suffer an interesting change. True crystallization begins on the larger particles, and the substance goes into solution at the small ones. It moves through the solution and continues to deposit on the large grains until

the small grains have completely dissolved and the large ones, fewer in number, have grown to considerable size. The plate is now **sulphated**, and if it is charged for the ordinary time, it by no means returns to its original condition of healthy charge. The large crystals of sulphate do not go into solution completely. In fact, they hardly dissolve at all, and long before the cell has been brought back to its charged state reaction has ceased and the current is merely producing gas. It is possible to restore a sulphated cell, but the charge must be continued so long that gassing breaks up the active material, and even when the remaining sulphate has all been forced to react, a large part of the original capacity of the cell has been lost. (See page 216.)

QUERY 5. Metallic lead in the form of a bar or plate is not dissolved by sulphuric acid under ordinary circumstances, and this is especially true of acid of the concentration used in storage batteries. The grids of paste plates and the main body of Planté plates resist the attack of the acid during the whole life of the plates. Lead is one of the metals which "protects itself" from solution in reagents by the formation of a dense layer of slightly soluble material on the surface. It is a familiar fact that lead pipes cannot be used for pure distilled water without danger of contamination, for in this case the substance formed is not dense and does not protect the

metal. The hydroxide which forms under these circumstances is fluffy and breaks away from the surface, and the plate rapidly dissolves. But if the water passing through the pipe is not pure,—if it contains carbonates, chlorides, and sulphates even in small amounts, — dense protecting coatings of carbonate, chloride, or sulphate are formed and the metal is no longer dissolved. It is safe enough to use lead pipes for ordinary water even if it is to be used for drinking purposes.

How is it, then, that the lead of the negative plate can pass easily and rapidly into the form of lead ion? Why do not the particles of lead so protect themselves and refuse to react? And if because of their very fineness the protecting layer which might be formed makes up a considerable part of the whole bulk of the grains, why does not the self-discharge necessary to produce this protecting layer greatly reduce the activity of the lead plate?

While it is quite true that the particles of lead on the negative plate are very small, they are still quite large in comparison with the protecting layer of sulphate which is sufficient to prevent further action. At the end of charge a part of the energy is lost by formation of sulphate at the lead plate, but in practice it is a very small fraction of the whole. But when current is passing through the cell in the discharge direction a very different state of things pre-

vails. Suppose our cell to be first on open circuit and that we are looking at what happens at the lead plate and able to see everything that occurs. Lead

changes to lead ion, Pb^{++} , and this goes into solution, leaving the plate **negatively charged**. The Pb^{++} finds SO_4^{--} waiting and precipitates as insoluble PbSO_4 , but it leaves 2H^+ behind it, and the condition of strain set up by the positively charged ion in the electrolyte and the negatively charged plate is not relieved (Figure 21). It only takes the presence of a very small concentration of ion in solution to set up an attraction so strong that no more ion leaves the plate.

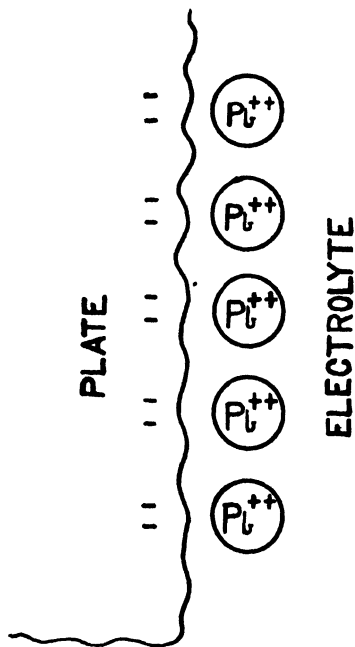


FIG. 21. — Electrostatic equilibrium about a lead plate.

The electrode is **in equilibrium** with respect to Pb^{++} . It has protected itself sufficiently by sacrificing a very minute fraction of its whole mass.

But as soon as the external circuit is closed and

current begins to pass, the H^+ is no longer bound by an electrostatic attraction. The lead plate can discharge itself through the wires and the H^+ can proceed on its way toward the cathode, carrying its equivalent of electricity with it. The electrode is no longer in equilibrium, and more lead goes into solution, becomes Pb^{++} , reacts with SO_4^{--} , and frees more H^+ . This continues as long as current is being taken from the cell.

CHAPTER VII

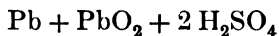
ENERGY RELATIONS

39. Any arrangement whatever which runs of its own accord and which can furnish energy for doing outside work as well must draw upon some store for the energy expended. A charged storage cell contains potential chemical energy. It differs in no way from any other galvanic cell in this, and if we knew of practical ways of manufacturing lead sponge and lead peroxide of exactly the same physical characteristics as those possessed by the active materials of our charged accumulator, we could build a cell just like it in every way without any charging process whatever. It merely happens that the very best way of manufacturing lead sponge and lead peroxide of exactly the right quality is to pass a current of electricity through a discharged storage cell. The materials themselves are no more electrical than the same substances in bottles on the laboratory shelf.

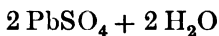
40. Transformations of Energy. — There is hardly a branch of science where we can be so sure of our footing as in calculations which involve the transformation of quantities of energy from one form to

another, especially in the calculation of **reversible** changes, and it is difficult to imagine any arrangement which could be more perfectly reversible than a storage cell. Small losses occur even in a big storage cell. Some gas escapes and cannot be taken into our calculation, and there is some local action at the plates with corresponding evolution of a little heat. But the same is true in any arrangement known to man, and in most cases the losses are very much greater than in our cell.

Electrochemical Reaction. — We can apply the law of the Conservation of Energy. Applied to our own particular case this law says: If we have at our disposal a system, represented by



and consisting of 207 gm. of lead, 239 gm. of lead peroxide, and 196 gm. of sulphuric acid, and this system changes of its own accord into another



consisting of 606 gm. of lead sulphate and 36 gm. of water, a definite and determined amount of energy will be set free, which can be utilized for doing work. If the reaction is perfectly reversible and no energy has managed to get away from us, we can restore the original condition of the system by expending the same quantity of energy on it.

Our own special interest lies in a chemical reaction, but the same law applies for any change whatever. The original condition might be represented by a certain mass of water at the top of a dam and the final condition by the same mass at the bottom. Here we would have no difficulty in calculating the quantity of work obtainable by the fall of the water, and the same amount of work would carry it back to the top, provided all our machines were frictionless and worked with 100 % efficiency.

41. Thermochemical Reaction. — Now for the next step. If we should take the amounts of the various materials on the left side of our fundamental equation, and should mix them all up into a pasty mass, we would not get any electrical current from it, but we would get a definite amount of heat set free. We will get the same total amount of energy from the reaction in either case, provided our cell does not itself heat up or cool down during the reaction of these amounts of its materials. In the one case we should measure the amount of available energy in heat units, or **calories**, and a calorie is the amount of heat required to raise the temperature of 1 gm. of water 1° C. In the other case we should measure the amount of available energy in electrical units, joules (volt-coulombs).

42. Heat Changes in the Cell. — If our cell does heat up while it is sending out its 96,540 coulombs, we

must remember the amount of heat which appears in this way, and we must expect to get less energy from the cell for use in the external circuit if a part of the total energy of the reaction has been used to heat the air of the room. If the cell **cools** while it is working, we might expect to get more than the calculated amount of energy, and to this point we will come back later.

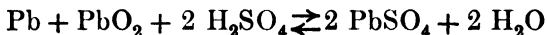
But if the cell neither heats nor cools during the passage of 96,540 coulombs, the law of the Conservation of Energy gives us our

First Fundamental Equation

chemical energy expanded = electrical energy produced.

Before we can go any farther we must know the numerical factor for transforming joules to calories (or *vice versa*), and this has been often determined. It takes 4.18 joules to raise the temperature of 1 gm. of water 1° C.

The determination of the heat of the reaction



cannot be carried out directly with accuracy because of the slowness of the reaction when the substances are mixed up together. It can only be determined by indirect measurement, and the best results have been obtained by using very **dilute** sulphuric acid.

Applying a correction to be explained immediately, the heat of this reaction for acid of density 1.044

(0.70 gm.-mol. H_2SO_4 per liter of electrolyte) is 87,000 calories. A cell containing acid of this density neither heats nor cools while it is working.

Now see how simple our calculation becomes:

$$87,000 \text{ calories} \times 4.18 = 364,000 \text{ joules,}$$

and this is the amount of electrical energy which becomes available when 207 gm. of lead and 239 gm. of lead peroxide have reacted with 196 gm. of sulphuric acid (in rather dilute solution) to produce 606 gm. of lead sulphate and 36 gm. of water.

If we arrange things so that the reaction can take place in a galvanic cell, $2 \times 96,540$ coulombs will pass through the cell by the time these amounts have reacted. These 193,080 coulombs will have given us 364,000 joules of work, and the **voltage of the cell** must therefore be

$$\frac{364,000 \text{ volt-coulombs}}{2 \times 96,540 \text{ coulombs}} = 1.90 \text{ volts.}$$

This agrees closely with the measured voltage of a cell containing this rather dilute acid as electrolyte.

While there is no doubt whatever about the correctness of this principle, there is often a great deal of difficulty in obtaining accurate data on the heats of reaction. In this case a number of reactions had to be used, and the final result calculated in a round-about way by eliminating the heats of the various

intermediate steps. Even in this case there is no doubt as to the correctness of the method, but the final result is always afflicted with a large experimental error.

43. Heating and Cooling of the Cell.—The ordinary practical storage cell contains acid of density about 1.210. It cools during discharge and heats during charge, and can therefore not be brought under the simple law we have just used. We can make some qualitative statements about it, however.

Since it cools during discharge, it must take into its system a certain amount of heat from the room during the passage of 96,540 coulombs. At least a part of this heat will be transformed into electrical energy. Since we **always** calculate on the basis of 96,540 coulombs, the voltage of this cell must be higher than it would be if it did not cool down while it was working.

During charge, the cell gets hotter than the room. A part of the energy supplied to charge it is used in heating the surrounding objects, and it therefore takes more energy to completely reverse the reaction than it would if the cell did not change its temperature during charge. Since we use the same 96,540 coulombs for the reversal, the charging voltage must be higher than it would be if the cell did not heat up.

44. The General Equation.—We can handle this case quantitatively just as easily as the simple previ-

ous one, for we have what is called the Second Law of Thermodynamics, which states

$$W = Q + T \frac{dW}{dT}.$$

For our case

W = available electrical energy.

Q = heat of the chemical reaction.

T = the absolute temperature.

$\frac{dW}{dT}$ = the temperature coefficient of available electrical energy.

Since all our calculations are based on gram-equivalents, 96,540 coulombs are always supposed to pass through the cell, and the electromotive force of the cell is therefore a measure of the available electrical energy.

If e = the electromotive force of the cell, we can put this formula into a form adapted specially for the case of galvanic cells.

$$e = \frac{Q}{F} + T \frac{de}{dT},$$

F being our 96,540 coulombs.

For an acid concentration corresponding to a density of 1.210 we have for Q (per gram-equivalent) about 43,000 calories.

$\frac{de}{dT}$ is positive and has a value of about 0.0003 at 20° C.

Numerically

$$e = \frac{43,000 \times 4.18}{96,540} + [290 \times 0.0003],$$

$$e = 1.86 + 0.087 = 1.95,$$

which is a little lower than the usual measurement of 2.04 to 2.06 volts.

The complete derivation of the formula will be found in the Appendix, page 255.

This is the general form of the expression for the electromotive force of a galvanic cell in terms of the chemical heat of reaction and the temperature coefficient of the electromotive force. It is perfectly general and suggests many interesting things. There are cells which warm up a good deal while they work. These are the ones whose electromotive force decreases rapidly when their temperature is raised. Others cool down, and the reverse effect is produced on these by warming them from without. In the first class, part of the energy of the chemical reaction is used to heat the room. In the second class some energy is taken from the room in the form of heat and converted in the cell into electrical energy. There are cells in which the heat of the chemical reaction is zero and in which all the electrical energy is produced at the expense of heat absorbed from the surrounding air. These are the "concentration cells," and they are very interesting and important

theoretically, even though none of them are used as practical sources of current.

45. Temperature Coefficient.—The usual commercial storage cell has a fairly large positive temperature coefficient—about 0.0003 per Centigrade degree. But it gains no energy from this fact because we

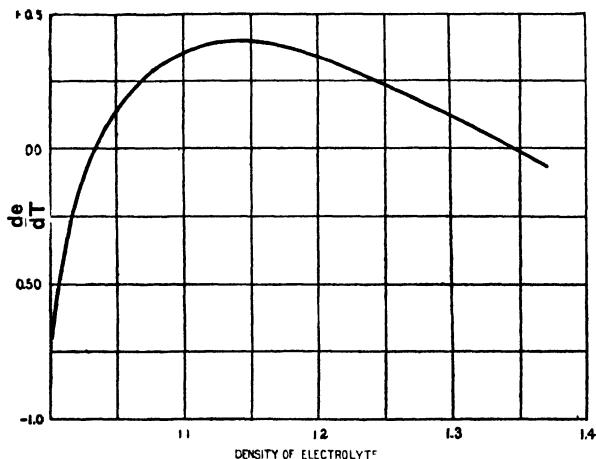


FIG. 22.—Change in the temperature coefficient of the e. m. f. of a storage cell with change in acid concentration (density).

reverse it when we charge it and lose from the negative coefficient during this part of the cycle. As far as this one factor is concerned we should charge it as cold as possible and discharge it as hot as possible. But as we shall see later, temperature has much larger and more important influence on other factors, and in comparison with them the change in

electromotive force with temperature is quite negligible. Figure 22 shows the change in the electromotive force of the cell with change in acid concentration, and the $\frac{de}{dT}$ of the formula can be taken from this curve. At acid concentrations higher than 2 gm.-mol. per liter the curve does not fit the measurements perfectly, and the values obtained by calculating backward from the heats of dilution are probably correct. The departure is not great, but requires explanation. It may be that the more concentrated acid attacks and combines with the lead sponge of the negative plate, even when no current is passing, giving out heat, and this loss of energy would of course mean that the electromotive force found by measurement will be too small.

46. The Heat of Dilution of Sulphuric Acid. — The determination of the heat of reaction for the materials of the storage cell was made in very dilute sulphuric acid. Under these conditions there would be set free in the calorimeter, besides the heat of the substances indicated in the equation for the cell reaction, the heat of dilution of 2 gm.-mols. of H_2SO_4 . This is a considerable amount of heat, as every one knows who has had occasion to dilute sulphuric acid by pouring the concentrated acid into water. If we used very dilute acid in our cells, we could also use the heat of reaction found in the calorimeter, but

since we use in practice rather concentrated acid, we evidently cannot expect to get any more energy than could be obtained from the heat of the cell materials plus the heat of dilution from pure H_2SO_4 to the acid concentration used in our cell.

The curves of Figures 23 and 24 show the heat of

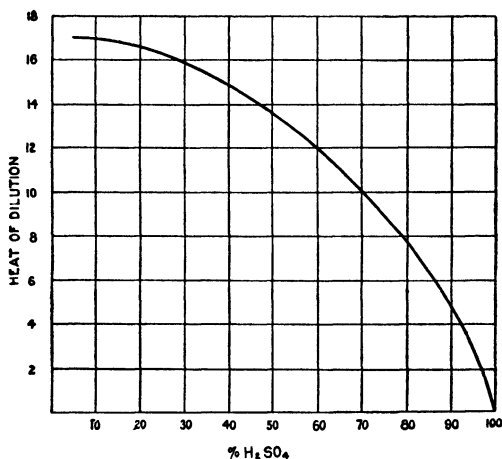


FIG. 23. — Curve showing the heat of dilution of a gram molecule of H_2SO_4 to various concentrations. Heat given in thousands of calories.

dilution of sulphuric acid. Along the bottom of the diagram of Figure 24 are given the densities of the solutions formed, and along the top the concentration of these solutions in gram-molecules of H_2SO_4 per liter of solution.

The Q which we use in our energy formula consists evidently of two parts, one being the heat of

reaction of the materials according to the fundamental cell reaction, the other the heat of dilution to the concentration used in the cell being tested. Since the temperature coefficient also plays a considerable part in our calculations of electromotive

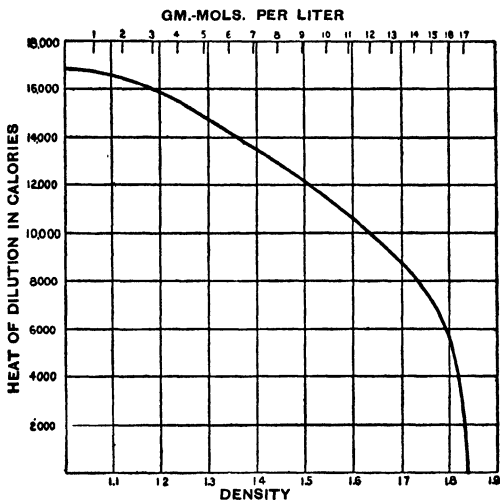


FIG. 24. — Curve showing the heat of dilution of H_2SO_4 to electrolyte of various densities (at bottom) and to various concentrations in gm.-mols. per liter (at top).

force, the easiest way of approaching the subject seems to be to choose as our starting point an acid concentration such that the cell has no temperature coefficient of electromotive force. This we did by choosing acid of density 1.044 (0.70 gm.-mol. per liter), and we thus made one factor constant.

47. Very Dilute Electrolyte. — 87,000 calories is the total heat of reaction when acid of this density is used in the cell, and this is already so dilute an acid that not very much more heat could be obtained by diluting it a great deal further. It will be seen from the curve (Figure 24) that the difference in the heats of dilution of 0.70 normal acid and 0.0 normal acid is small. It is only a couple of hundred calories at the most. Q will therefore be about 87,200 calories for the most dilute solution in which the cell electromotive force could be measured.

From Figure 22 we see that the temperature coefficient for very dilute acid is negative, and that it is rapidly increasing in the negative direction as the acid density approaches zero. Dolazalek has measured this coefficient for very dilute acid (0.0005 gm.-mol. per liter), and he finds it about -0.0025 volts per Centigrade degree.

From these data we can calculate the electromotive force of a storage cell having this very dilute acid as electrolyte.

$$e = \frac{Q}{F} + T \frac{de}{dT},$$

$$e = \frac{87,200 \times 4.18}{2 \times 96,540} - [290 \times 0.0025],$$

$$1.87 - 0.72 = 1.15 \text{ volts,}$$

which is close to the measured value.

48. Concentrated Acid. — Passing to concentrated acid, the agreement between the simple theory and the measurements is not by any means so close. This will be at once evident from an examination of the curves of Figures 22 and 24 in connection with

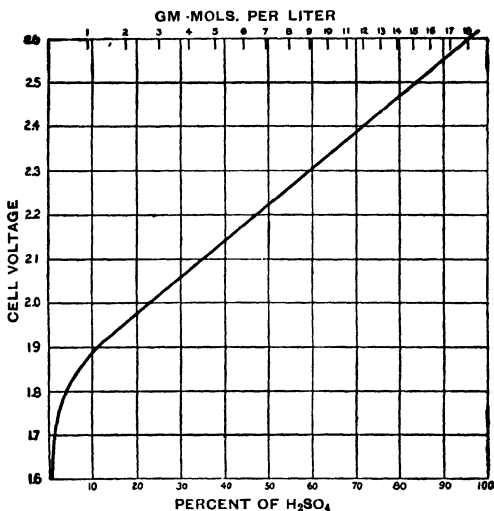


FIG. 25. — Variation of cell voltage with change in acid concentration (in percent of H_2SO_4 at bottom, in gm.-mols. per liter at top).

the results of measurement on cells with various acid concentration, given in the curve of Figure 25. Measurement shows that the electromotive force of a cell is nearly a linear function of the acid concentration, only departing from a straight line in the region of dilute acid, and certainly approximately straight for all acid concentrations used in practice.

Figure 24 shows that Q decreases with increasing acid concentration, since the heat of dilution to be subtracted from the constant part of Q becomes greater and greater as the acid concentration increases. On the other hand, the change in electromotive force with change of temperature is in the right direction to counterbalance this only as far as acid of density 1.15. Beyond this both the Q and the $\frac{de}{dT}$ of our energy formula are decreasing, while the measurements show that the electromotive force is constantly increasing.

At acid density 1.15 the formula still holds accurately enough.

$$e = \frac{85,700 \times 4.18}{2 \times 96,540} + 290 \times 0.00036,$$

$$e = 1.85 + 0.14 = 1.99.$$

For the higher densities we can no longer expect close agreement, if we take the data of our curves. But at the usual acid density of 1.210 the agreement is still fairly close.

$$e = \frac{85,000 \times 4.18}{2 \times 96,540} + 290 \times 0.00032,$$

$$e = 1.84 + 0.093 = 1.933,$$

noticeably lower than the measured value, which is 2.06 volts.

49. This lack of agreement of course arouses sus-

picion of our data. The fundamental theory has been so well and thoroughly proven in hundreds of cases that we need hardly fear any trouble there.

While the thermochemical data for the heat of reaction and the heat of dilution are hard to obtain and undoubtedly fraught with considerable experimental error, there is nothing in the course of the curves expressing them to excite any suspicion of the correctness of their general trend.

The curve connecting the temperature coefficient of the electromotive force with the acid density (Figure 22) is the one which seems to contain the doubtful data. The droop in the value of $\frac{de}{dT}$ comes

in those concentrations of acid where lead is rather rapidly attacked and dissolved. Manufacturers have stopped increasing the density of their electrolyte at about 1.200, because they found local action to be a factor just beyond that point. If there is local action at the negative plate, and the acid is being used up there as a result, the average density in the cell would not be the same as that at the point of cell activity. And since there is no current passing when these measurements are made, diffusion alone must replace the exhausted acid. This would certainly account for at least a part of the discrepancy, but this still remains a point which demands further investigation.

CHAPTER VIII

REACTIONS AT THE ELECTRODES

50. In our discussion of the action of the Daniell cell (page 26) we decided that we could get

$$1.1 \times 96,540 \text{ volt-coulombs}$$

of work from the cell when 32.7 gm. of zinc went into solution as Zn^{++} and 31.8 gm. of copper changed from Cu^{++} to metal. There are a great number of possible cells of the same type, for we can replace either zinc or copper or both by any other metals immersed in solutions of their salts, and in this way make cells quite similar to the prototype.

51. Cells of the Daniell Type. — The following list indicates a few of the combinations and their electromotive forces. These are measured with the metal immersed in a solution which is **normal** with respect to the **metallic ion**. The Daniell cell itself contains 65.4 gm. of Zn^{++} per liter of solution about the anode and 63.6 gm. of Cu^{++} per liter about the cathode. Whenever we use silver as electrode, we measure it in a silver salt solution containing 107.9 gm. of Ag^+ per liter.

	e. m. f.	
Cu/Cu ⁺⁺ /Zn ⁺⁺ /Zn	1.10	Cu cathode, Zn anode
Cu/Cu ⁺⁺ /Cd ⁺⁺ /Cd	0.750	Cu cathode, Cd anode
Cu/Cu ⁺⁺ /Fe ⁺⁺ /Fe	0.986	Cu cathode, Fe anode
Cu/Cu ⁺⁺ /Ni ⁺⁺ /Ni	0.926	Cu cathode, Ni anode
Cu/Cu ⁺⁺ /Ag ⁺ /Ag	0.469	Ag cathode, Cu anode
Zn/Zn ⁺⁺ /Cd ⁺⁺ /Cd	0.350	Cd cathode, Zn anode
Zn/Zn ⁺⁺ /Fe ⁺⁺ /Fe	0.113	Fe cathode, Zn anode
Zn/Zn ⁺⁺ /Ni ⁺⁺ /Ni	0.173	Ni cathode, Zn anode
Zn/Zn ⁺⁺ /Ag ⁺ /Ag	1.568	Ag cathode, Zn anode
	etc.	

If a very little cross-calculation is undertaken, some interesting things will be found. We did not need nearly all these statements to cover the facts, for we can calculate from

$$\begin{array}{r} \text{Cu/Cu}^{++}/\text{Zn}^{++}/\text{Zn} = 1.10 \\ \text{Cu/Cu}^{++}/\text{Cd}^{++}/\text{Cd} = 0.750 \\ \hline \text{Cd/Cd}^{++}/\text{Zn}^{++}/\text{Zn} = 0.350 \end{array}$$

and others in the same way. We can also calculate a good many combinations which we have not put down. For example, —

$$\begin{array}{r} \text{Zn/Zn}^{++}/\text{Ni}^{++}/\text{Ni} = 0.173 \\ \text{Zn/Zn}^{++}/\text{Ag}^{+}/\text{Ag} = 1.568 \\ \hline \text{Ni/Ni}^{++}/\text{Ag}^{+}/\text{Ag} = 1.395 \end{array}$$

and in the same way for any other combination.

All these connected facts suggest a possible simplification. Why not calculate the work at the two

electrodes separately? For the Daniell cell: (1) the work available when 31.8 gm. of copper changes from ion to metal, and (2) the work available when 32.7 gm. of zinc changes from metal to ion. And of course we would not stop here. We would go on and determine the work available when 107.9 gm. of silver passed a silver electrode, and so on for all the single electrodes. Dividing the work in joules in each case by 96,540, we would then have a series of single electromotive forces, and from this series we could pick out any two we wished to combine to make a galvanic cell.

52. Standard Electrode.—Before we can begin to make such a series we must in some way fix a value for one single electromotive force metal/ion. There has been a good deal of trouble in scientific circles about this, but fortunately it does not make the least difference for our elementary work what this standard metal/ion electrode is, or what we take for its single electromotive force. If we should put any one of the single metal/ion combinations equal to 1, and then measure all the others against this, we would arrive at exactly the same figures as those given in our series on page 81. As a matter of fact we have a so-called “normal electrode,” and its electromotive force has been determined separately in various ways. Measured against this single electrode, it has been found that the electromotive

force Zn/Zn^{++} has the value 1.053 volts, the zinc passing from metal to ion through the electrode. It is given the negative sign and is written $\text{Zn}/\text{Zn}^{++} = -1.053$.

Cu/Cu^{++} is $+0.046$, measured against the same standard.

Using these values, and our series of cells of the Daniell type, it is a very easy matter to write out a list of the single potentials of all the metal/ion electrodes which appear in that list.

Zn/Zn^{++}	-1.053	} Daniell cell 1.099
Cu/Cu^{++}	$+0.046$	
Fe/Fe^{++}	-0.940	
Ni/Ni^{++}	-0.880	
Cd/Cd^{++}	-0.703	
Ag/Ag^{+}	$+0.505$	

and we might add from other measurements

Pb/Pb^{++}	-0.431
H/H^{+}	-0.283
Hg/Hg^{++}	-0.467 , etc.

53. Work done at an Electrode. — So here we have the way opened for the calculation of the work done at each electrode. We need only to multiply the single electromotive force by 96,540 and the result is the number of joules furnished by that half of the cell during the change of a gram-equivalent of the metal to ion, or *vice versa*. There would not be much

need for any more minute theory of the process if the single electrodes did not change their electromotive force considerably when the ion concentration about them is changed. For instance, if we are using Ag/Ag^+ as one of our electrodes and silver is going out of solution, this half of the cell furnishes $0.515 \times 96,540$ joules of work. But if we change the concentration of the ion from 107.9 gm. per liter to 10.79 gm. per liter (from N to $\frac{N}{10}$), the half cell only furnishes $0.457 \times 96,540$ joules for the same amount of silver.

At the anode a change of concentration has the opposite effect. $\text{Zn}/\text{Zn}^{++} N$ has 1.053 volts. $\text{Zn}/\text{Zn}^{++} \frac{N}{10}$ measures 1.082 volts.

Nernst has suggested a generalization which makes the whole subject matter easy to remember and which at the same time opens the way to many interesting and important numerical relations. .

54. Nernst's Theory of Solution Pressure. — Let us think of the question in this way: Each metal has a **tendency** to send ions into solution, and does it. The ions carry with them a definite quantity of electricity of $+$ sign, for the metallic ions are all cations. If the electric circuit is not a closed one, this leaves the metal with $-$ charge, and before the concentration of ions has reached a very high value,

a true static attraction is produced between the $-$ charged plate and the $+$ charged ions in solution. Unless this condition of things is relieved by discharging the plate, the concentration of the ion in solution no longer increases, and we have equilibrium. (See Fig. 21.)

Theoretically, at least, we can reverse this process by using a metal with a comparatively slight tendency to go into solution, and placing it in a concentrated solution of its ion. Since a very small concentration of ion is necessary to balance the **solution pressure** of the metal and we have purposely made the ionic concentration high, ion will change to metal under these circumstances and the plate will take on a $+$ charge until static repulsion causes equilibrium. So far this is rather hypothetical. But measurements show that it fits the facts very closely indeed. If a metal is going into solution as part of a galvanic arrangement, we can better the electromotive force of the cell by surrounding this anode with an ionic concentration as small as possible. The single electromotive force of the electrode goes up as the solution about it is diluted. If a metal is to go out of solution as part of a cell, we can assist it by increasing the concentration of its ion to as high a value as possible.

55. Electrode Equilibrium. — A few simplifying assumptions lead us to still more exact numerical

relations. Let us assume that the solution pressure of each metal is constant and that when it dips in a solution it is constantly held in equilibrium by a layer of charged ions about it. Then the passage of 96,540 coulombs through the cell results in the change (suppose this is the anode) of a gram-equivalent of metal into ions of this definite equilibrium concentration and subsequent diffusion of these ions from the more concentrated solution about the plate into the main body of the electrolyte. The whole work of the electrode has been expended in maintaining this ion concentration about the plate. We can calculate the total work of the electrode as merely the **osmotic** work corresponding to the change of a gram-equivalent of the ion from its equilibrium concentration to the average concentration of the electrolyte (see Appendix, page 256).

56. Osmotic Work. — The osmotic work available as the result of such a change in concentration is

$$RT \ln \frac{C_1}{C_2},$$

where C_1 is the concentration in the equilibrium layer about the electrode, C_2 the concentration in the main body of the cell, R is a constant for all dilute solutions — numerically the same as the gas constant R , T is the absolute temperature, and $\ln$ is the sign indicating a logarithm to the natural base e .

C_1 was the concentration which exactly balanced the solution pressure of the metal. As far as we are concerned we could put P , the **solution pressure** of the metal, in place of C_1 , since the electrode is in equilibrium.

Now let a gram-equivalent of the metal change to ion and diffuse into a very large cell, in which the ionic concentration is C_2 .

The osmotic work is

$$RT \ln \frac{P_a}{C_2},$$

and since a gram-equivalent has been used, 96,540 coulombs have passed through our electric circuit.

Electromotive force $\times$ 96,540 = osmotic work

$$= RT \ln \frac{P_a}{C_2}.$$

The electrode electromotive force

$$= \frac{RT}{96,540} \ln \frac{P_a}{C_2}.$$

If we put in the numerical values, using the gas constant for R and changing it to joules, measuring everything at 17° C., and changing to the ordinary system of logarithms, we get

$$e = \frac{0.0575}{n} \log \frac{P_a}{C_2},$$

n being the **valence** of the ion.

This for one electrode. At the other we will have a precisely similar set of relations except that at the cathode the change is from ion to metal, and the electromotive force will therefore have the opposite sign. The electromotive force of the cell as a whole will be the **difference** of the two expressions.

$$e = \frac{0.0575}{n} \log \frac{P_a}{C_a} + \frac{0.0575}{n} \log \frac{P_c}{C_c}.$$

57. Effect of Concentration on Electromotive Force. — Evidently if we want our cell to have a high electromotive force, we must choose

as anode, a metal with a high solution pressure;

as cathode, a metal with a low solution pressure.

And we must also make

the ion concentration about the anode low;

the ion concentration about the cathode high.

58. Application to Lead Accumulator. — In the case of the lead accumulator we have evidently chosen a favorable set of conditions, for it has about as high an electromotive force as any practicable cell. It is a matter of interest to examine this particular galvanic combination from the new point of view.

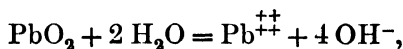
No difficulty is found in applying it to the lead plate. This is the anode during discharge, and we can be quite sure that this electrode is reversible with respect to the ion Pb^{++} . We have insured a low concentration of this ion in the main body of the

electrolyte, for lead sulphate is a very slightly soluble substance. The only electrolyte which I can think of that would possibly increase this single electromotive force would be a soluble sulphide, for lead sulphide is even less soluble than the sulphate.

For the lead plate, we have

$$e = 0.0288 \log \frac{P_{\text{Pb}}}{C_{\text{Pb}^{++}}}.$$

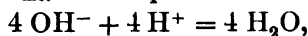
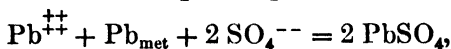
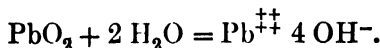
59. Theory of Le Blanc. — When we examine the peroxide plate we find it a much more difficult matter to decide upon our active ion. Whatever it is, it must be present in the electrolyte in exceedingly small concentration and quite beyond the limits of chemical analysis. Two theories have been proposed, one by Le Blanc and one by Liebenow, and while each assumes the existence and importance of a quite different ion, the final result is much the same in each. Le Blanc's reasoning is in this form. Lead peroxide has a small but perfectly definite solubility in water, and reacts with it in the reaction



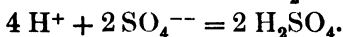
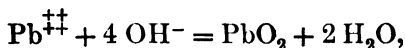
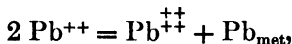
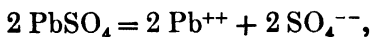
forming a quadrivalent lead ion Pb^{++} , and OH^- ion.

During discharge the quadrivalent lead ion changes to ordinary lead ion Pb^{++} , and this meets with SO_4^{--} and is precipitated as solid lead sulphate.

The entire course of discharge is therefore given by the set of equations —



and during charge these reactions are completely reversed:—



The total result of these reactions gives a reaction just like our fundamental one —

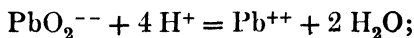


for during discharge we lose lead and lead peroxide and gain 2 of lead sulphate and 2 of water, and during charge the reverse change takes place. As far as the chemical facts of the reaction are concerned, Le Blanc's theory fits very well.

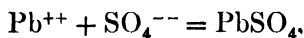
The quadrivalent lead ion Pb^{++} can be shown to exist, but we have not much data as to its concentration in the electrolyte of a lead accumulator.

60. Liebenow's Theory.—Liebenow's theory is in several ways a more acceptable one than Le Blanc's.

He assumes that the lead peroxide electrode is reversible and that the electrolyte contains PbO_2^{--} ion. Then during discharge this ion goes into solution at the cathode (it is a negative ion) and reacts with the H^+ ion of the acid to form Pb and water



the lead ion finds SO_4^{--} ion waiting for it,



and precipitates as solid lead sulphate (see Figures 14 and 15).

The reaction at the anode is the same as before, and the sum of the whole is again our fundamental reaction.

PbO_2^{--} undoubtedly does exist in perfectly measurable concentration in strongly alkaline solution, and theoretically must also be present in the acid of the cell. In the Appendix (page 261) will be found the complete calculation, which leads to the remarkable result that the concentration of PbO_2^{--} in an ordinary cell acid is about 4×10^{-50} gm.-mols. per liter. In the same electrolyte the concentration of the Pb^{++} ion is about 2×10^{-8} .

While it is true that 10^{-50} means only a few molecules in a volume equal to the oceans of the world, this is the number we need to express the concentration ratio in our cell. It must be remembered that

these ions only have to pass over molecular distances and that the reservoir of sulphate from which they are drawn can supply them as fast as they are needed. In such statistical matters as this the unit may make a great difference. There is nothing surprising about the statement that ten children are born per year in a certain village. The same fact is represented by the statement that 0.00000031 children are born there per second.

In terms of Nernst's theory and Liebenow's hypothesis, we have for the lead peroxide electrode

$$e_{\text{PbO}_2} = -0.0288 \log \frac{P_{\text{PbO}_2}}{C_{\text{PbO}_2^{--}}},$$

and for the entire cell

$$e = 0.0288 \log \frac{P_{\text{Pb}} P_{\text{PbO}_2}}{C_{\text{Pb}^{++}} C_{\text{PbO}_2^{--}}}.$$

61. Conclusions to be Drawn. — This equation gives interesting qualitative relations. Evidently we can hardly do better than to retain sulphuric acid as our electrolyte. We are also to use it as strong as the life of the plates will permit; for while lead sulphate is more soluble in concentrated acid than in dilute, and we will therefore lose a little at the lead electrode, the PbO_2^{--} concentration decreases as the fourth power of the hydrogen ion concentration, and we should much more than make up for the loss. As a matter of fact, manufacturers have gradually

increased the commercial concentration of their electrolyte, with a corresponding increase in the electromotive force of their cells. Ten years ago electrolyte of density 1.15 was the rule. Now nearly every one uses a density of 1.210, and for special work as high as 1.225. In portable cells where the limit of weight is fixed and a small total mass of electrolyte must be carried, the density is permitted to go as high as 1.27.

We can also see from this formula that an alkaline electrolyte, with its high concentration of PbO_2^{--} , would greatly decrease the electromotive force of the cell. In caustic soda solution it does in fact go as low as 0.75 volt. An electrolyte containing a large concentration of Pb^{++} will also lower the electromotive force, and if we could manage an electrolyte which was both strongly alkaline and high in Pb^{++} , we could reach a very low value indeed.

CHAPTER IX

CHARGE AND DISCHARGE

62. Up to now we have been considering the cell as independent of the current flowing through it. This point of view is necessary for a theoretical discussion, because the whole cell is changed as soon as current passes. From a rather simple system, quite open to formal investigation as long as it stands on open circuit, the cell changes to a very complex system as soon as it begins to work. The only way to study this complicated thing is to keep all the factors but one as constant as possible, and follow the change in that one. Each factor in turn can sometimes be taken up in this way and the whole problem cleared up. But in the case of our cell we shall find that this general method of solving scientific puzzles is hard to apply. So many of the factors which are active in a storage cell are not within our direct control. For these reasons it is easiest to follow the changes in an accumulator by study of **curves** and families of curves. A single such curve shows the mutual effect of two things. A family of curves shows a great deal about three factors and their re-

lations. Let us take first of all the curves which show how the voltage of an accumulator changes with time, while it is being charged and discharged at a constant rate.

In all that follows, the general theory of Chapter VIII should be kept clearly in mind. Large changes in voltage appear during complete charge and discharge, but every change can be explained satisfactorily and completely by reference to changes in the **concentration** of the active ions.

The electromotive force of the Pb/Pb^{++} electrode is given by the formula —

$$e_{\text{Pb}} = 0.0288 \log \frac{P_{\text{Pb}}}{C_{\text{Pb}^{++}}},$$

and that of the $\text{PbO}_2/\text{PbO}_2^{--}$ electrode by —

$$e_{\text{PbO}_2} = 0.0288 \log \frac{P_{\text{PbO}_2}}{C_{\text{PbO}_2^{--}}},$$

at every point of a charge, discharge, or recovery curve.

The only variables are the concentrations of Pb^{++} and PbO_2^{--} .

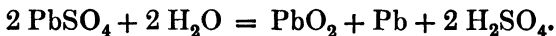
It should also be kept clearly in mind that the Pb^{++} ion concentration varies inversely as the acid concentration at the point of activity, and inversely as the square of the H^+ ion concentration, while the PbO_2^{--} ion concentration varies inversely as the

square of the acid concentration and therefore inversely as the fourth power of the H^+ concentration (see Appendix, page 260, for the complete statement of the theory).

63. Charge Curve. — Our cell has been fully discharged at a rather low rate. Lead sulphate has been formed through each plate wherever sulphuric acid of sufficient concentration was available for reaction. Lead peroxide and lead sponge have been more or less completely exhausted and partially covered with a layer of sulphate. Sulphuric acid has been taken from the electrolyte, which has a lower acid concentration than before the discharge.

We connect the terminals of the cell with a source of current, and proceed to charge it.

The reaction is



The reservoir of lead sulphate supplies material, and water is taken from the electrolyte as well. The reactions described on page 55 begin, and sulphuric acid is set free in the two plates.

If the cell has been recently discharged, this reaction begins immediately, and the voltage rises slowly until diffusion balances the concentration of the acid at the point where the reaction is taking place. But if the cell has been rather completely discharged, and has been standing for some time, the layer of

sulphate, which has had time to change into the firmer and more stable modifications, must first be broken through. In this case the charging voltage overshoots a little just at first (Figure 26). It rises rapidly for a short time, and then drops again slowly to the value corresponding to the concentration of

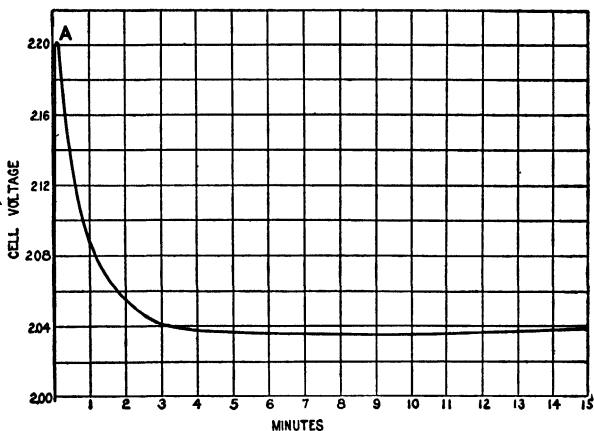


FIG. 26. — The very beginning of charge on a completely discharged plate. (Vertical scale large.)

the acid at the active point in the plate (see *A*, Figure 27). There is no positive evidence that this kind of lead sulphate is an insulator or even a very poor conductor. Measurements of the internal resistance of a discharged cell show that there is no increase at this point sufficient to account for this little rise in voltage. It seems much more probable

that the acid concentration is, as usual, responsible, and that the layer of sulphate merely prevents easy diffusion until it has been broken through. It may act for the moment as a semi- or nearly impermeable membrane, retaining the concentrated acid, and so causing the rise in electromotive force.

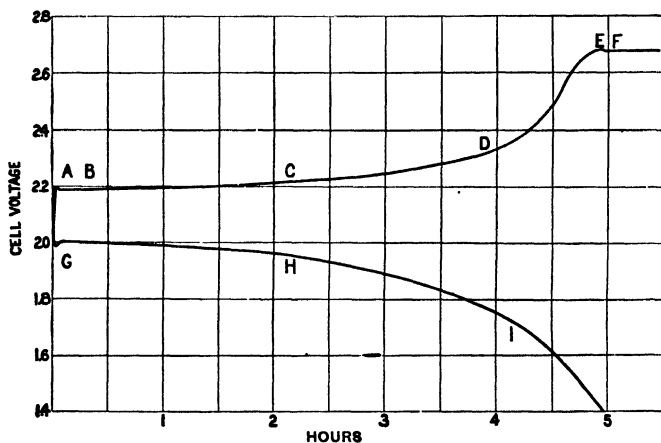


FIG. 27.— Changes in cell e. m. f. during charge and discharge at the 5-hour rate.

In any case the electromotive force of our cell very soon reaches a definite value, characterized by the factors :—

- (a) Acid density.
- (b) Temperature.
- (c) Rate of charge.
- (d) Type of plate.
- (e) Previous history.

64. Peculiarities of the Charge Curve. — At the point marked *B* on the charge curve (Figure 27) this definite condition has been reached. The condition is only momentary, and, as charge proceeds at constant rate, the electromotive force increases slowly throughout the part of the curve marked *C*. Sulphate is being transformed into lead and peroxide, and acid is being produced throughout the plates. Diffusion is becoming more and more difficult, for it must take place through ever-increasing distances, and along tortuous and minute passages. The slope at any point in this part of the curve is also a function of the five factors, and the condition of the cell as to charge can always be seen by one acquainted with the type of plate, by merely reading the voltmeter, and taking into account the time the cell has been on charge.

At *D* there comes an evident change. The curve begins to rise much more rapidly, and gas is evolved more freely. The curve rises through *E*, then drops slightly at *F*, and runs along parallel to the time axis. From this time on the cell is merely a machine for the electrolytic manufacture of hydrogen and oxygen.

The rapid change of curvature at *D* is significant. It cannot be due to any further increase in the acid concentration inside the plates, for they are nearly completely changed into lead and peroxide by now, and very little acid is being formed. What little is

formed is greatly assisted in circulation and dilution by the gas bubbles now rising from the plates. This acts as a vigorous stirrer and equalizes the acid concentration through the whole cell. The rapid rise at *D* must have another cause. Refer to the equation on page 89.

Up to the point *D* we had plenty of lead sulphate to work on, and the solution has always been thoroughly saturated with PbSO_4 , except perhaps immediately about the grains on which Pb and PbO_2 are depositing. But at *D* we begin to clear out the last of the solid sulphate and from that point on the solution becomes less and less concentrated in Pb^{++} . Part way up the curve at *E* there is so little Pb^{++} present that it is just as easy to cause hydrogen gas to leave the solution as it is to force out solid lead. This means a high electromotive force (page 92). At *E* the last of the more concentrated acid and of lead ion as well hold up the electromotive force for an instant by their presence inside the plates; they are then cleared away by streams of gas bubbles, and the charge is complete.

65. Now for the factors *a*, *b*, *c*, *d*, and *e*, and their effect on the charge curve.

(*a*) *Acid density.* The effect of various concentrations of acid on the open circuit electromotive force of the cell is shown in Figure 25. The effect at any point in the charge curve might also be found, but

it would be so very lively and changeable a factor as not to be very valuable as a criterion. From what we have already learned of the effect of acid concentration on electromotive force (page 92) we can be sure that something like the following picture expresses the factor in question. Diffusion is a function of **gradient**. Acid will diffuse out of the plate into the ambient electrolyte at a rate proportional to the difference of concentration at these two places. But acid is produced in the interior of the plate in direct proportion to the current which is passing, and regardless of acid density in the electrolyte. The same current will therefore give a greater gradient with a weaker acid in the cell than with a strong one, and the effect of the average acid on the electromotive force will be less for high than for low concentrations.

(*b*) *Temperature*. This has an important effect on diffusion. At the higher temperature diffusion is rapid, and the concentrated acid formed in the plate is rapidly removed. The voltage required to charge our cell will be lower and the whole charge curve will be changed in position and shape. This effect is, of course, quite aside from any effect of temperature on the electromotive force of the cell (see page 72), and the latter factor is for any practical cell so small as to be almost negligible, while the former factor is by no means a small one. The temperature coefficient of diffusion is about 2 % per Centigrade de-

gree and is for certain types of cell of great importance. In electric vehicle work, for instance, winter temperatures are most trying, and the effect is to reduce the apparent capacity of the battery by a considerable fraction. This almost wholly because of voltage limits imposed by the slowness of diffusion at the

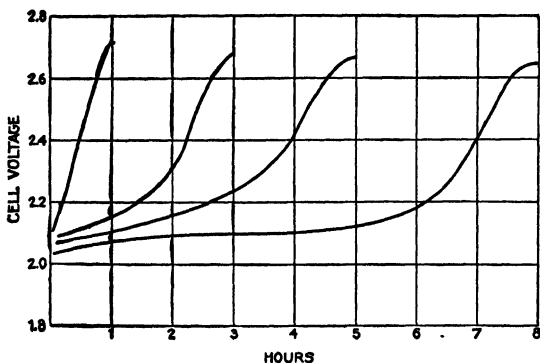


FIG. 28.— Charge curves on the same plate at various rates.

low temperature. (See page 253 for data on practical cells.)

(c) *Rate of charge.* This determines the rate at which acid is formed at the place where the action is going on. Diffusion determines how fast this acid shall be removed. At high rates the whole charge curve is steeper. (See Figure 28.)

(d) *Type of plate.* The position and slope of the charge curve vary with the plate tested. Surface, thickness of active material, hardness, are all factors.

A large-surface Planté plate, with a comparatively small content of active material, shows a curve like *A* in Figure 29. An intermediate type has the characteristics shown by *B*, in the same figure. The extreme of high capacity, a light grid with a large

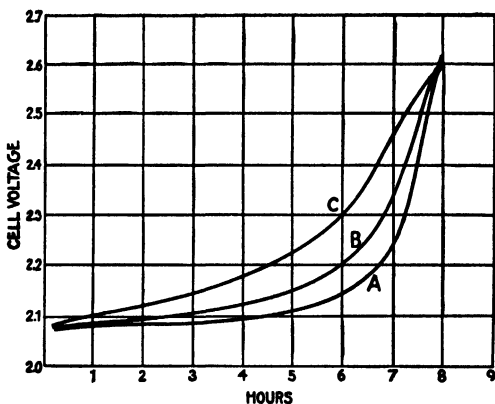


FIG. 29. — Charge curves for plates of various types.
A. Planté plates. *B.* Mixed type. *C.* Paste plates.

percentage of active material, gives curve *C*; all other factors of course being constant for the three cases. Here, as in every other case, the concentration of acid at the point of action is the deciding factor. The large surface plate is pretty freely open to the acid. Diffusion is easy, since it takes place largely through the main body of the electrolyte and not through the pores of a packed mass of active material. In the mass plate we have the other extreme.

Diffusion, except at the very outside surfaces, must proceed through long capillaries in a comparatively thick mass of active material and is correspondingly slow and inefficient.

66. Recovery after Charge.—Our cell is fully charged. The last remnants of available lead sul-

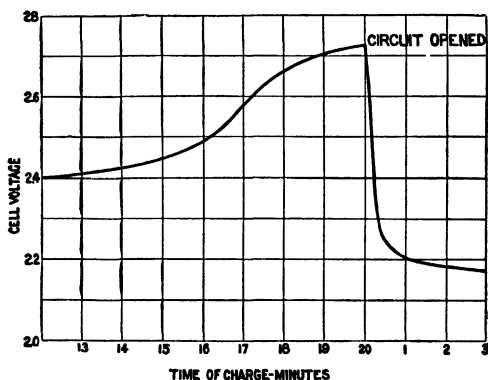


FIG. 30.—Curve showing end of charge and recovery after opening circuit.

phate have been attacked and removed and the plate is nearly pure lead or lead peroxide. Whatever sulphate is left in the plate lies too deep to be easily reached or is encapsulated with active material. When the charge circuit is broken the electromotive force drops along a **recovery curve**. Lead sulphate will now go into solution until saturation is reached, and the process of solution of the sulphate in the quiet electrolyte is largely one of diffusion. The

curve is very much like a diffusion curve, dropping rapidly at first and then more and more slowly toward a limit. (See Figure 30.)

67. Discharge.—If current be now drawn from the cell by closing the circuit through an external resist-

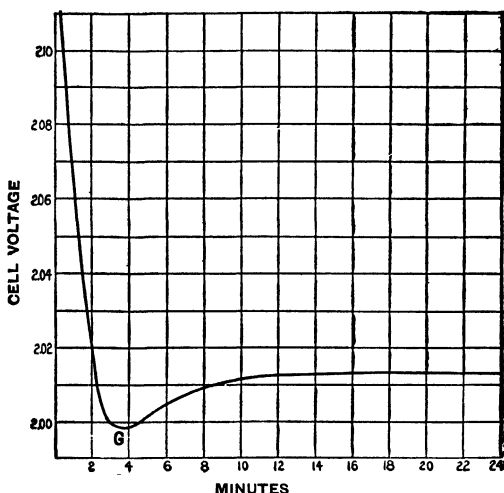


FIG. 31.—The beginning of discharge after complete charge. This curve is an enlargement of the first part of the lower curve in Figure 27.

ance, the electromotive force passes through the stages shown in the curve of Figure 27. The little hump in the curve at *G* (see Fig. 31) appears only under certain conditions, and it may be due to the formation of a supersaturated Pb^{++} solution and a correspondingly low electromotive force. This could

occur in very fully charged plates where there is not enough lead sulphate near the surface to release such a supersaturation. And, as a matter of fact, it only does appear in fresh and active plates which have been very fully charged immediately previous to taking the discharge curve. This peculiar twist can last but an instant, for then the limit of supersaturation is passed and PbSO_4 begins to deposit everywhere. The electromotive force then rises to its proper value, corresponding to the concentration of the acid (now being depleted) at the point of activity, and the curve proceeds smoothly. As discharge goes on along the curve at *H*, diffusion (now of acid *into* the plate) becomes more and more difficult. The active concentration of acid droops, and at the point *I* the cell is for practical purposes **discharged**. Its electromotive force is still 1.7 volts, and it could be run for some time longer at low rates before dropping to zero. As storage batteries are used in practice, 1.7 may be taken as the limit of useful discharge at a low rate. (See page 118.)

The five factors of page 27 are just as important during discharge as during charge and for the reasons given at that place. Acid density determines starting point and position of the curve, and simultaneous examination of discharge voltage and density, as given in the curves of Figure 32, enables one to decide upon the condition of the cell as to charge or discharge

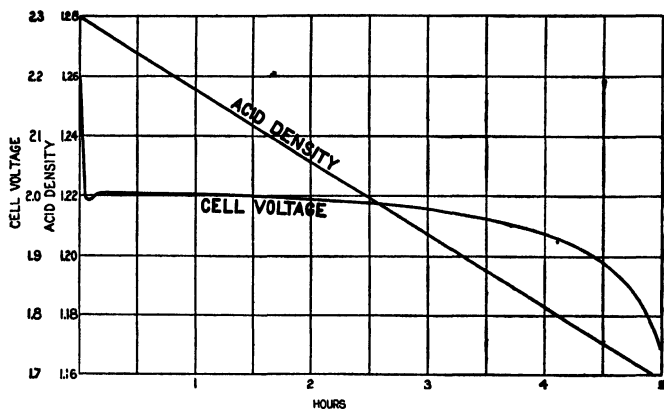


FIG. 32. — Discharge curves showing change in acid density and in voltage.

from acid density as well as from voltage. Temperature affects diffusion and therefore acid concentration at point of action and electromotive force. It

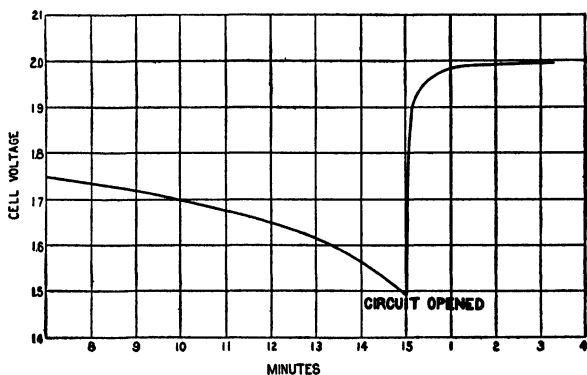


FIG. 33. — End of discharge and recovery.

also affects the electromotive force directly. Rate of discharge determines acid concentration and therefore the concentration of the active ions. Type of

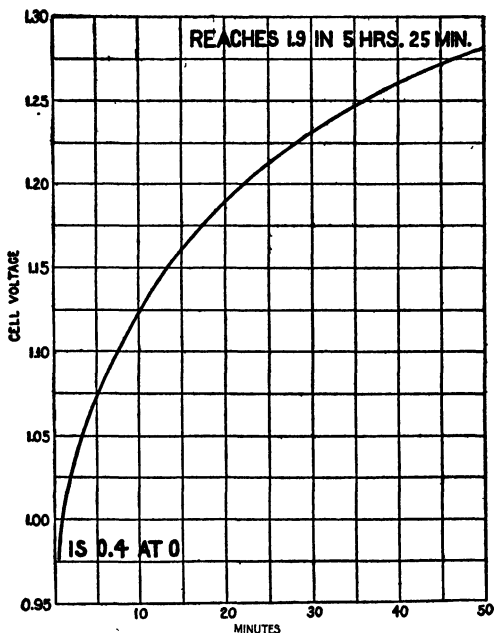


FIG. 34. — Recovery after very long and complete discharge.

plate enters and previous history of the cell. (See page 113.)

68. Recovery after Discharge. — The curve along which recovery takes place after discharge is shown in Figures 33 and 34. It is very much like a diffusion curve, and represents the rate of return to the

normal concentration of acid in the cell on the part of the acid in the deep interstices of the plates. It is not quite the right shape for a pure diffusion curve, and the equalization of concentrations throughout the cell is undoubtedly assisted by local action.

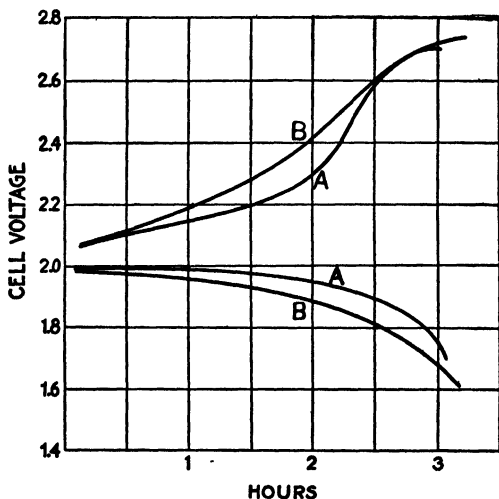


FIG. 35.—Charge and discharge curves of [A] Planté and [B] mass plates.

69. Special Peculiarities of Charge and Discharge Curves.—The two extreme types of plate — large surface Planté on the one hand, and thick mass plates on the other — show evident differences in their curves of operation. Figure 35 indicates the general character of these differences, and a résumé of the theory of the inflections of these curves will be found to

agree with the physical characteristics of the plates. It is quite possible to get composite curves from composite plates. An interesting example is the type of ribbed Planté plate now very common all over the world and used for the hardest kind of



FIG. 36. — Full discharge curve of ribbed Planté plate.

work. Figure 36 shows the full discharge curve of a Gould plate. For the greater part of its discharge it behaves like a large surface plate, which it is. Then the action reaches that part of the plate where there is a considerable mass of active material, much of it at about the same distance from the main bulk of acid in the cells. Here the droop is stopped for a short time, and only when the action has penetrated

far into this last reservoir of material does the final drop begin. And the final drop, instead of being like that of a large surface plate, is much more like a mass plate. The only reason why these peculiarities are not noticed every day is because they lie at

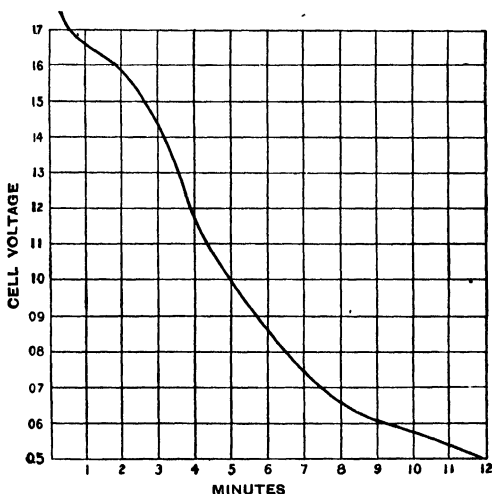


FIG. 37.—End of curve of complete discharge at constant rate (semi-Planté type).

voltages lower than those of practical service conditions. (See also Fig. 37.)

70. Charge and Discharge at Various Rates.—Figures 38 and 39 show series of curves of charge and discharge for two types of plates at various rates. They hardly require detailed discussion, for they fit very closely the general principles so often invoked in

explanation of changes in cell electromotive force. The charge curves have much the same general char-

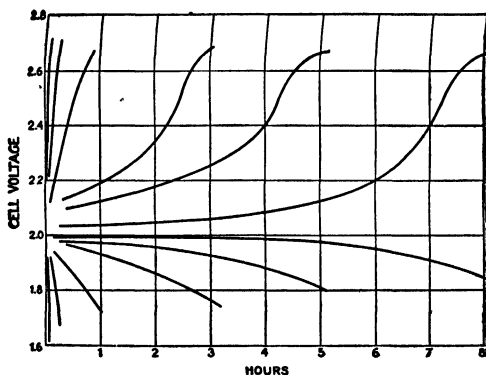


FIG. 38. — Curves of operation of Planté plates at various rates.

The rates for the curves of Figure 38 are

For 8-hours of charge or discharge 1 ampere

„ 5	„	1.4	„
„ 3	„	2.0	„
„ 1	„	4.0	„
„ 20 minutes	„	8.0	„
„ 5 minutes	„	16.0	„

These are the rates usually specified in practice.

The capacities corresponding to these rates are

For 8-hour charge or discharge 8 ampere-hours

„ 5	„	7	„
„ 3	„	6	„
„ 1	„	4	„
„ 20 minutes	„	2.67	„
„ 5 minutes	„	1.33	„

acteristics at different rates, but show more rapid changes as the rates are raised. The most interest-

ing thing about the set of curves is the information it gives about the last factor in our list — the “previous history” of the cell. It makes a great difference in the discharge curve of a cell whether the cell has been charged at a high or a low rate, and just as great a difference in the charging curve, whether the

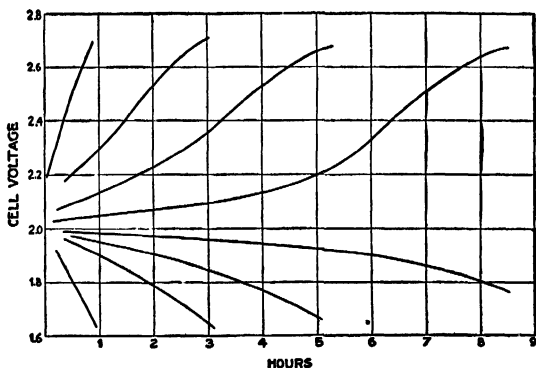


FIG. 39. — Curves of operation of mass plates at various rates.

previous discharge has been fast or slow. Take a single case. Suppose a fully charged cell has been discharged at the 5-minute rate. It is evident from the figure that only 1.3 ampere-hours have been drawn from it. We only need to return a little more than this to the cell to charge it completely. In the same way, if our cell has been completely discharged at a low rate, and then charged at the 5-minute rate, we can only get about 1.3 ampere-hours into it. It may be fully charged for a 5-minute discharge, but it is

by no means fully charged for a 3-hour discharge. When we come to the chapter on operation we shall have another side of this same problem to look at — the one which deals with the effect of charge and discharge rates on the *life* of the cell.

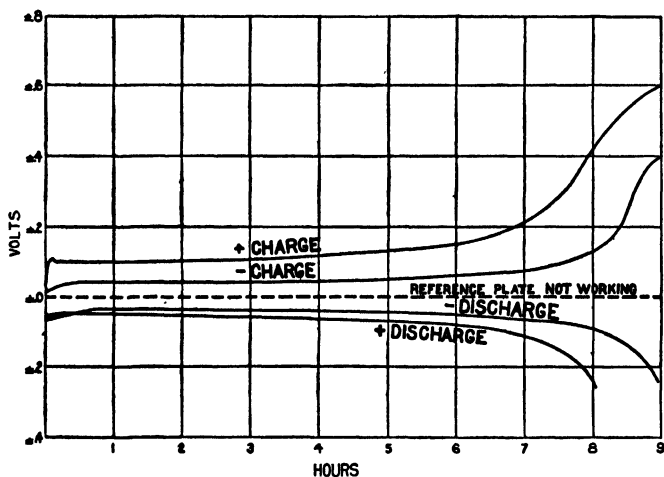


FIG. 40.— Charge and discharge curves. Peroxide and lead plates measured against an auxiliary electrode (lead plate).

71. Use of Auxiliary Electrode.—It is very frequently desirable to segregate the two plates in a cell, so that the course of charge and discharge may be followed for each separately. Several forms of auxiliary electrode have been suggested, and the one in most common use is metallic cadmium. A stick of this metal is used as one electrode, and the electro-

motive force Cd/dilute Cd^{++} against one of the plates is measured.

It is evident that this is not the most stable of electrodes, for its readings are dependent on the amount of current flowing through the cadmium circuit and also on temperature and other factors. It answers very well for most practical purposes, however, and some of the curves for single plate potentials which are given in this book were made with its aid.

Another way of following the single electromotive forces at the two plates is to use an idle lead or peroxide plate as a third electrode, measuring each of the working plates against it. Figure 40 gives charge and discharge curves for working positive and negative plates, measured against an idle lead plate.

CHAPTER X

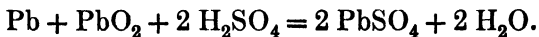
CAPACITY

In our observations on the curves of charge and discharge we found that at least five factors were active in fixing the shape and position of these curves. These same factors, together with the limit of voltage set by practical experience, determine the **capacity** of a storage cell in the sense in which this term is usually applied.

The lower limit of voltage—the point to which the cell is discharged in actual service—is not by any means invariable. At low rates, as in telephone and train lighting service, it is about 1.8 volts. In regulating power plant loads, and in much of the other regular work which a battery does, it is about 1.7. At very high rates, as when an emergency battery is called upon to take the entire load of a large station, it may be carried as low as 1 volt. Just for the present we will assume 1.7 volts as the limit below which we cannot usefully discharge our cell, and we will base its capacity on this point.

72. Faraday's Law and Capacity.—Of course capacity, in the basic sense of the word, is given by

Faraday's law, and can be calculated directly from the equation



207 gm. of lead sponge
239 gm. of lead peroxide
196 gm. of sulphuric acid

} give $2 \times 96,540$ coulombs,

and if we keep the current small enough, it might be possible to get this theoretical current yield at 2 volts.

Since one ampere-hour is 3600 coulombs, we will need for one ampere-hour, 3.86 gm. lead, 4.45 gm. lead peroxide, and 3.6 gm. H_2SO_4 , and these are the amounts of active materials which are really used up in any storage cell during the passage of current to the amount of one ampere-hour. In actual practice the voltage of the cell would have fallen to zero long before all the material in the plates and the electrolyte had been acted upon, and in any actual cell there is always a very large excess of all three of the constituents, even at the time when the cell is "discharged." Besides, there must always be supports for the active lead and lead peroxide, and these supports must in practice have strength and weight enough to enable them to withstand many complete cycles of charge and discharge. As we shall see later, there are useful types of cells in which the materials which really enter into reaction

only make up 10 or 15 % of the total weight of the plates, and only 6 or 7 % of the total weight of the installation.

73. End Voltage determines Capacity. — There is no doubt whatever about our oft-repeated fundamental principle that it is the acid concentration within the

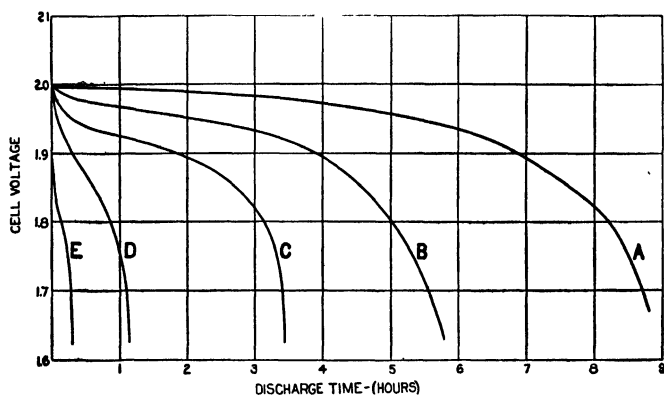


FIG. 41. — Discharge curves at various rates.

pores of the plates, at the point where the action is taking place, which determines the voltage of the cell. At a high rate of discharge, the acid density at the active point in the plate is low, and the voltage curve drops after a comparatively short time. It becomes too hard for the electrolyte to get to any more active material, even though there is plenty in the plates, and useful discharge must be stopped.

Figure 41 gives a set of discharge curves made

in actual test on a large cell. This cell was charged each time at a constant and low rate, in order that the charging part of the cycle might not be a variable factor. It was then discharged at constant temperature at the rates given. If we take as the

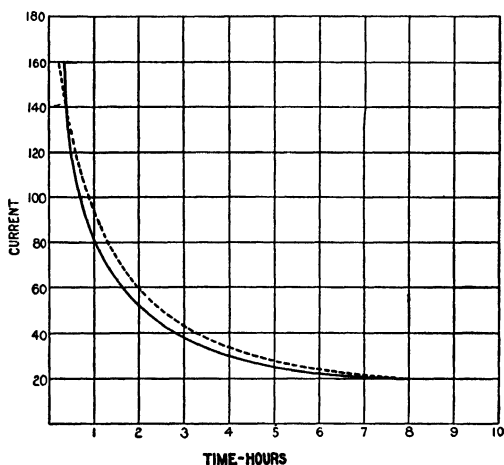


FIG. 42. — Capacity curves, theoretical (dotted), and experimental (full-line).

voltage for stopping discharge 1.70 for most of the curves, and 1.65 for the 1 hr., and 1.6 for the 20 min. discharges, we get the following table: —

CURRENT	TIME OF DISCHARGE	CAPACITY IN $A-H$
20 amp.	8 hours	160 $A-H$
40	3	120
80	1	80
160	20 minutes	53

These values can be equally well expressed by means of a single curve, for there are really only two things to be related, — current and time. The expression of the capacity in a separate column is merely for the sake of having a direct statement of capacity. Figure 42 contains this curve. It is the one which is drawn as a full line.

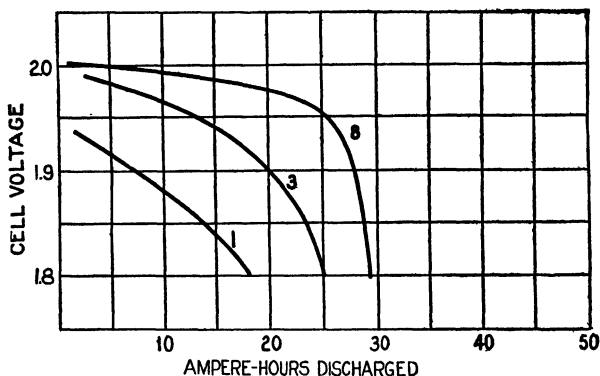


FIG. 43. — Discharge curves of Planté plates at the 1, 3, and 8-hour rates.

Figure 43 gives discharge curves for Planté plates at various rates, Figure 44 similar curves for semi-Planté plates, and Figure 45 curves for thick mass plates. In the three cases plates were chosen with the same capacity at a medium rate of discharge (3 hours). It is evident that the large surface Planté plates are best at the high (1-hour) rate, and that they are by no means up to either of the other types

explanation of changes in cell electromotive force. The charge curves have much the same general char-

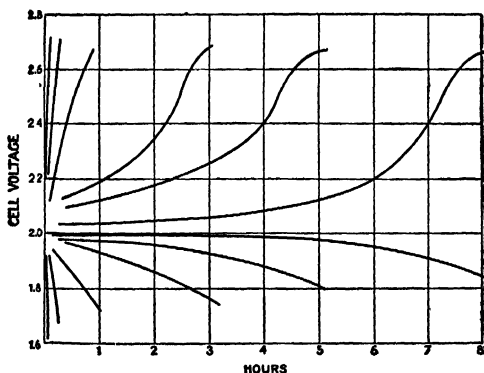


FIG. 38. — Curves of operation of Planté plates at various rates.

The rates for the curves of Figure 38 are

For 8-hours of charge or discharge 1 ampere

" 5	"	"	1.4	"
" 3	"	"	2.0	"
" 1	"	"	4.0	"
" 20 minutes	"	"	8.0	"
" 5 minutes	"	"	16.0	"

These are the rates usually specified in practice.

The capacities corresponding to these rates are

For 8-hour charge or discharge 8 ampere-hours

" 5	"	"	7	"
" 3	"	"	6	"
" 1	"	"	4	"
" 20 minutes	"	"	2.67	"
" 5 minutes	"	"	1.33	"

acteristics at different rates, but show more rapid changes as the rates are raised. The most interest-

The mass plates of Figure 45 are very short of capacity at the 1-hour rate, but they are far better than the Planté type at the low (15-hour) discharge.

The semi-Planté plate lies between the other two.

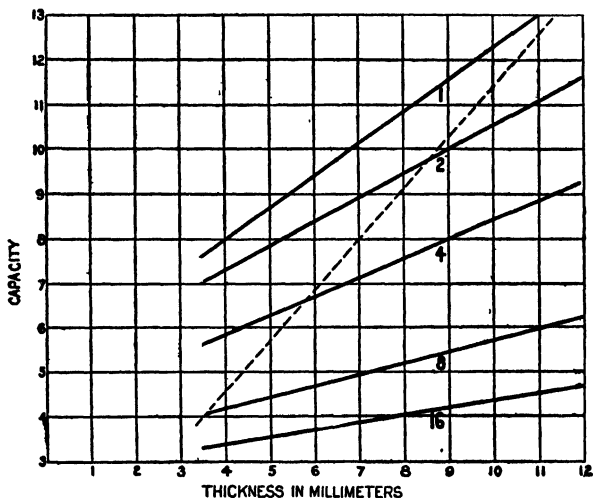


FIG. 46.—Capacity as a function of the thickness of a paste plate, at various rates. Peroxide plates against auxiliary electrode.

The useful end voltage has been placed at 1.8 volts in this case.

It is evident from these curves that the thickness (and structure generally) of a plate is a factor of importance in its working capacity. Experiments with paste plates of the same surface and varying thickness give the results shown in Figures 46 and 47, the former for positive plates and the latter for negative.

The five curves in each figure are for different rates, from 1 to 16 amperes.

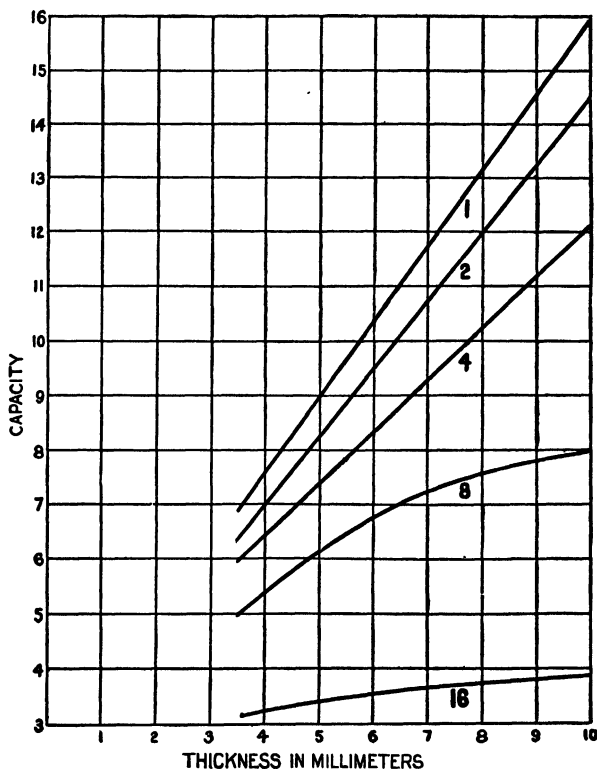


FIG. 47.— Capacity as a function of thickness of plate. Negatives against auxiliary electrode.

The dotted line in Figure 46 is for an infinitely slow rate — capacity directly proportional to thickness.

74. Formula for calculating Capacity at Various Rates.

—It is usually possible to find a not very complicated mathematical formula to fit a curve which looks like Figure 42 and the dotted line in this figure is plotted as an expression of the formula

$$I^n t = \text{constant.}$$

n for this particular type of plate is 1.45, and the constant is determined by putting in the actual values for our plate at one rate and solving the equation. See **75**, below.

This exponent n is rather a good measure of the physical qualities of a plate. It is large for thick, dense, massive ones and becomes smaller and smaller as the plate is given a larger surface in proportion to its content of active material. It goes as high as 2.0 for some plates of the most thick and tender kind, and as low as 1.20 for the most active types of large surface plates. See also Figure 48. A little calculation will show what kind of a family of discharge curves at different rates will be characteristic of each of these extremes. The one with exponent 2.0 is the easiest to calculate.

75. Let us go through the course of the calculation of such a curve for the simple case where $n = 2.0$. Assuming that the cell gives 10 amperes for 8 hr.

$$i^2 t = \text{constant}$$

$$10^2 \times 8 = \text{constant}$$

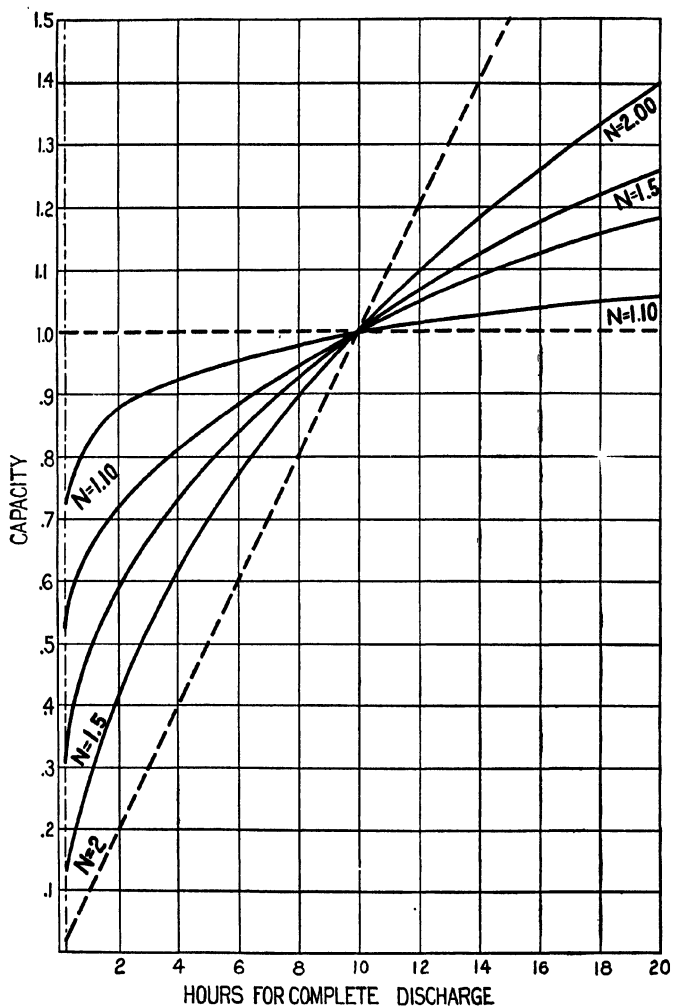


FIG. 48.

	$i^2t = 800$		
$t = 3$	$i^2 \times 3 = 800$	$i^2 = 267$	$i = 16.3$
$t = 1$		$i^2 = 800$	$i = 28.2$
$t = \frac{1}{3}$		$i^2 = 2400$	$i = 49$
$t = \frac{1}{12}$		$i^2 = 9600$	$i = 98$

and from this, when,

current is = 10,	capacity is 80.
current is = 16.3,	capacity is 49.
current is = 28.2,	capacity is 28.2.
current is = 49,	capacity is 16.3.
current is = 98,	capacity is 8.2.

If *capacity* is plotted vertically in place of *current*, the family of curves for various exponents becomes still more expressive. Figure 48 gives the calculated curves for values of n from 1.10 to 2.0.

It is also possible to derive a curve like the one in Figure 42 with the aid of the theory of diffusion, but the assumptions necessary are far-reaching, and the final formula is in fact only an empirical one like our own. Diffusion has the chief rôle to play, however, here as at every other point in the theory of the lead (and any other) accumulator.

76. Liebenow's Diffusion Experiment. — Liebenow, one of the most brilliant of the students of the lead cell, made an interesting experiment on the effect of merely allowing acid to flow through a plate which was discharging. His arrangement is shown in

Figure 49. A negative plate was used in his test, and it was found that without flow it gave 14.4 ampere-hours. With flow it gave 41.6 ampere-hours. Such experiments have frequently been performed of late, and it is a most interesting thing to see a plate which has been exhausted without flow, so that its voltage is zero, pick up and come to life again as soon as acid begins to flow through it. Its voltage rises to nearly 1.7, and it is capable of doing a great deal more work.

The object of the flow through the plate is to keep the acid concentration **up during discharge** and **down during charge** at the place in the plate

where the reaction is actually taking place. Practical applications are numerous. Large surface plates are necessary where charge and discharge rates are high. They contain much less total active material than paste plates of the same weight, but the material in them is in a thin layer, and diffusion is easy to all

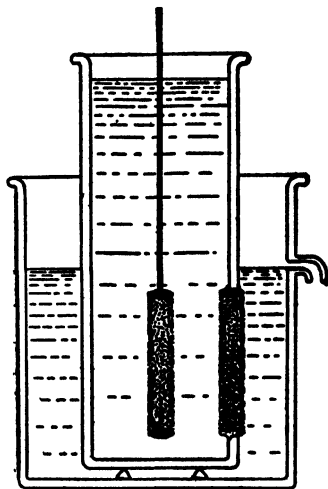


FIG. 49.—Liebenow's experiment to show the effect of forcing electrolyte through the plate during operation.

parts of it. Then, too, thin paste plates give a far larger capacity per weight than thick ones operating on the same rates and to the same end voltages. Aids to diffusion are perhaps the most important improvements which can be made in storage battery work with the exception of the all-important one of a reasonably long life under hard service conditions.

The positive plate needs help more than the negative, for besides using up or producing sulphuric acid, water appears or disappears at that point. It will be seen that it needs help 1.6 times as badly as the negative. In spite of this need it is harder to send it the necessary relief; for while negative plates can be made both tough and porous, the positive active material, lead peroxide, persists in being merely a dense but rather loosely interlocked mass of fine grains. Some rather rough measurements on the rate at which acid diffuses into positive and negative paste plates are given in Figure 50. These are resting plates, however, and do not take into account the greater need for acid of the peroxide plate during action.

Lead grows on the negative plate as real trees and sponges, and this can often be clearly seen in venerable negatives on which the lead has been deposited and redissolved thousands of times. The positives in the same cells look lean, for they have lost much of their original material, and if they are healthy, and

of the kind that have proven themselves capable of hard work, they have manufactured more active material to take the place of that lost. It is easy to apply Liebenow's principle to the negative plate. It

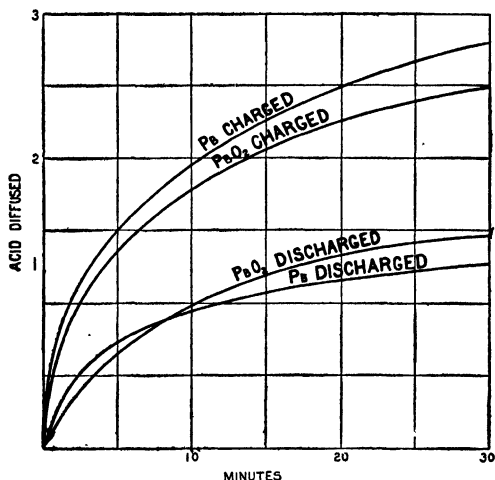


FIG. 50. — Diffusion into resting positive and negative plates.

is much harder to persuade acid to flow through one of lead peroxide.

77. Diffusion. — To digress for a moment to the general subject of diffusion. A substance in solution can move about from point to point in either of two ways — by convection or by diffusion. The difference in velocity with which a given amount of a substance can be transported from one place

to another by the two methods is enormous. Suppose a tall cylinder with a couple of inches of a strong solution of a colored salt (copper nitrate, for example) in the bottom, and with pure water filling the rest of the cylinder. By convection we could mix the whole to a homogeneous average solution in ten seconds, by violent stirring or shaking. By diffusion alone the same degree of mixing would take months.

The process of convection could be delayed in the cylinder by filling it with glass or cotton wool. In this case the transfer of material from the concentrated solution out through the dilute one has to take place through spaces in the inert substances. It is much as though the cylinder were a mile long instead of a foot. Diffusion will also be delayed by the inert filling, but in much less degree. The difference becomes still more evident if we fill the cylinder, not with pure water solutions, but with solutions which set to a jelly, such as gelatine or agar—a concentrated gel below; a pure water gel above. Now convection is entirely stopped and diffusion has all the work of transportation to do. The process becomes a very tedious one indeed.

78. Diffusion and Convection in the Cell.—In the storage battery the real transport of all material is a matter of diffusion. Solid material is there in plenty, but the acid of the electrolyte is just as

necessary for the reaction as the solids, and it has to come to the solid by diffusion through the fine pores of the active material. At certain portions of the cell cycle convection comes along to help, especially when gas is being evolved in the plates. The gas bubbles stir everything up and assist greatly in bringing materials to the point where they are needed. The difference in density between the concentrated acid formed during charge and the average acid of the cell also gives rise to convection currents, which can be clearly seen by looking across the face of a plate toward a bright source of light. If the cell is charging, a thin stream of denser electrolyte can be seen running down the face of the plate and curling up on the bottom of the cell. The more dilute acid can also be seen rising up along the face of the plate during discharge.

79. Recovery Curves and Diffusion Curves. — The curves in Figures 30, 33, and 34 are very nearly like diffusion curves. When the circuit is closed for discharge, material is rapidly exhausted near the solid particles which are active. The concentration gradient becomes steep and acid begins to diffuse toward that point. Lead sulphate is formed in the solution and presently a state of very dynamic equilibrium is reached. Acid is being transported by diffusion just fast enough to supply the demand at the point of reaction; and lead sulphate is being removed by pre-

cipitation as fast as it is formed. The curves referred to are, of course, voltage curves, but the relations of page 92 show clearly that the curves can equally well express the average concentration of reacting materials at the point of action. The recovery curve of page 133 is of the same nature. At the lower part, at the beginning of the recovery curve in Figure 33, we have the final condition described above. Materials are being supplied at a rate just able to maintain the concentration at a rather low and constantly decreasing value. When the circuit is opened, consumption of material ceases. But the concentration at the point where the reaction was going on was different from that outside in the body of the cell. Diffusion, therefore, continues and the concentration differences become smaller until diffusion becomes indefinitely slow.

Theoretically these curves take an infinite time to become perfectly flat, but practically they approach very near to a final value within a few minutes. One exception to this last statement will occur to every one who watches storage cells closely. A very fully charged cell, which has been gasing freely, takes a long time to return to its open circuit electromotive force (see Fig. 51). This cannot be due to any high concentration of acid in the pores of the plates, for practically all the materials have long since been disposed of and only an infinitesimal amount of acid is

being produced. There is another reason for this slow approach to the normal open-circuit voltage. At the end of full charge, practically all the dissolved sulphate has been driven out of solution. Opening the circuit at the end of such a charge permits lead

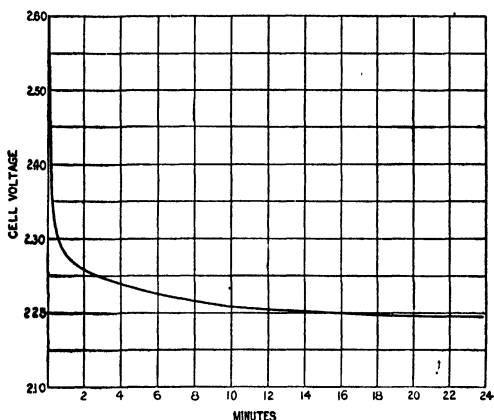


FIG. 51.— Recovery curve after complete charge.

sulphate to form. Local action takes place at the places where support and active material are in contact. So lead sulphate is soon present inside the plate. But before it reaches its normal maximum concentration at all points in the plate it has to saturate the entire electrolyte. The drop in voltage is therefore not so rapid as it would be if only acid diffusion were to be considered. Besides the diffusion of an already dissolved substance, we have to wait in this case for its formation.

80. The Effect of Temperature on Capacity. — Since capacity is determined by a fixed voltage limit as well as by other factors, we must expect to find that the effect of temperature will be a considerable one. Figure 52 gives a set of discharge curves at the same rate but at the different temperatures indicated on

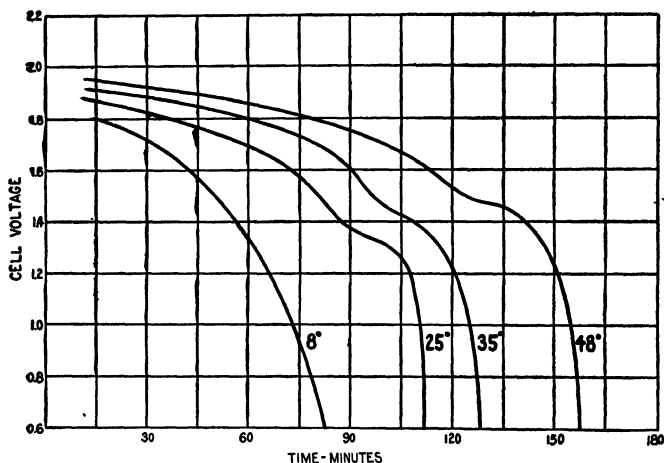


FIG. 52. — Discharge curves. All made at same rate but at various temperatures.

the curves. This was taken with constant charge conditions. The cell was in every case charged at 25° C. Its temperature was then changed by heating or cooling the thermostat in which it was kept, and after remaining constant for five or six hours, charging at a low rate all the time, the discharge was taken. The rate was such as should give complete

discharge in one hour under normal conditions of service, and the 25° curve shows this. The voltage dropped to 1.7 in just about one hour. At 48° the same cell ran for an hour and three quarters; at 8° for half an hour. A difference of over 100 % for quite possible limits of temperature, and of over 300 % within temperatures not really dangerous to the life of these cells!

This is a very high temperature coefficient, to be sure, but it is hardly possible to make a cell which has not a coefficient of at least one per cent per degree in the ordinary working range of temperatures.

Everything combines to make the storage cell work better and more efficiently at the higher temperature. For the usual acid concentration the temperature coefficient of electromotive force is positive, and has a value not far from 0.0003 volt per Centigrade degree. This, of course, has nothing to do with the **ampere-hour capacity** of the cell, except to raise the voltage a little, and thus lengthen the time of discharge a little. Examination of the discharge curves at various temperatures will show how very little this affects the total number of ampere-hours which can be taken from the cell. A difference of 30° C. means 0.0003×30 , or a rise of only 0.009 volt in the fundamental cell electromotive force due to the higher temperature, and this is not even measurable

on a curve which is drooping as rapidly as the low-temperature curves of Figure 52.

81. Reaction Velocity. — But the other two factors are highly important. One of these is the diffusion, which we have discussed at length. The other is not less important, probably, though it is much more difficult to isolate and examine. This is the **increased reaction velocity**. Whatever the reactions which are basic for the action of the cell, we have found very good evidence that the transport through the electrodes is cared for by ions which are present in very small concentration.

The velocity with which these ions are formed from the solid material of the plates, in reaction with the electrolyte, is a determining factor of importance. As a matter of fact the temperature effect on the cell is too great to be ascribed to diffusion alone. And while in most cases reactions between ions take place so rapidly that they are quite unmeasurable, it is not impossible that the effect should be evident in such a case as this, where the ionic concentrations are so very small.

82. Effect of Acid Density on Capacity. — Measurements of the capacity of a cell with varying acid density, and with all the other factors which might affect its behavior kept as constant as possible, give a very simple and interesting result. The cell shows its maximum of capacity for an acid of maximum

conductivity. This is in both cases, for sulphuric acid, of density about 1.22. (See Figure 53.) We shall be better able to explain the reason for this coincidence when we have discussed the facts about the

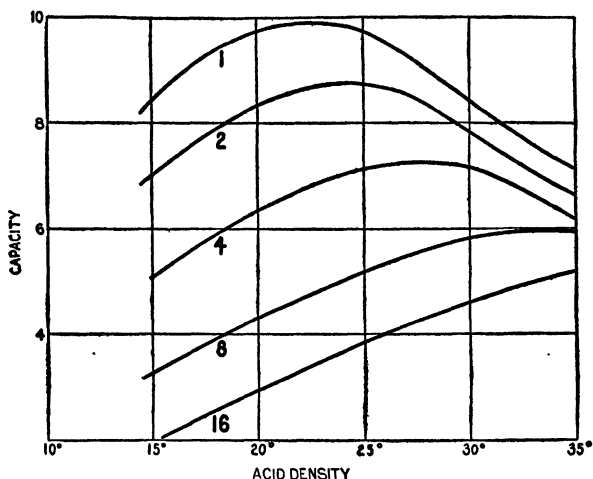


FIG. 53.— Change in cell capacity at various rates (1, 2, 4, 8, and 16 amperes) with various acid concentrations. (See also Figures 72 and 73).

internal resistance of our cell, and we will therefore leave it until we reach that chapter (page 167).

83. Watt-hour Capacity.— It is, of course, the energy capacity, or watt-hour capacity, of the cell which really interests us. This is found by multiplying the ampere-hour capacity by the average voltage of discharge. The curves of Figure 54 are the same as those of Figure 41, and on each a straight

line was laid out along the average cell electromotive force during the time of discharge. The areas under these lines, including everything from time zero to time-end of discharge, and from the line of average electromotive force down to zero electromotive force, give watt-hours if we multiply in

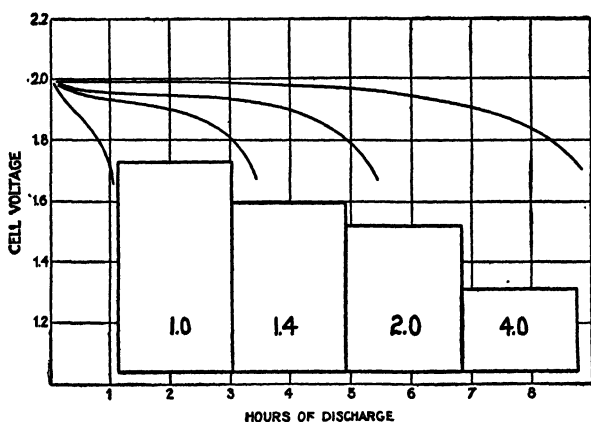


FIG. 54.— Watt-hour capacity areas at various rates, and discharge curves from which they were taken. Discharge at 1, 1.4, 2, and 4 amperes.

each case by the discharge current. The rectangles give the set of areas so produced, merely as visual indication of the variation in energy capacity of a storage cell with change in discharge current. The same differences are given in Figure 55 for temperature variation, for one type of cell only. Other curves for these same relations will be found on page

253, in the discussion of various types of cells under actual working conditions.

84. Weight Capacity.—For most purposes where the battery has to be carried about the energy capacity per pound of battery is a very important ratio. This is especially true of batteries which are used for electric vehicles, and for submarine boats. The calculation of this factor is very simple. Divide the total watt-hour output of the battery at the desired rate by the total weight of the battery and connections. Data on actual tests will be found in chapter XVIII, page 254.

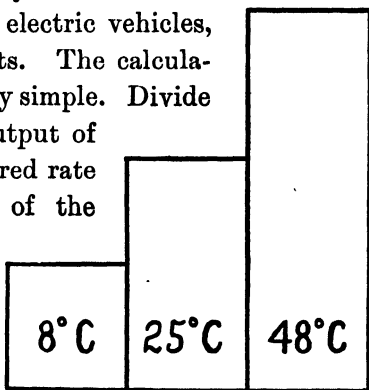


FIG. 55.—Watt-hour capacity areas at various temperatures.

This factor is not one of much interest

to the buyer of a large stationary battery, but it is a matter of interest to the manufacturer who has to pay for the lead used in making the battery, and therefore has a good deal to do with the price which he is obliged to ask for a battery to do a certain kind of work. The modern tendency to install paste plates in large emergency batteries is a good example of this fact. The paste plates give a much larger watt-hour efficiency per pound of total battery, and

as they are also much cheaper to make per killowatt-hour, they can be sold cheaper than the large-surface plates of the same total capacity. It becomes merely a question of life and cost of maintenance whether this type, or the perhaps longer-lived Planté plates, shall be used for this work.

CHAPTER XI

EFFICIENCY

85. There are two ways of stating what is called the **efficiency** of a storage cell. One of these is in terms of ampere-hours; it is the ratio of the number of ampere-hours which can be taken out of the cell to the number which must be put into it to bring it back to its original condition. The other efficiency is expressed in terms of watt-hours — the ratio of the watt-hours taken out to those put in. The first kind of efficiency is more or less misleading as a criterion of the quality of a cell, but the second is of decided interest and importance.

86. Ampere-hour Efficiency. — From what we have already said about the behavior of a cell in charge and discharge it is evident that the ampere-hour efficiency of most cells under the usual conditions will be high — it will be nearly 100%. For the only way in which current is lost is by local action and by the evolution of gas during charge. If charge is carried on at a very low rate, gas does not begin to form on the plates until very near the end of charge. The *DE* part of the charge curve (see Figure 27)

is steep and occupies only a small fraction of the whole time. Gas begins to form rather suddenly, and at this time the cell is practically fully charged. Under these conditions the ratio

$$\frac{\text{ampere-hours taken out}}{\text{ampere-hours put in}}$$

is very nearly unity.

Even at fairly high rates the production of gas only involves the expenditure of a comparatively small fraction of the current sent into the cell, and for working charge rates it leads to ampere-hour efficiencies of 90% to 95%.

The losses due to local action are very small if the cell is charging and discharging with only a small interval of rest. And this is usually the case where efficiency is a factor of importance. If a battery is standing on open circuit for a long time, with only an occasional charge to keep it in good condition, and with a rare discharge at a very high rate (as in the case of a stand-by or emergency battery), efficiency as such is not a factor which need be considered at all. The interest on the battery investment on this latter case is so much greater than all the coal expended on it that the latter item disappears completely. The factor which is of importance in such an emergency battery is **watt-hour capacity**, and if this could be attained conveniently with a cheap battery of

efficiency 20%, we would see this type of battery installed in stations which require this kind of "insurance."

Formally, ampere-hour efficiency is

$$AE = \frac{i_{\text{disch}} t_{\text{disch}}}{i_{\text{charge}} t_{\text{charge}}},$$

and for most purposes in service it will be found to be from 90% to 95%. As far as this is concerned the battery is about as efficient as any of the ordinary electrical machinery.

87. Energy Efficiency. — The other and more important kind of efficiency is **energy** efficiency, and this is the ratio of the energy which can be taken from the cell to that put into it. Or,

$$EE = \frac{\text{watt-hours taken out}}{\text{watt-hours put in}}.$$

This is also evidently expressible as

$$EE = \frac{i_d t_d e_d}{i_c t_c e_c},$$

where i and t have the same meaning as above and e_c and e_d are the average cell voltages of charge and discharge respectively.

88. Data for Efficiency Calculation. — The most direct way to get data on the value of EE is for us to examine sets of curves like those in Figure 41 and Figure 53 and calculate ampere- and watt-hour

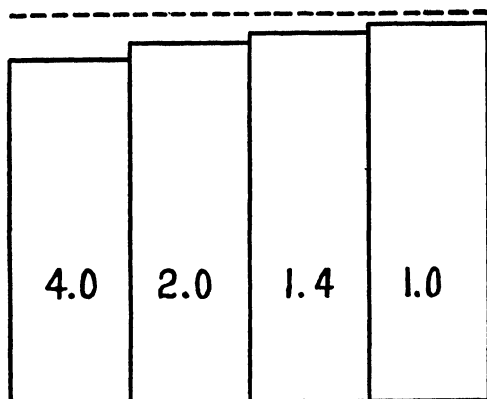


FIG. 56.— Ampere-hour efficiencies at various rates. Planté plates discharged at 1, 1.4, 2, and 4 amperes. Charge at 1 ampere.

efficiencies from them. Figures 56 and 57 give areas so calculated from a similar set of charge and dis-

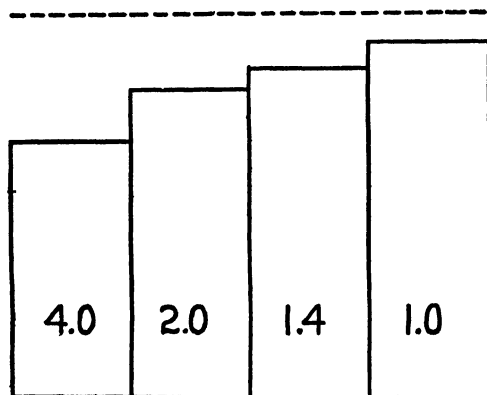


FIG. 57.— Watt-hour efficiencies at various rates. Planté plates discharged at 1, 1.4, 2 and 4 amperes. Charge at same rate as discharge.

charge curves. It will be noticed that while the ampere-hour efficiencies are good enough even at the higher rates, the watt-hour efficiencies fall off pretty rapidly, going as low as 60 % at the highest rates of charge and discharge. These are rather extreme cases, however, for storage cells in hard service are

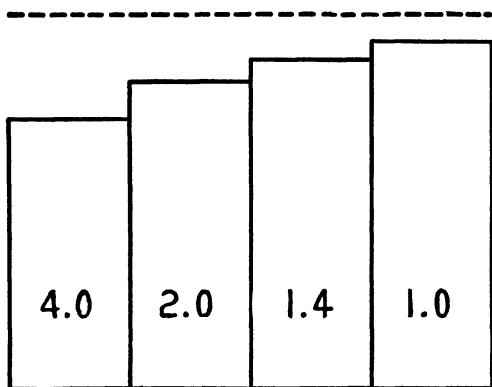


FIG. 58.

rarely charged as fast as they are discharged, and the actual figures are a little higher than those obtained by holding rigorously to a charge rate as high as that of discharge. This will be very evident if we take a medium rate for charge and determine efficiency for this rate and various discharge rates. Figure 58 gives these data. Here we have assumed the one-hour rate of charge, and taken the corresponding curve through-

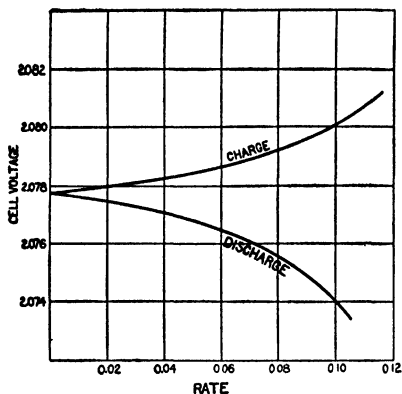


FIG. 59.—Charge and discharge voltages at very low rates.

out. At very low rates the charge and discharge voltages may be nearly the same throughout the whole cycle of operation. Figure 59 shows the change in cell voltage at the various low charge and discharge rates given.

At the lowest rates the cell shows an efficiency of nearly 100 %.

Figure 60 shows charge and discharge voltage at practical rates.

In batteries which are worked severely every day and all day, at rates which average perhaps as high as the one-hour rate of discharge, the matter of efficiency is worth careful consideration. Under

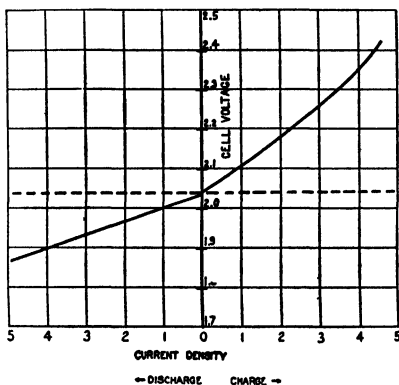


FIG. 60.—Average voltages of charge and discharge at various practical rates. Planté cells.

these circumstances the difference in the coal bill for an efficient and an inefficient battery may be of the same order as the depreciation and maintenance of the battery for the same length of time. In vehicle batteries which are worked on regular runs leading to a full discharge every day or oftener, the same relations will be found to hold. A difference of 10 % in watt-hour efficiency will be of the same importance in dollars and cents as the depreciation on the battery for the year. It is on such points as this that choice must be made between two types of battery. The battery with the slightly higher depreciation or shorter life is sometimes to be chosen for the sake of the saving which can be made with it on account of its higher watt-hour efficiency. We can of course discuss matters of price and cost only in the most general way, but we shall often have occasion to call attention to points like this.

CHAPTER XII

INTERNAL RESISTANCE

89. Practical Cells.—The internal resistance of a storage cell of commercial dimensions is very small indeed and may frequently be entirely neglected in calculations on the circuit containing a battery of cells. Even in small portable cells the resistance seldom rises above 0.05 ohm and in large stationary cells it may be as small as a few hundred-thousandths of an ohm.

90. Specific Resistance.—In calculating and stating the resistance of a substance we always take as reference a cube of the substance 1 cm. on an edge, with electrodes covering the two opposite faces. This **specific** resistance once known, we can calculate the resistance of a wire of any size or length made from the same material.

$$R = K \frac{l}{q},$$

where K is the specific resistance, l is the length, and q the area of the cross-section of the conductor, and R is the required resistance.

The table on page 263 gives the specific resistance

of some important substances. All pure metals have positive temperature coefficients — they increase their resistance when they are heated. All electrolytes, on the contrary, decrease in resistance with rise of temperature. An alloy may behave in either way or

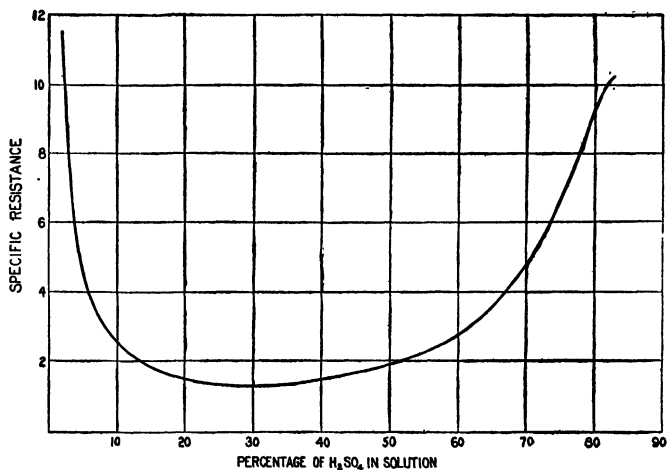


FIG. 61. — Specific resistance of sulphuric acid solutions containing varying percentages of 1.842 acid.

may have a positive coefficient at one temperature and a negative one at another.

In the storage cell the solid substances all have positive coefficients like metals. The electrolyte is of course a member of the other class. The specific resistance of sulphuric acid of various concentrations is given in Figure 61.

For many calculations it is more convenient to

use the reciprocal of the resistance, the conductance, and the corresponding specific conductance. The conductance of electrolytes forms one of the most interesting chapters of general electrochemistry, but we shall not have occasion to use many of its principles, and it must therefore be looked up in some other book.

Unit conductance and unit resistance refer to the same thing. A wire with resistance 100 ohms has conductance 0.01, and so forth.

91. Acid Resistance in the Cell. — Let us calculate the approximate resistance of the electrolyte alone in some cells of very different size. First, a sparking cell with three plates each 3 in. square (7.6×7.6 cm.) and 0.4 in. apart (1 cm.). The total acid area is

$$7.6 \times 7.6 \times 2 = 115 \text{ sq. cm.}$$

The specific resistance of sulphuric acid of cell strength is about 1.5, and since the plates are about 1 cm. apart, the resistance of the cell will be

$$1.5 \times \frac{1}{115} = 0.013 \text{ ohm.}$$

The second calculation will be for a fairly large cell such as would be used in a regulating battery. It contains thirty-one plates, each 15 in. square and with 0.4 in. separation. The acid area is in this case

$$42 \times 42 \times 30 \text{ cm.} = 17,000 \text{ sq. cm.,}$$

and the acid resistance of the cell is

$$1.5 \times \frac{1}{17,000},$$

or a little less than 0.0001 ohm.

About the largest cells which are in common use have perhaps 131 plates about 15×30 in. In such a cell the acid area is therefore about 290,000 sq. cm. and the acid resistance is about 0.000005 ohm.

92. Acid Resistance and Temperature. — The change of resistance of the cell acid with temperature is shown in the dotted curve of Figure 62, and it is also given quite accurately by an equation of the form

$$R_t = R_0(1 + \alpha t + \beta t^2)$$

where α and β are calculated from measurements made at two temperatures.

93. Acid Resistance and Cell Losses. — It may be taken as an approximate general statement that the total internal resistance of a cell is about double the acid resistance. This approximation is usually sufficiently close to be useful in the calculation of losses inside the cell due to resistance.

Suppose we are drawing an average current of 2000 amperes from our biggest cell just considered. The losses in the cell are

$$i^2r = 2000 \times 2000 \times 0.00001,$$

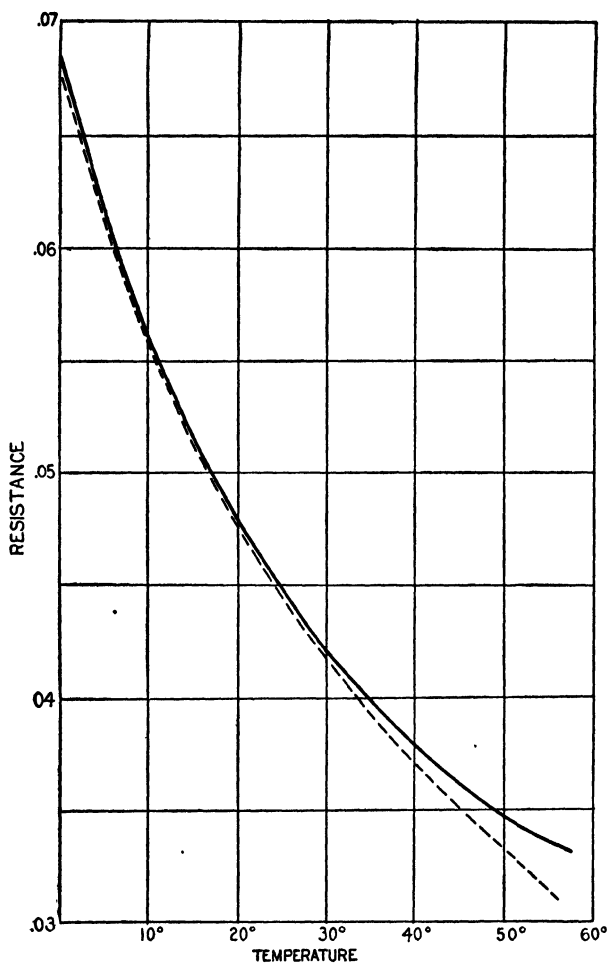


FIG. 62.— Change in resistance of cell acid with temperature (dotted line).

40 watts in all. The cell is furnishing $2000 \times 1.8 = 3600$ watts, and our resistance loss is therefore just about 1%. This is so small in comparison with the normal working losses of the cell at this rate (about 25 %) as to be negligible.

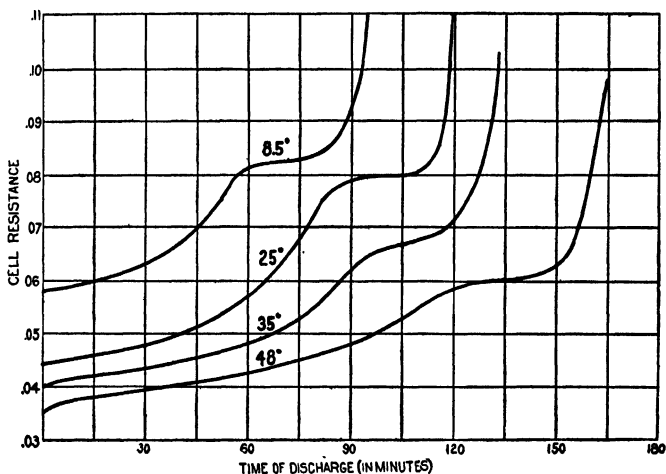


FIG. 63. — Resistance curves of Planté cell during discharge at various temperatures.

94. Resistance Curves. — It is quite true that the internal resistance of a storage cell is usually negligible as far as loss of energy is concerned. There are, however, many things of great theoretical (and therefore practical) interest about this factor. Hardly anything about a lead cell gives so clear an insight into its internal workings as its internal resistance. Even its voltage curve cannot tell more

about the minute phenomena of charge and discharge than can be seen from its resistance curve. Figure 63 gives a set of curves of resistance taken during the discharge of a Planté cell at various temperatures, and Figure 64 gives both voltage and

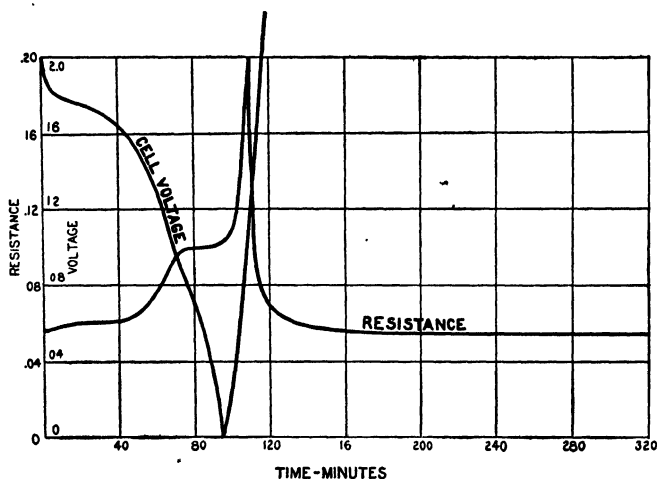


FIG. 64. — Curves of resistance and voltage during complete discharge and partial reversal of a Planté cell.

resistance for the same cell at one temperature. It will be noticed that the change in resistance is considerable, if the cell is discharged down below its usual end voltage—say down nearly to zero. Figure 65 gives voltage and recovery curves during partial discharge and recovery curves after open circuit immediately following the discharge.

95. Factors of Resistance. — The total cell resistance is evidently made up of at least three distinct parts as indicated in the diagram of Figure 66: —

A. Support plate.

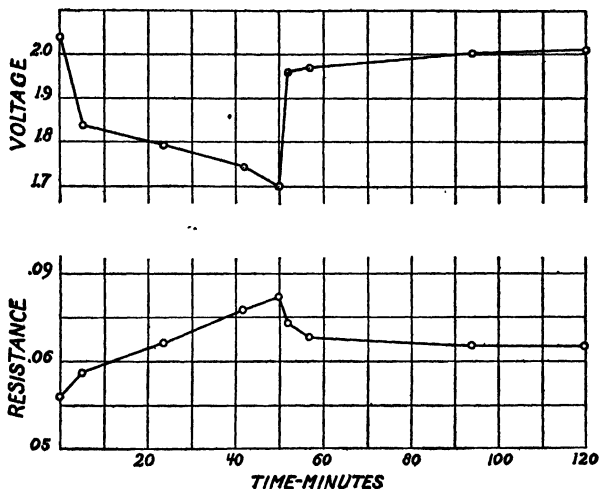


FIG. 65. — Curves of resistance and voltage during discharge and recovery. Planté cell.

B. Active material, including electrolyte in the pores.

C. Main body of electrolyte.

A and *C* we can consider practically constant, and if *C* changes, we can calculate the amount of the change from the data of Figure 61, which gives the relation between resistance and acid concentration. *B* is the variable part of the system.

During charge the active material first to react is near the surface of the plate, and the electrolyte does not have to diffuse far through the narrow channels of the mass. As the diffusion path increases and the cell becomes more fully charged, concentrated acid is produced in the pores. But all through the

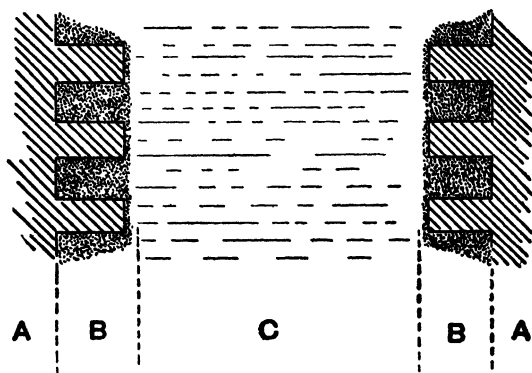


FIG. 66.—Diagram of the parts of a Planté cell.

charge it is the solid plate itself which does most of the conducting, and the change of resistance to be expected during charge is therefore not great.

During discharge a very different state of affairs exists. In this case also the action begins at the surface, where there is plenty of both electrolyte and active material. But as discharge proceeds the area of activity moves back deeper into the mass, acid is used up within the plate and must be replaced by diffusion. The acid concentration becomes much

lower at the point of activity, and there is added to this the loss of conductivity by the solid plate itself. The particles of lead and lead peroxide in the outer layers have now become covered with a layer of lead sulphate and have been more or less insulated from each other. The result is as if the distance between the plates had been increased, for the plate surface which is actually carrying the current has moved from the surface back into the interior of the plate. The surface of the plate in contact with electrolyte has also been greatly decreased by this displacement of the active plate surface.

Such changes as these are quite sufficient to account for the change found in the resistance of cells under the usual conditions of charge and discharge. We should not expect, and we do not find, any very large or very rapid changes in cell resistance.

96. Sulphation. — On long standing, a storage cell may acquire a very high resistance indeed as the result of complete "sulphation." This means that the active lead sulphate formed during normal discharge has gradually changed into the inactive crystalline form, and that crystals of this inactive modification have completely covered the particles of lead and lead peroxide with an insulating coating. Authentic cases are known of large cells with internal resistance as high as 10 ohms.

As usual, it is hard to make things act properly

when you want them to. I have left a completely discharged cell for six weeks or more, carefully following its internal resistance every day, and found no change of more than a few per cent in its resistance. It seems very likely that the ordinary cases of sulphation, which are rather common and most annoying in their results, do not lead so much to a very high internal resistance as to poor contact between particles of active material. The electrolyte can get into the plate or the grid well enough, and the internal resistance of the cell can therefore not be very high. But the capacity of the plate has suffered because a good deal of what ought to be available active material has been incapsulated by sulphate and removed from the reach of plate activities.

In ordinary practice, the cell is discharged only until its electromotive force sinks to about 1.7 volts. This means that only perhaps a quarter of the active material of the plates has entered into reaction, and that the increased resistance in the active mass is due rather to separation of particles by sulphate coatings than to complete transformation of the active material at any place into insulating material. During the charge, sulphate coatings and bridges are rapidly broken down, and the decrease in resistance during charge is therefore more rapid than could be explained by a change in concentration of electrolyte within the pores of the plate.

After a period of discharge, with corresponding increase in resistance, the cell recovers its original electromotive force along a curve nearly like a diffusion curve when the circuit is opened. It also recovers its original resistance along a very similar curve. (See Figure 65.) This fact indicates the dynamic nature of the equilibrium which causes the cell to have any particular electromotive force or resistance at a particular place in its discharge, charge, or recovery curve. The particles of active material cannot have been completely covered by insulating sulphate, for on standing, the plate returns to its original condition as far as we can measure it by an examination of either electromotive force or resistance.

We must evidently think of the lead sulphate as swelling up and almost plugging canals which lead to unchanged lead and lead peroxide. The density of the sulphate is much less than that of the materials from which it is formed, and while the particles of lead or peroxide may have had plenty of space between them at the end of charge, the sulphate must shut off much of this from activity at anything like a practical rate of discharge. As long as no current is flowing, acid does make contact with the remanent active material and the active plane in the plate draws out toward the exterior.

In Figure 62 the full-line curve gives the open circuit resistance of a small Planté cell at various

temperatures. The dotted curve shows only the **shape** of the curve for the electrolyte, and not its true value, which would be only about half that of the cell at any point. The acid curve was plotted in this way to show how the cell resistance departs from the acid resistance at higher temperatures. Probably the solid resistances of grid and active material begin to make themselves felt, and as these have positive temperature coefficients, the increased resistance makes the cell take a sharper turn than the electrolyte. That the resistance of the plate material becomes a factor is shown by the fact that pasted plates of slightly greater area, placed as nearly as possible the same distance apart, show a decidedly greater resistance on open circuit than the Planté plates. The cells with paste plates have about 25% higher resistance.

97. Effect of Distribution of Material on Resistance Curves. — The curves of Figure 49 speak for themselves. The only queer thing about them is the flat place which appears after 60 to 80 minutes of discharge. This is characteristic of Planté plates with ribs, and does not appear in the curves for paste plates. The ribs of these plates are formed into active material, which lies close to the ribs at their tops, but which forms a solid mass down at the bottoms of the ribs. (See Figure 67.) During the first part of the discharge the electrolyte finds active material on the

ribs, and diffusion takes place largely through the open space between them, and only for a small distance through active material. As this easily available material is used up, the action moves farther down into the plate and presently reaches the mass of material at the bottom of the grooves. Here for a time there is material enough at a nearly constant distance from the surface of the plate, and after this has been passed the resistance rises very rapidly and the plate potential shows that the cell is completely discharged.

If there is anything in our fundamental theory of the dependence of electromotive force on acid concentration, the curves of electromotive force of these cells ought to show a corresponding flat place somewhere near the same point in the discharge curve. The curves of Figure 52 show it clearly except in the one for 8° C. We missed it here by not taking points near enough together, for it shows clearly in the curve of Figure 64, which was made on the same cell at another time. This curve gives the course of electromotive force and resistance during a complete discharge followed by partial re-

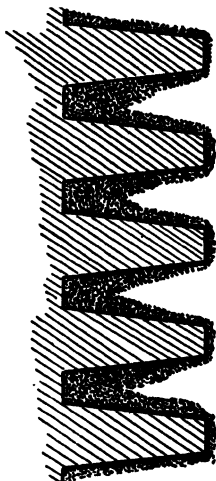


FIG. 67. — Diagram of distribution of active material on ribbed Plante plate.

versal. If our explanation is correct, the resistance ought to decrease very rapidly after passing through a maximum at about the end of complete discharge. The curve is in agreement with this idea.

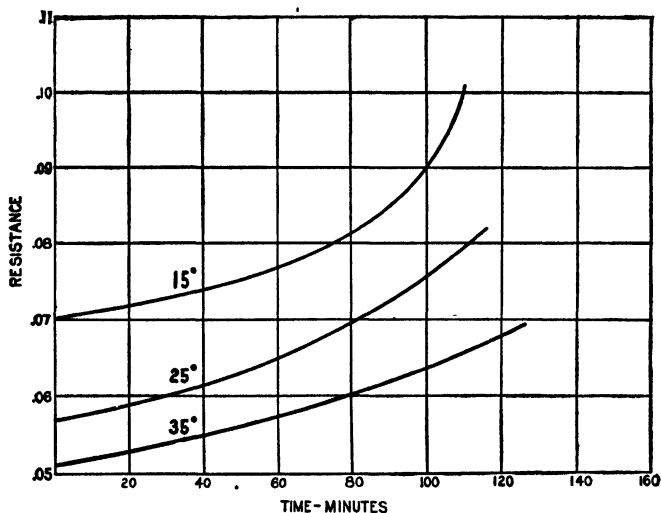


FIG. 68.— Change of internal resistance during discharge at various temperatures. Paste plates.

98. Paste plates show smooth curves of resistance, as shown in Figure 68.

Our resistance curves should also be characteristic when taken for different rates, and Figure 69 shows this for the same Planté plate cell at constant temperature.

99. A most interesting idea of the lively dynamic

nature of the momentary equilibrium existing in the cell at any time during the cycle is obtained by plotting curves of **constant composition** at various times and temperatures. The curves of Figure 63

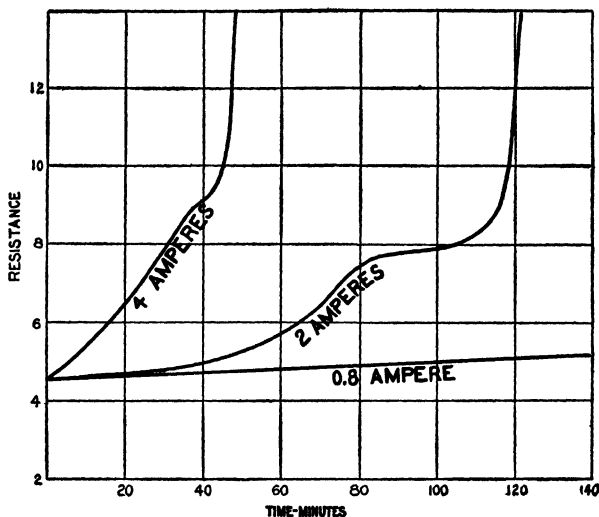


FIG. 69.—Change of internal resistance at various discharge rates. Planté cell.

are isothermal curves. Each one shows the course of the change of resistance during discharge at constant rate and constant temperature. Since Faraday's law is true, the cell contains exactly the same amount of lead, lead peroxide, lead sulphate, sulphuric acid, and water at the end of the same time of discharge. Curves of constant composition will

therefore result if we cut these isothermal curves at times 30 min., 1 hr., 2 hr., etc., and plot the values so found — resistance against temperature. Figure 70 shows a set of curves so found. The curve $T = 0$ is for open circuit, and it gives the temperature

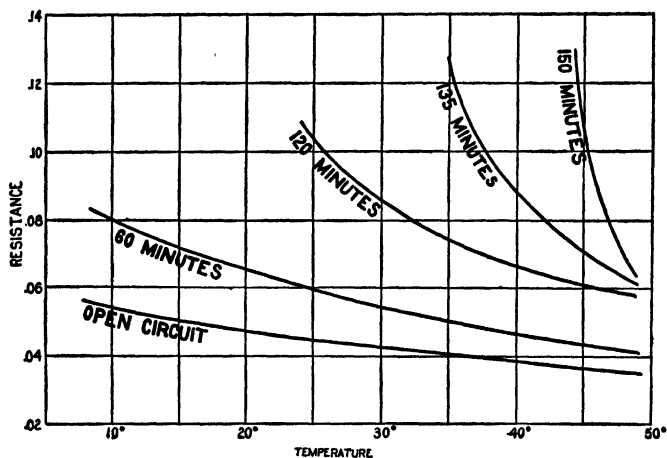


FIG. 70. — Resistance curves corresponding each to constant composition of plates and electrolyte made by cutting the curves of Figure 63 at various times.

[For example, after 60 minutes of discharge at 25° C, the cell had a resistance of 0.06 ohm.]

resistance curve for the cell, like the full curve of Figure 62, but on a different scale.

The slope of the curve $T = 0$ gives the temperature coefficient of resistance on open circuit at the temperature corresponding to the point where the slope is determined. The slope at any point on one

of the other curves is the temperature coefficient corresponding to the temperature where the slope is taken. For all the curves except $T = 0$ the condition of the cell is one of momentary dynamic equilibrium. The materials are in the cell, without any doubt, but their **distribution** depends to a great extent on the temperature at which discharge has taken place.

100. Temperature Coefficient during Activity. — The open circuit temperature coefficient is about 1.5% per degree. The coefficient after 150 min. of discharge is 23 % per degree. This latter value is of course not like an ordinary temperature coefficient, but it is most expressive of the lively nature of the factors which determine the condition of a lead storage cell at any moment in its life.

Corresponding curves for cell voltage are given in Figure 71.

101. Capacity and Acid Density. — At this point we are prepared to examine the question left unanswered on page 137. Why does the capacity of our cell reach a maximum for acid of density about 1.22, as appears from the measurements?

The statement requires elaboration. It is not true at all if the cell is examined at various working rates, and if we measure merely the acid density in the main body of the cell. It may very well be the truth, if we take into account the dilution of the

acid in the pores of the active material, and if we base our calculation on the density of acid inside the plate.

The curves of Figure 53 show how the capacity of the cell changes with the acid concentration in the

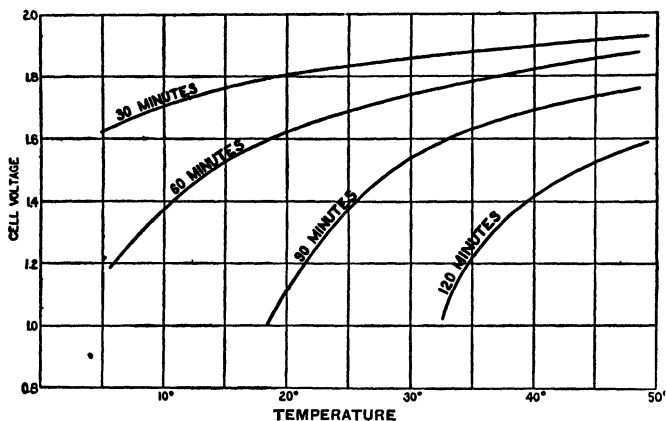


FIG. 71.— Voltage curves corresponding to constant composition of plates and electrolyte.

[For example, after 60 minutes of discharge at 25° C, the cell showed a voltage of 1.69.]

electrolyte. This particular set of curves was made with paste plates, and corresponding curves for large surface Planté plates would show some difference in shape and would have their maxima at other points. But it is very evident in every case that the maximum of capacity shifts toward the region of higher acid density as the rate is raised. Rate must evidently be taken into account in making any state-

ment about the relation between capacity and acid density. This becomes still more evident if we examine into the change of capacity of positive and negative plates separately. Figure 72 gives data for the positive plate and Figure 73 for the negative.

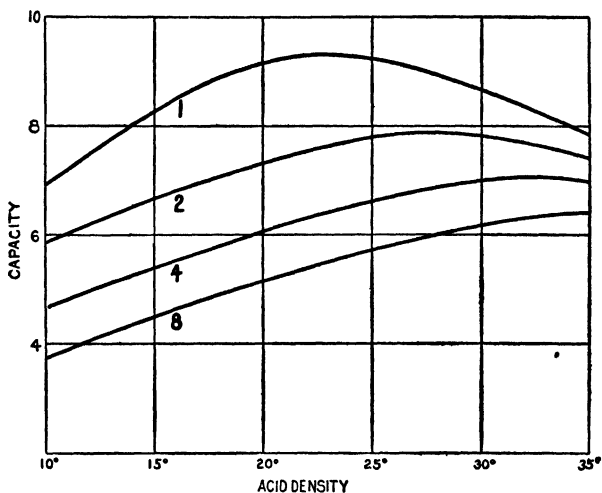


FIG. 72. — Change in capacity with variation of acid density. At discharge rates of 1, 2, 4, and 8 amperes. Paste positive plates, measured against auxiliary electrode.

It is evident that as far as the positive plate is concerned we must go up to a very high value of acid density to reach the maximum of capacity, while for negatives at ordinary rates we need only acid of ordinary density to bring us out to the maximum. For the positive we should have acid of

density 1.32 and higher. For the negative we need only to go as far as 1.2, which is well within the range of practical operation. The facts have somewhat the appearance of contradicting the explana-

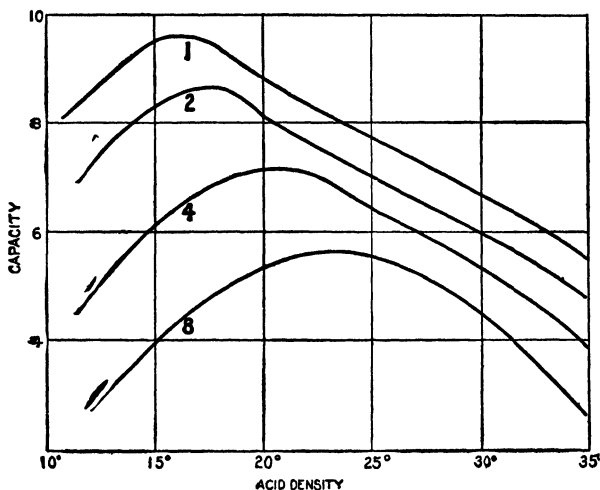


FIG. 73.— Change in capacity with variation in acid density at various rates. Negatives.

tion which Dolazalek gives for the appearance of this maximum. He says:—

“At the beginning of discharge the current lines enter only the outer layers of the active material, where they find the least resistance. As the change in concentration develops polarization in the outer layers, the current lines penetrate deeper and deeper into the plate, and these lines have density such that

everywhere in the pores the drop in potential (ir) is equal to the polarization prevailing in the outer layers. This condition must of necessity be fulfilled, for the active material, lead as well as lead peroxide, is a good conductor, and the potential must therefore be the same in the pores and out near the surface of the plate. If the polarization in the outer layers has reached 0.2 volt, the potential of the whole accumulator has also fallen by the same amount, and this would be the point at which discharge would be stopped. At this time the current lines have penetrated so far into the active material that the drop of potential in the pores — the product of current and pore resistance (ir) — has also reached the value 0.2 volt.

“But the resistance of the pores is determined by the conductivity of the acid which fills them. The better the acid conducts, the later the moment will appear when the product (ir) reaches the value 0.2 volt, and therefore the greater the capacity of the cell. The conductivity of sulphuric solution increases at first with increase of concentration, reaches a maximum at 30% of H_2SO_4 , and then decreases again. The above discussion shows that the capacity must also reach its maximum for 30% acid, and this is splendidly confirmed by the measurements.”

As a matter of fact, it is quite evident from the curves that the measurements do not confirm this

conclusion at all, if we confine our measurement of acid density to reading a hydrometer placed in the cell electrolyte between the plates. But if we consider at the same time the difference between the density of the acid in the pores and that in the main body of the electrolyte, — this same difference which we have already had occasion to mention so often, — Dolazalek's hypothesis fits much better.

102. The Concentration of the Active Ion. — The ion which really determines the electromotive force at the cathode (the peroxide plate during discharge) is H^+ , and the current is driving this ion toward the peroxide, $2 H^+$ for each SO_4^{--} sent in the opposite direction, and five times more rapidly as well, because of its greater migration velocity. The reaction at this electrode requires $4 H^+$ for each PbO_2 , and $2 H_2O$ is formed as the result of the reaction. Besides the lowering of acid density due to the formation and precipitation of $PbSO_4$, we are diluting our electrolyte by the addition of $2 H_2O$. Acid of maximum conductivity is about 1 of H_2SO_4 to 19 of H_2O , and it may very well be possible that the acid concentration out in the cell is **much** higher than it is in the pores at the place where the reaction is taking place.

At the negative plate (the lead plate) things are not so bad. Here SO_4^{--} is the determining ion, and it is used up in the pores to form $PbSO_4$, more being

sent along as an ion by the current. Here we do not have the formation of water to dilute the acid at the point of reaction, and in spite of the fact that the SO_4^{--} moves much more slowly than H^+ , there is less change of density inside the plate. A smaller excess density in the main body of the electrolyte is sufficient to maintain the concentration at the point of action.

CHAPTER XIII

PHYSICAL CHARACTERISTICS

103. So far we have been considering the chemical processes in the cell and the behavior of the elements of the cell under varying conditions. We have not paid much attention to the physical nature of the plates and we have been judging them by their works rather than by their looks. It is interesting to examine the plates of our cell somewhat more closely — they sometimes give a good deal of valuable information.

Most of the hard battery service is done by plates of the Planté type. This name does not now mean the lead sheets used by the inventor, but indicates that the active material of the positive plate has been formed from metallic lead and not from a paste of lead salts. For the hard service into which these plates are called certain fundamental properties are necessary. Most important of all is the power to deliver current at a high rate with a reasonable efficiency. A reasonable life must also be given under these service conditions.

The type is a comparatively simple one. It may

be represented diagrammatically by Figure 66. Its special characteristics are:—

Large surface.

Active material near conducting plate and electrolyte.

Reserve of metallic lead for further formation in service.

A certain minimum of mechanical strength.

A new positive plate of this type should have just enough peroxide on it to give its rated capacity, without much to spare. This peroxide has been formed in the factory under the most favorable conditions, and it may even contain a little cement sulphate from its rapid formation. If it goes into good hard service, it probably loses a full quarter of this original peroxide in a few months. Whatever there was on the plate that was at all loose or liable to become so, has been knocked off by the rapid evolution of gas during charge. By this time the original material, whatever its nature may have been, has been replaced by a firmly adherent and dense layer of peroxide which hugs close to the lead of the plate. Ribs, rosettes, and pores have opened to better diffusion of the electrolyte, and the plate with its rather "skimpy" but readily accessible peroxide layer, is in the pink of condition for hard work. Its capacity at the high rate at which it is working is perhaps even increased, in spite of the fact that it has lost a good

quarter of the active material with which it started to work and has probably regained but a very small fraction of the loss. .

If this same positive plate has gone into slow and easy service, it will also change, though not so much in external appearance, after a few months of service. Its ribs or rosettes will become filled with peroxide, and it will increase in total capacity. Too low a charge rate is liable to crowd the spaces in the plate and produce buckling or twisting.

In either case the plate seems to adapt itself as well as it can to existing conditions—to its “environment.” It increases its capacity at the rate at which it is called upon to work. If now the high and low rate plates were to be interchanged, the one going into easy service instead of hard, and *vice versa*, there might be trouble for a while. The “skimpy” skin formation, which was just what was needed at the high rate, will not give the low rate capacity which the other plate has been easily delivering. And the low rate plate will nearly explode when it is first put on at the high rate. It throws off excess active material for a time and as remanent sulphate, always present in a plate worked at very low rates, is cleared away, action on the support plate itself may be severe for a time. Buckling or stretching may appear. If the plate passes this danger point safely, it settles down to the high rate pace and becomes

before very long much like its predecessor. In the meantime the former high rater, which made so poor a showing during its first few cycles at the low rate, has picked up gradually. More material forms from the reserve lead under the low charge rate, and most of this remains in the plate. Gradually the capacity rises until it is quite sufficient for the work, and by this time the two plates have completely interchanged their natures and looks. It seems to be generally true that a plate that has been working at high rates is in no special danger when put on easier work. The reverse is not true by any means. It is a ticklish operation to break in a plate for high rate work which has been in operation for a long time in very easy service.

104. Densities. — If we examine the densities and the relative volumes occupied by lead, lead sulphate, and lead peroxide, it is immediately evident that shrinking and expansion are sure to occur during charge and discharge. The following table gives the data:—

DENSITIES

Metallic Lead	11.4
Peroxide, hydrated	7.4
Peroxide, dry	9.4
Lead Sulphate	6.2
Litharge	9.3
Red Lead	8.9

A good many pretty mysterious occurrences in battery practice should be referred directly to these differences of density. For instance, most Planté plates, during the process of making them from pure lead, grow in length. Some of those with long vertical ribs without many breaks in them may grow an inch in length per foot of plate. There is every reason to believe that this stretching is caused wholly by the crowding of sulphate as it is formed from lead. A properly forming plate has its sulphate in the form of a very dense and firmly coherent layer, and as this is formed from the soft lead of the ribs it hangs to them and crowds. The cumulative effect is proportional to the length of unbroken rib along which the crowding takes place, and the stretching is proportional to this factor also. It is also very different for various forming agents, probably because the coherence of the sulphate to the lead of the plate is different for each.

It will be noticed from the table of densities that the peroxide layer which is finally formed on the positive as the result of formation is denser than the sulphate from which it came. So the properly formed Planté plate has a peroxide layer with just about the right degree of porosity. If its active material were more porous, it would be at the expense of coherence; and if it were denser, diffusion would be poor, and the plate would give low capacity at high rates.

Metallic lead is the densest of the materials in the table, and negative plates, which are to be porous, too, if they are to have reasonably good capacity, must be made to have very large and highly developed surfaces. This can be more or less successfully attained in the case of Planté plates by the natural method of forming them. True Planté negative plates are always made by formation first as peroxide, by attack of a forming agent and action of the current on the pure lead of the grid. They are subsequently completely reversed to sponge lead and are then finished negatives. The surface is, of course, enormously increased by the formation of grains of peroxide from the solid lead, and when the reversal is given to the negative condition, sponge lead is formed right where the grains of peroxide were. Since its density is greater, it only partially fills the space occupied by the particle of peroxide or sulphate, and as a matter of fact it is more like a mere slender network when the plate is finished than like the dense solid from which it came.

Paste plates make natural negatives. Litharge and red lead are dense compared with sulphate, and if the paste plate is allowed to sulphate as completely as possible before formation and is then reduced to lead, the resulting sponge has passed through the state of lead sulphate, with its greater volume, and has then gone on to become metallic lead, shrinking

all the time during this latter change, and opening pores everywhere during the final change.

The extremely small solubility of lead peroxide probably accounts for the fact that it is always present in fine grains, which never grow to any size, even after many cycles of service. It cannot stay in solution long enough to move about and look for a place to settle where there is already a crystal of peroxide. Lead sulphate is comparatively soluble, and when metallic lead is formed from it, the lead ion has a chance to look for a nucleus of lead on which to precipitate. The result is that negative plates increase in average size of grain with service, and finally show a much decreased capacity as compared with their original one. Not because there is less lead in the plate, but because the available surface has become smaller.

CHAPTER XIV

FORMATION OF PLANTE PLATES

105. In the early days of lead storage cells, formation was a very slow and expensive process, requiring a month or more for its completion and the expenditure of a great deal of primary battery material. For at that time the primary cells were the only source of current for the purpose, and primary cells have never been very cheap as a source of power. The plates of those early batteries were really **plates** of lead, either quite flat or with slight corrugations which enabled them to hold a little more active material on the roughened surfaces. These plates were set up in their final cell positions in dilute sulphuric acid, usually in acid much more dilute than we now use for the purpose. The cells were then subjected to a series of reversals — they were charged first in one direction and then in the other.

When the acid is poured into the cells, thin layers of lead sulphate form on both plates, and this process ceases as soon as the layer has become thick enough to protect the plate from further action. Charge is begun in either direction, as the plates are just alike

and there is no reason to decide, at this point, which plate is eventually to become peroxide and which is to become sponge lead. Under the action of the current the lead sulphate layer at the anode is changed into peroxide and that at the cathode is changed to sponge lead. The thin peroxide layer is then a complete protection against further action and the other plate is cathode, and needs no protection. As soon as charge has been carried this far, the cell becomes a gas generator and nothing more. All the current is used to produce hydrogen at the cathode and oxygen at the anode.

The capacity of such a cell is very small indeed. It will give a spark if it is short-circuited, but not much more. For the amount of lead sulphate which is formed before a lead plate protects itself against further action by the acid is minute, and no more sponge lead can be formed at the negative than corresponds to the original quantity of sulphate on it. At the peroxide plate there will be action on the lead of the plate and formation of somewhat more sulphate than was originally present, but this action takes place only during a part of the charge, and before long the dense peroxide layer shuts off the lead plate completely from further attack.

If now the cell be immediately put on charge in the opposite direction, the results are not good. The active material formed during the first charge turns

over very quickly and the plates reverse their polarity, but only a little more active material is produced. It took Planté only a short time to find out that much better results were obtained by letting the cell stand discharged before each reversal. After standing at rest, discharged, for a day or so, the cell is reversed. Not much is gained in the way of capacity this time, but when the cell is again reversed it is found that considerable gain has been made. Local action, especially at the peroxide plate, has resulted in deeper attack on the lead, and subsequent reversals and periods of rest give finally an active material layer of useful thickness. The two plates look different after they have been formed. There is a layer of brown peroxide on one and a layer of gray sponge lead on the other.

If the capacity was forced too far by more formation, the peroxide layer was liable to slough off and fall to the bottom of the cell. To be sure, more was formed to take its place, but the battery has reached its maximum capacity and further formation was merely a waste of current—an expensive article in those days.

This was during the first stage in development. Before long it was found that ribs and in general mechanical development of the surface of the lead plates permitted of much more formation and so gave higher capacity. Then before long came the

idea of rapid formation — the use of chemical agents to aid and hasten the electrolysis, and along these lines the modern “rapid forming processes” gradually came into use. There are many points about the older process which are interesting and which lead directly to an explanation of the theory of the later methods of formation.

The first point to be remembered is that lead sulphate does not form a dense enough layer on lead to protect it from the action of an electric current in sulphuric acid. A plate is quite protected by such a layer, provided no current is passing, but it has no power to resist the more active attack of the anion, backed by the driving force of the current.

The second point is that a connected layer of peroxide does protect against attack, even when the plate is anode and current is passing through the cell. The other point to be kept in mind is that the positive plate can discharge itself by “local action” while it is at rest. In the case of the Planté plate, with its thin coating of active material, this self-discharge may be pretty nearly a complete one in the time of rest recommended for Planté formation.

The curve of Figure 74 shows how rapidly this action takes place in the case of a plate which has been subjected to only a few Planté cycles, and which has therefore a very thin layer of peroxide on its surface.

It is the most natural thing in the world that such a plate should discharge itself on standing, for it is really a whole storage cell. Lead plate, peroxide plate, sulphuric acid, all are present in every peroxide plate, and the surface of contact is very large in proportion to the mass of peroxide. It discharges during its period of rest wherever lead and peroxide are in contact, and lead sulphate is formed at these points. During the subsequent reversal all the material on the peroxide plate is converted into sponge lead, and this in-

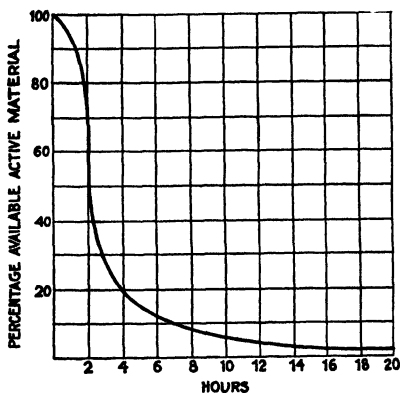


FIG. 74. — Self-discharge of original Planté plate.

cludes new sulphate formed from the plate itself as a result of the local action following the previous peroxidation. During the rest now taking place after reversal local action is increasing the sulphate content of the other (peroxide) plate, and so on.

The pertinent query arises: Why does not every peroxide plate discharge itself by local action? It does, but only to the same extent that the older Planté plate would. Where lead and lead peroxide

are in contact every positive plate discharges itself, but the amount of material in contact in a modern plate is so small in proportion to the total amount of active material in the plate that the amount of action on the plate is comparatively small, and only a low percentage of the total capacity of the cell is lost through the effect. The action is, however, strictly proportional to the surface of contact between lead and peroxide, and the modern high-rate plates are subject to much greater losses from this cause than are the paste plates. Fortunately the efficient large surface plate does its important work under conditions of rapid reversal—discharge and charge follow each other very rapidly, and the cell is never standing at rest for more than a few minutes at a time.

106. Modern “Rapid Planté” Formation. — After the first excitement over Planté’s discovery had passed, it was not very long before the small capacity of the flat plates was felt to be a drawback. The surface was increased by corrugating or otherwise roughening it. At this same time the original method of forming by a series of reversals began to seem slow and wasteful of current. So methods were sought which should permit of attaining the same or better results more easily and rapidly, and these methods were:—

1. To begin the attack on the lead by treating the

plate with an etching agent, nitric acid, for example, which dissolves some of the lead and roughens the surface of the plate. This treatment was followed by regular Planté formation, but the process went on much more rapidly than in the original method.

2. To produce on the surface of the lead plate some compound which could afterward be changed into peroxide by a single charge. One of these ideas was to subject the plate to the action of sulphur. Lead sulphide was formed, and this was changed first into sulphate and then to peroxide during the period of charge.

3. To add to the sulphuric acid used in formation an agent which should attack and dissolve the lead of the plate. This resulted in formation, first of a soluble lead salt, then of sulphate by reaction with the sulphuric acid of the electrolyte, and finally of peroxide by the usual effect of the current.

This last method is the usual one nowadays, and the great majority of all Planté plates are now formed from lead plates by electrolysis in a sulphuric acid solution containing a "forming agent." The most efficient method of applying this principle seems to be to use as agent a substance which can furnish an anion capable of forming a soluble lead salt.

The common soluble lead salts are: the nitrate, acetate (chloride), chlorate, perchlorate, and sulphite, and these are (or have been) all used for the purpose.

It is not our business to examine technical recipes or to study the minutiae of manufacturing processes. But we can state a general theory of formation which will be found applicable to all the different processes.

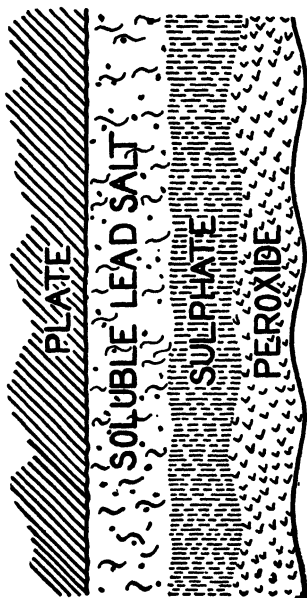


FIG. 75. — Diagram to show modern "rapid Planté" formation.

107. Theory of Rapid Formation. — Figure 75 gives a diagrammatic picture of the different zones and stages in the formation of a lead plate. All plates are formed into peroxide first, if they fall into this class at all, even if they are eventually to become negatives; so this one picture covers all the cases.

The solution contains sulphuric acid and the forming agent, which has as anion an ion which can yield a soluble salt of lead. The charging current started, this forming ion and SO_4^{--} migrate toward the plate. The velocity of the forming ion may apparently be either greater or less than that of the SO_4^{--} ion without making any difference in the process. At any rate, we will suppose that the two

ions reach the plate at the same time. A layer of soluble lead salt in solution is formed at once, but this lasts only an instant. SO_4^{--} is there and lead sulphate is immediately precipitated. The regular charging reaction then comes into play and the sulphate is transformed into peroxide. In the meantime the forming ion has been freed, and it bores into the plate again to form more soluble material, which is precipitated by SO_4^{--} , and so on.

This insures formation, but the relative concentrations of the two active ions must be carefully balanced if it is to proceed far enough to make it a practical success. If there is too little forming ion in proportion to the sulphate ion, sulphate will precipitate as a dense layer clinging closely to the plate, and peroxidation follows so closely that the plate soon protects itself. If there is too much forming ion relative to the SO_4^{--} ion, an actual layer of solution, containing a considerable concentration of the soluble lead salt, forms between the plate and the layer of precipitated sulphate. The sulphate layer is thus kept from close contact with the plate at all points, and when peroxide forms, the whole sheet of active material, partly sulphate and partly peroxide, is so loosely attached that it flakes off at the least provocation, leaving the plate bare.

The formation of a tough and coherent peroxide demands careful attention to the relative concentra-

tions of the active ions. It may be taken as a general rule that there is no one acid concentration and no one forming ion concentration that produce correct formation. For each acid concentration there will be, however, an optimum concentration of the forming ion, and other considerations usually make it advisable to use a rather low acid concentration for the forming solution.

Formation to a practical depth usually requires eight or ten times the number of ampere-hours afterward to be required of the plate in service. This is quite natural, for as we have seen in Chapter X, we use in service only about 10 to 30 % of the total active material of the plate. If the plate is an old-fashioned thin-layered flat Planté plate, the maximum proportion of the total will be brought into use. If it is a modern plate with ribs or rosettes, a smaller part of the total peroxide will be turned over in practice.

108. Low Voltage Formation. — A special mode of formation has been invented and patented by Pollak, and while it has apparently not been adopted as a manufacturing method, it is of interest as an example of a principle we have frequently applied. Lead sulphate cannot protect a lead plate from attack when current is passing and the plate is anode. If we can prevent the formation of lead peroxide and continue to form sulphate, there is no reason why

formation without any special agent should not be carried as far as we choose.

Peroxide is not formed from sulphate except at cell voltages higher than 2 volts. If therefore we send current through the cell at a voltage slightly lower than this value, only sulphate will result, and the plate will continue to be attacked. This condition of things is best attained by connecting the lead blank which is to be formed to a fully charged peroxide plate of capacity sufficient to complete formation. This means a charged peroxide plate of eight or ten times the capacity desired for the finished plate we are making. When enough sulphate has been produced to give final capacity, the sulphate-formed plate is taken out of this cell and formed to peroxide in another cell, either against negative plates or flat lead dummies. In the meantime the auxiliary forming positives are receiving a new charge to get them ready for the next formation. There seem to be practical reasons why this idea has not been generally adopted. Theoretically and as a laboratory experiment it works quite perfectly.

109. Changes in the Forming Agent during Formation. — It is much to be desired that the activity of the forming agent should cease as soon as the plate is brought up to its proper capacity. If some of this dangerous substance remains in the plate, it will

continue its original behavior and attack the lead of the peroxide plate during each period of charge. Of course this attack is much weakened by the fact that the plate is completely peroxidized and also because it is never discharged to such an extent that much of the peroxide in contact with the lead support is changed to sulphate. But a lead cell must have a life of several years and must go through a great many cycles of charge and discharge, and even a small amount of action can be cumulatively harmful.

Some of the forming agents mentioned in the list are only too ready to eliminate themselves. When chlorine ion is used either as hydrochloric acid or as a chloride, chlorine gas is evolved nearly quantitatively at the anode, and the forming agent must be replaced accordingly. Chlorates are also broken up with evolution of chlorine, but not so completely as Cl^- ion. Nitric acid is reduced at the cathode, first to nitrous acid and finally to ammonium sulphate. This necessitates renewal during formation and final saturation of the electrolyte with ammonium sulphate. This means that small quantities of nitric acid, left in a plate as the result of formation, are perfectly eliminated from the cell during its first few cycles of active operation.

An interesting suggestion is that of Beckmann. Sulphur dioxide in water solution forms some sul-

phurous acid, H_2SO_3 , and this gives a forming ion SO_3^{--} , because lead sulphite is a fairly soluble substance.

During formation this ion leads the attack on the lead plate as described, but it is itself oxidized rather readily to SO_4^{--} , and so a few cycles are sufficient to remove completely every trace of extraneous ion from the cell. This also seems rather difficult to apply as a practical forming process, as SO_2 is not a pleasant substance to have about in large quantities.

Acetate ion, $\text{C}_2\text{H}_3\text{O}_2^-$, is most persistent and can cause great damage if any of it is left in the plate after formation. Even this is gradually destroyed as the result of cell activity.

Perchlorate ion, ClO_4^- , is apparently the only substance in the list which is perfectly resistant to the effects of the current. It is therefore the most effective of all forming agents, as it does not need to be renewed at all in the forming tanks. For this same reason it might become a dangerous factor in the cell after it goes into service. Fortunately the limits of proportion between which perchlorate ion can act as a forming ion in sulphuric acid solution are narrow. In electrolyte the sulphuric acid concentration is comparatively high, and the little remnant of perchlorate is therefore a very small fraction indeed. Under these conditions it hardly has any power of attacking lead, and while in proper propor-

tions it is perhaps the most active of all forming reagents, it is much less dangerous than many of the others in the conditions of ordinary service.

110. Planté Negatives. — The negative Planté plate is made in exactly the same way as the positive. It is formed as a positive, with the aid of a rapid forming agent, and is then reversed completely, so that all the peroxide is changed to sponge lead under the action of the current.

Such a plate has all the good qualities of the large surface positive, especially during the first part of its life. It is easily reached by the electrolyte and can give large discharges without danger. Later in its life it loses a considerable part of its original capacity because of increase in size of grain and loss of porosity. It must therefore be made to have a much larger original excess capacity than the positive, which increases its capacity by local action and slow formation in service. Most Planté negatives are made to give nearly 100 % excess capacity when they go into service. This excess is rather rapidly lost during the first six months or so of service, and at the end of the first year the plate will usually show an excess of only about 25 %.

The curves of Figure 76 show how light Planté positives and negatives change in capacity in service. The curves are of course only averages, and different types would show somewhat different curves, but

these can safely be taken as representing the general course of events.

Many makers use pasted negatives entirely, even in batteries which are to be called on for the hardest

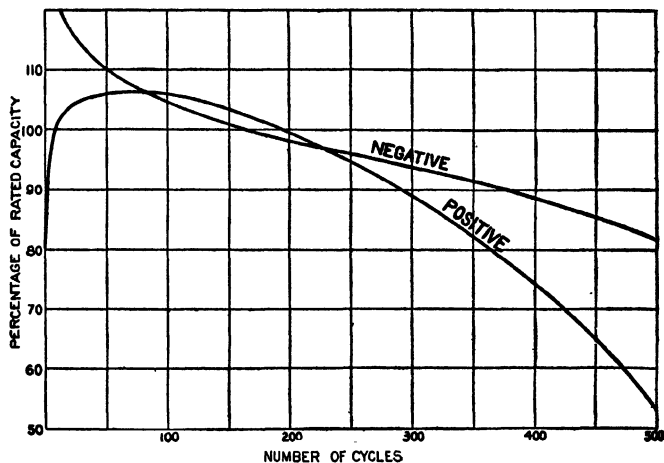


FIG. 76. — Change in capacity in hard service. Light Planté plates.

service. Their life is sufficient, and their excess capacity is so great that no fear need be entertained that the negatives will ever limit the discharge of the cell.

CHAPTER XV

PASTE PLATES

III. It was Faure who first conceived the idea of producing active materials for accumulator plates by the electrolysis of lead compounds instead of from the lead of the plate itself, and he began the evolution of what are called paste plates. Faure probably reasoned somewhat like this: Planté produces lead sponge and lead peroxide by a wearisome and expensive attack on the solid lead. It would certainly be much better to cover a lead plate with a mass which can then be easily and completely converted into lead at the cathode and lead peroxide at the anode, and such a plate can be made to have capacity enormously greater than the thin-skinned plates of Planté. Some triumphs and not a few troubles for many people began just at this point in the history of galvanic cells. As we now know very well, Faure's invention was not able to push Planté's out of the field. Each of the two types of plate has a perfectly definite place and service of its own, and while the two types appear to cross into each other's territory now and then, there is always some very definite reason for the apparent intrusion.

The process of making a paste plate is a very simple one. Perhaps the people who find most difficulty in the process are the ones who have to actually manufacture the plates for the market. The difficulties are all practical ones and so minute and difficult to sort out and describe and remedy that we can only hope to touch the more evident and fundamental ones.

Suppose it is desired to make a set of fairly light plates to be used in an electric automobile. They must have good capacity per unit of weight, mechanical strength sufficient to withstand the jar of road service, and a fairly long life (say 250 to 300 cycles), if they are to compete with other plates already on the market. We will make the positive plates first.



FIG. 77. — Ribs of positive paste plate.

For positives, a grid which can hold the peroxide in place somewhat is usually considered best. Lead peroxide has very little coherence and drops off the plate surface very easily unless it is kept in some way from doing so. We should therefore choose a grid of the general form shown in Figure 77, having ribs with inward dovetails to keep the material in the plate. It is usual to cast the grids of 6 to 10% antimony alloy. This gives a much stiffer grid than pure lead and prevents attack by the acid of the electrolyte. Molds we will assume—they are not

within the province of our discussion — and we will also assume that we have a supply of grids ready cast. The next thing is to paste them.

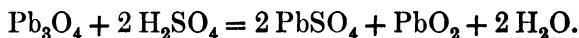
Recipes for positive pastes are legion. A very simple one which can be made to give good results is made by mixing litharge (PbO), or red lead (Pb_2O_3), or a mixture of the two, with rather dilute sulphuric acid. A paste is made of the constituents, just thick enough to permit of its being worked into the holes and hollows of the grid. If then a plate so pasted is set in the air, it dries and at the same time sulphates, setting to a hard mass. Better results are obtained by soaking the freshly pasted plate in dilute sulphuric acid for several days. During this time what is perhaps the most important thing in the whole life of the plate takes place. It **cements**.

Lead peroxide is a powdery, non-coherent mass at best, and a plate pasted with pure peroxide has very little mechanical strength compared with the plate which has been treated in the way just described. But lead sulphate, crystallizing into a firm, connected mass all through the interstices between the grains of oxide and peroxide, can become a most useful binding material. Just a word about what we mean by the general term **cement**.

A cement sticks things together. It does this by first of all penetrating, as a liquid, all the irregular holes and crannies and spaces between the solid

particles to be held together. It then afterward hardens to a solid and fills all these irregular spaces, thus dovetailing the various pieces of the whole mass into a single piece. The resulting solid is as strong as its two final constituents—one of them the original solid which was to be bound together, the other the new solid formed by the hardening of the cement.

If red lead is used in the paste, the following reaction takes place partially as soon as the acid used in mixing has a chance to react:—



The plate therefore contains lead peroxide, red lead, and lead sulphate, as soon as it has set and before formation is begun. If litharge alone has been used in the paste, the unformed plate contains only lead oxide and lead sulphate. The lead sulphate reacts quickly, and within a few minutes or at most a few hours after the plate has been placed in the cementing acid bath, the sulphation of the plate is quantitatively complete. But the second and equally important step—the locking together of the plate by the sulphate—takes place much more slowly. It depends on the recrystallization of lead sulphate and is an action very like the dreaded “sulphation” which is so often the cause of trouble in the vehicle batteries all over the country. The fine particles of sulphate are more soluble than the larger ones, and the latter grow

at the expense of the smaller ones. As the crystals grow they interlace and lock themselves together, as growing masses of crystals always do. One sulphate crystal, growing out from between grains of oxide or peroxide, touches the one growing out from the neighboring opening and the two coalesce. The result of this crystalline growth and interlocking is the cementing of the plate. It becomes hard, sounds hard when it is struck, can be used as a hammer and pounded on the floor without losing any paste except at the place where the lead grid is actually bent or broken. It is now ready to be formed.

112. Formation of Paste Positives. — The plate, destined to become a positive, is now hung in a bath of rather dilute sulphuric acid and made the anode for the passage of the forming current for perhaps 60 hours. Figure 78 shows the changes which take place in its composition during this time. At the start the plate contained : —

PbO	55 %
PbO ₂	25 %
PbSO ₄	20 %

The lead oxide begins to turn to peroxide right away as soon as charge is begun, but the sulphate content of the plate rises for several hours. This may be because the plate is becoming more porous as formation proceeds, so that the acid finds unused

oxide ready to hand as it enters new channels. But before long the sulphate also passes over into peroxide

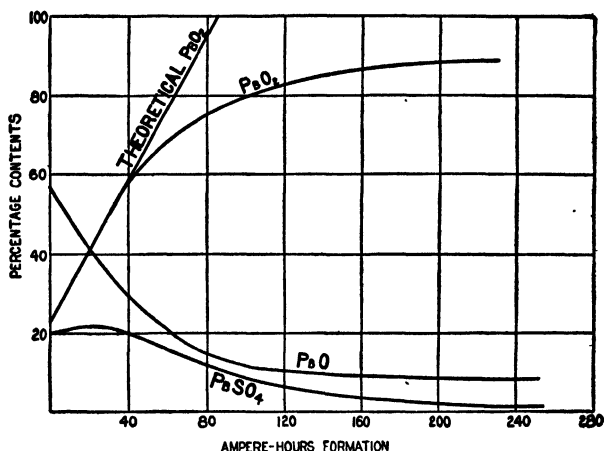


FIG. 78. — Changes in composition of a paste positive during formation.

and at the end of the period of formation the active material consists of :—

PbO 9 %
 PbO_2 88 %
 $PbSO_4$ 3 %

Our cement is nearly gone. But even this 3% is a potent factor in the life of this positive plate, and if formation has been carried on at the right current density, there is also some cementing, or rather loose interlocking, of the particles of peroxide.

It seems probable that this remanent lead sulphate

is never removed from the plate under proper conditions of charge and discharge and that it forms a network which really helps to hold the peroxide together. During each discharge sulphate is deposited on this nucleus, and the plate may perhaps be partially held together by the binding action so produced during the succeeding period of charge, which is so trying to the paste plate.

Surely this cannot be the whole story of the making of a paste positive? There are hundreds of secrets carefully guarded, and hundreds of patents and recipes for pastes. A glance at the patent literature shows the nature of the various things that might be added to the positive paste — alcohols and organic acids, salts and sugars, and almost anything else that one could think of. The intention of these additions is to aid in producing either one of two desirable things : —

(a) An increase in the hardness of the plate, and therefore increased life.

(b) An increase in porosity, and therefore its efficiency.

The organic acids — carbolic acid, for example — hasten the cementing action. Probably a lead phenolate or some such substance is formed and lead sulphate is then rapidly produced from this. The soluble lead salt would naturally hasten sulphation just as a forming agent hastened it in the case of

Planté plates. The addition to the paste of a soluble salt like magnesium sulphate has not much effect unless the plate is allowed to dry after pasting and before formation. The salt crystallizes all through the plate while it is drying and setting, and is then dissolved again during formation, leaving spaces in the formed active material and thus increasing porosity. A good many manufacturers probably still feel the need of a "hardening agent" or a "porosity agent," or both. But it seems perfectly possible to get along without either of them. And perhaps the final result is just about as satisfactory if only lead oxide and sulphuric acid are used instead of the more mysterious and cabalistic formulæ of some of the inventors in this field. It is, as a matter of fact, very hard to see how any good effect of the addition of any of these agents to the paste can remain after the resulting plate has been through fifty cycles of hard work. Long before that time the hardening agent has been completely decomposed and removed from the cell so completely that chemical analysis will often fail to show a trace of it. The porosity agent is of course dissolved out and diluted through the cell as a part of its activity. The active material of the plate has been turned over and over and has disposed itself in new ways—filling up the old pores and channels and making new ones for itself. All that is left is a very small trace of lead oxide and the

normal proportion of lead peroxide and lead sulphate. Whatever coherence the paste now has is due to these two substances, and as we have already seen, lead peroxide is not inclined to bind together to give much mechanical strength. The remanent network of sulphate is all that holds the plate together. Whenever particles of peroxide lose contact at the surface of the plate their fate is to fall off sooner or later and collect in the bottom of the containing jar. The cementing sulphate has no chance to persist at the surface. It is transformed almost completely into peroxide at each charge. So the peroxide plate naturally loses active material by "shedding," and the rapid evolution of gas which accompanies the end of each charge helps to throw off all the loose particles. It is the fate of all paste positives, even the most healthy, to finally become a mere skeleton — a grid — with nothing left on it but a few bunches of peroxide clinging to its ribs.

113. Paste Recipes. — Every manufacturer has his own particular recipe for positive paste. This and other facts lead to the conclusion that the proportions are not of great importance. Many manufacturers make good plates, and they use —

1. Pure litharge.
2. Pure red lead.
3. Mixtures of litharge and red lead in all proportions.

Some makers mix their paste with strong sulphuric acid; some use it weak. Evidently there is much in knowing how to paste, dry, cement, and form — much more than in any secret of proportions or materials.

This statement might almost be taken as an axiom in battery manufacture.

114. Paste Negatives. — The finished negative paste plate has a very different set of characteristics and a very different life history from its weaker positive brother, but it begins in very much the same way. Since it is to become spongy metallic lead, it may as well be made of litharge unless there is some special reason against this, for the step from PbO to Pb is the easiest possible one and takes less energy than the one from Pb_3O_4 or PbO_2 to Pb . No hardening agent is needed, for the negative has plenty of coherence. But it does need porosity, and a good many makers use either a soluble salt like magnesium sulphate, or an inert substance like graphite, in making their negative paste. It seems doubtful whether the effect of the soluble salt is lasting, and there seems to be a belief that graphite and the other space-filling inert substances which are suggested may be harmful in the ordinary open-grid negative plate. So we will make our negatives as simply as possible, using only litharge and rather dilute sulphuric acid, and allowing the plate to set and cement

very much as though it were to become a positive. It sulphates to the amount of about 30 % of the whole mass, and during formation the changes shown in Figure 79 take place. In this case the plate was about 20 % sulphate before formation, and 80 %

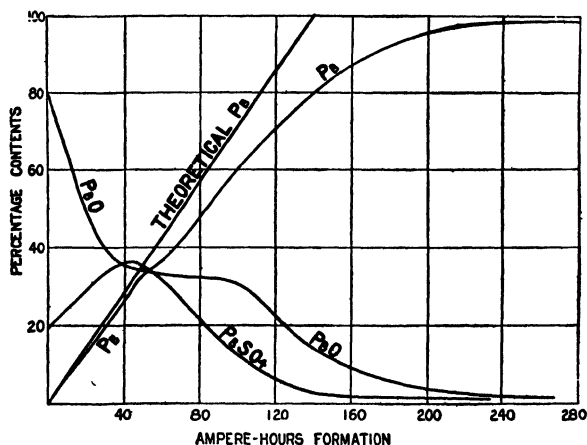


FIG. 79. — Changes in composition in a paste negative plate during formation.

litharge. Lead begins to form immediately when the current is started, but notice how the sulphate content also rises during this period — almost as fast as lead is formed. The pores are opening. Metallic lead occupies much less space than either the oxide or the sulphate, and the acid has a chance to reach and attack new oxide in the deeper pores of the plate. Before long the sulphate reaches its maxi-

mum, and then it seems to reduce faster than it is formed from the oxide. Finally the plate stops when it contains about 98 % of metallic lead, the rest being mainly oxide, with a very small remnant of sulphate.

Lead sponge made in this way is tough, coherent, and well interlocked all over the plate, and a properly made negative has a chance of much longer life than the positive made in about

the same way. It is usually said that one set of negatives will just about outlast two sets of positives.



FIG. 80. — Rites of paste negative.

The rites of negative grids are

often made with dovetails as shown in Figure 80, the intention being to hold the contracting material in better contact with the support.

115. "Chloride" and "Box" Negatives. — Two variants on the usual processes have been of importance. The "chloride" negative was made by casting a lead grid around pellets made from molten lead chloride. The whole plate was then reduced to sponge lead, and the active material so formed had many good qualities. This process is no longer in use. The other plate in this class is the "box" negative, originated by the most important of the German battery companies and now used in this country by the Electric Storage Battery Company. The appearance of the finished plate is shown in Figure 91.

Pellets containing litharge mixed with some lamp-black or other "expander" are made outside of the plate and dropped into place in the openings. They are then covered by the other sheet of perforated lead, and the plate is complete. This particular active material has no coherence at all, and would fall out of the openings in an ordinary grid in a few days of service, but by protecting it with this perforated cover it can be made to give good capacity and life.

CHAPTER XVI

DISEASES AND TROUBLES

116. Frequent mention has been made of action between the peroxide and the lead support in the positive plate, resulting in self-discharge proportional to the quantity of material affected. Lead sulphate is formed at the surface of contact. This action is a perfectly normal part of the activity of every positive plate. It is a large factor for the original flat plates of Planté, fairly large — quite measurable at any rate — for modern large surface plates, very small in paste plates.

While this action is a normal one, and essential in its nature, it may be so exaggerated by wrong operating conditions that it becomes a source of danger.

Between sponge lead and solid lead the difference of potential is so small that self-discharge is very slight. But in many of the modern negative plates there are other things than lead. Many have graphite in them to give contact, insure porosity, and make the active material a better conductor. With this substance in the negative material there is a good

deal of local action, and the negatives may discharge themselves quite as fast as the positives in the same cell.

These normal effects of self-discharge we must take with our storage cell, for they are a part of its nature. There are many other substances which might be in the cell—impurities—and which can greatly increase the local action. Some of these are so strong in their effects that they are dangerous to the life of the cell.

Suppose, for example, that a very stable and persistent forming agent has been used in the manufacture of the plate and that this has not been carefully removed after formation and before the plate is put into service. During each charging period this forming agent will bore into the peroxide plate (anode) and continue formation at a rate determined by the concentration of the forming ion. From our discussion of rapid formation it will be remembered that maximum rapidity of formation, and density and coherence of material formed, result from using a definite value for the ratio—

$$\frac{\text{concentration of forming agent}}{\text{concentration of acid}},$$

and that the velocity of formation dropped very rapidly when the concentration of forming ion was carried much below the value indicated by this ratio.

In the working cell there is not much likelihood of enough of our stable and persistent forming agent remaining in the plate to approach this value. If such an agent were present at anything like the optimum concentration, the positive plate would have a total life of only a few cycles. By that time the lead support would be completely peroxidized, and the plate would fall to pieces.

Large surface plates attain a life of 1000 or more discharges. If a plate is to compete on these terms, even a minute amount of forming action makes a difference in results, and so manufacturers have learned to carefully remove the forming agent before sending their plates into service:

Another thing helps very much. Most active forming agents are soon completely decomposed by the electrochemical action of the cell. Nitric acid has been frequently used as an active forming agent. It is reduced to ammonia at the cathode and remains in the cell only as a slight impurity of ammonium sulphate in the electrolyte. While this latter substance is not to be prescribed as good for the cell it is not actively dangerous.

This danger is confined to the peroxide plate, and the most unhealthy impurities are the forming agents of the list given on page 185. Of course the dangerous ions turn and go to the negative (lead sponge) plate during discharge, but the voltage is

much lower and the plate appears well able to protect itself by a layer of sulphate.

117. The lead sponge plate has its own class of uncomfortable impurities — the metals — and they have no power to affect the life of the plate. They merely cause self-discharge. This they do by settling on the plate and causing little local cells. During charge the lead plate is cathode. All the metallic ions in the cell wander over to this plate, and if they can go out of solution at the voltage of charge and under the existing conditions in the cell, they deposit as metal on the lead plate. Little cells

metal/sulphuric acid/lead

discharge as soon as the voltage is removed, and the current used in their discharge is lost as far as external work is concerned. The cell appears on test to have lost capacity.

Evidently the noble metals will be the chief offenders, for they go out of solution very readily and give a local cell with a good big electromotive force for self-discharge. A very little platinum will keep a negative plate from taking in more than a minute fraction of its proper charge. This unpleasant effect does not persist for many cycles; for while the noble metals are ready enough to go out of solution, they are not ready to go back in again. At any rate,

when the lead plate is cathode (charge) the noble metal goes out before the lead does, and the latter plates it over and eventually covers it away out of reach. As the negative naturally increases the size of its grain in service, the noble metals are gradually encapsulated in the heart of the lead grains, which no longer react completely to the very center at each reversal.

Copper, silver, and gold can act in the same way as platinum. Copper is not very active, and the activity increases to the other end of the list.

118. There is still a third class of impurities which can cause self-discharge, though its representatives have no direct effect on the plates. This class includes those ions which can exist in two stages of oxidation and which are easily converted from one state to the other. Iron is the commonest example. Suppose a workman drops a pair of pliers into a storage cell during its installation. When the electrolyte is poured into the cell, these pliers dissolve gradually to form ferrous sulphate, and now the cell contains Fe^{++} ferrous ion. This travels about in the cell, and during discharge it migrates along with the H^+ to the cathode, now the peroxide plate. When it meets with lead peroxide, it is oxidized to Fe^{+++} ferric ion. Even if the cell is on open circuit, the action will take place as fast as Fe^{++} reaches the peroxide plate, and as soon as a little Fe^{++} has been

oxidized to Fe^{+++} a slight concentration gradient is set up which hastens the motion of Fe^{++} toward the peroxide plate and the removal of Fe^{+++} from the neighborhood. In the meantime Fe^{+++} has wandered over to the lead plate, and there it is reduced to Fe^{++} , setting up a diffusion gradient there in the same direction as the one at the other plate. Everything conspires to aid in the discharge so produced. No metallic iron is deposited, but every bit of Fe^{++} and Fe^{+++} in the cell keeps busily at work running from one plate to the other and discharging the cell. Even a small amount of pliers in a large cell will cause a considerable self-discharge in 24 hr. This is, of course, an effect which is especially noticeable on open circuit. If the cell is working hard, charging and discharging every few hours or every few minutes, the loss of energy will be negligible.

Probable Impurities. — The list includes: —

Forming agent. From rapid forming process.

Iron.

Copper.

Tin.

Arsenic.

Antimony.

Platinum (noble metals in general).

119. A certain amount of depreciation must be expected in a battery, even if it is kept in the best possible condition. The effects of local action cannot

be avoided, nor can the negative active material retain its original porous structure throughout the whole life of the cell. Plates shed their active material. Positive peroxide loses its coherence and falls off the plate even in the case of the toughest of Planté type, and to a much greater extent in paste types.

These normal disturbances may be greatly magnified by poor operating conditions. We will make a list of the common diseases which are especially apparent in Planté types.

1. *Loss of capacity.* — This is due to wholly different causes in positive and negative plates. A Planté positive should retain its capacity almost unchanged up to nearly the end of its life. It has great power of recuperation and can re-form lost active material and should remain healthy for the rate at which it is operating if it is carefully handled. Toward the end of its life all the reserve lead will become exhausted. If it is made with rosettes, like the Manchester type, all the pure lead in the strips becomes changed into peroxide, and the plate then becomes like a rather low-surface paste plate. The grid remains unattacked, but the capacity has reached a maximum, and from this time on peroxide will be shed and no more can be formed to replace it. Events follow much the same course in a ribbed Planté plate. The ribs will become entirely peroxidized and the main supporting webs have not sufficient surface to keep

up the supply. *The ribs finally disappear, as do the rosettes of the Manchester type. The plate is approaching the end of its useful life.*

120. The Planté negative has a more peaceful existence and an almost indefinite life, but it diminishes rather rapidly in capacity during the first hundred cycles or so of service and continues to lose more and more unless it is regenerated by some means. This loss of capacity has been spoken of before (page 192). It is due to the increase in size of grain and the general decrease in surface which results from many cycles of charge and discharge. The large grains persist and are not completely transformed into sulphate during discharge. The lead deposits on them rather than to form new grains. Then, too, the smaller grains are more soluble than the large ones, and these two effects taken together combine to produce a continual and considerable droop in capacity with service. One way to bring back the original condition of the plate is to completely reverse it to peroxide and then back to lead again, but this is not very frequently feasible in practice, where the plate is set up with many other positives and negatives in a large cell.

121. Another way of restoring the original capacity of a Planté negative is by means of a process called "Permanizing." The plate is soaked in a rather strong solution of sugar and then heated to about

300° C. for a time. The sugar is quite completely carbonized at a point below the melting point of lead, and the pores of the active material are filled with very finely divided carbon. This carbon prevents the pores from filling up with lead, and the grains may also act as centers on which lead can precipitate. At any rate, plates treated in this way seem to retain their capacity longer than usual, and a plate which has lost a part of its capacity by service has most of it restored by the treatment.

2. *Deformation.* — All Planté plates are more or less subject to buckling or fracture. If they are made of pure lead, they twist and stretch when any strain is put on them, and if they are made of anti-mony alloy, they are liable to crack instead. In the case of pure lead plates, buckling may be caused by improper formation. If one side of the plate is formed more deeply or completely than the other, the changes of volume which occur will twist or bend the soft lead and the plate buckles. Almost all Planté plates with ribs grow in length considerably during formation, and if the resulting peroxide is dense and firmly attached to the lead of the support, the stretching may be as much as an inch or more. It is almost wholly along the rib—much less marked across the plate; a perfectly normal effect, and known and allowed for by all manufacturers who make this type of plate. Lead is so soft a metal that the

material produced, which is greater in volume than the lead from which it is made, and which adheres strongly to the surface, exerts force sufficient to stretch the whole plate.

Certain operating conditions may tend to cause buckling. For example, if a battery has been on very high rate work, its ribs and pores are very open. If now it is changed over and put on low rates, especially of charge, its plates are very liable to buckle. Much new peroxide will be formed away down near the central support of the plate, and this can easily fill the available space between ribs too full.

And sulphation, in the evil sense of the word, can cause plates to tie themselves almost into knots. Here the change of volume is as great as possible, and all the pores and spaces in the plate are overcrowded with material. It may be taken as a general rule that any treatment which can cause more than the normal change of volume in the deeper active material of the plate will give rise to buckling or fracture.

3. *Sulphation*. — This is a “waste-basket word” among all the people who have to deal with storage batteries. Whenever anything whatever seems wrong with a cell, the first diagnosis is “sulphated.” Lead sulphate usually has something to do with the difficulty, but its connection may be of the most remote. The most common cause of trouble is lack of

proper charge. In days not so long past, batteries were often sent out a long way into the country, to a point miles distant from the power house, and allowed to "float" on a trolley line to help the voltage and save copper feeders. These lonely batteries often had a hard time as far as proper charge was concerned, and some of them furnished examples of sulphation and buckling of the most aggravated nature. Engineering practice has improved since then, and boosters and feeders have been found economical compared with the rapid depreciation of batteries used in this way. In the case of station batteries properly operated, there is not nowadays much cause to use the word "sulphation."

4. *Impurities and local discharge.*—Before the danger of very low charging rates and the worse danger arising from a net discharge were clearly appreciated, many of the troubles with plates were sought for in the presence of "impurities" in the cells. Every rapid forming agent was suspected, and water, acid, and even air were examined with great care for possible explanations of trouble. It will be evident from what has been said about the elimination of the forming agent and its comparative action in very dilute solution that these analyses and examinations were without positive result. A storage cell should contain **nothing** but sulphuric acid; but it takes a long time to accumulate troublesome

impurities if reasonably pure water is used to fill the cells, and many of the troubles mentioned appeared within a few months of service. It seems now fairly certain that the whole effect could be explained by undercharge, by the fact that the plates got a net discharge, and by the fact that the charging rates were much too low. Certainly these factors can cause sulphation and buckling, and even destruction of a whole battery, in the way these troubles used to occur.

5. *Shedding of active material.* — Planté positives shed. So do paste plates, but the shedding is a more healthy thing for the Planté plate, and is a part of its physiology. On page 174 there was pictured the way in which well-made Planté plates adapt themselves to the rate at which they are working. No plate can do this so well as the simple ribbed type of positive. Even the Manchester plate, nearly universal in its application though it may be, cannot compete with the simple ribbed pure lead type in adaptability, and especially in lively response to the demands of very rapid rates. At low and intermediate rates the sensitive pure lead plate is at a disadvantage, for it is endangered by low charge rates, and is by no means so excellent at low discharge rates as at high ones.

Planté negatives have none of these weaknesses. Their only failing is the one already described —

rapid loss of capacity. As far as health and toughness are concerned, they are beyond criticism.

6. *Short circuits in the cell.* — The almost universal use of wood separators has nearly removed this once common source of trouble. Any large surface plate develops strips and flakes of surface sulphate or other surface material. This drops off and sometimes reaches across from positive plate to neighboring negative. Often these delicate bridges are quite innocuous, but they occasionally become formed part way or all the way across, and the result is a complete short circuit in the cell. Local action may be very great indeed at the two points of contact of this bridge, and many a plate has had a hole eaten right through it by the very high local current within a few days after the accident occurred. Rigorous inspection is the only way to avoid such an accident, and the acid density is the very best indicator of trouble. In small glass jars it is easy to see whether anything has occurred, but in the big lead-lined tanks used for large batteries it would be a great deal of work to look down between each of the ten thousand or more pairs of plates every day. If the cell is not working properly, its acid density will not rise during charge to the proper value, and this may always be considered a sign of trouble.

As a battery grows old much sediment forms in the bottom of the cells, and if this is not removed,

the plates will eventually short-circuit across their bottom edges. Pure carelessness or laziness only can account for such a condition.

7. *General debility.* — The “storage battery man” learns to judge pretty well about the condition of a battery by looking it over. “She don’t **look** right,” is reason for a careful investigation. If a battery has been doing well and then begins to show signs of ill health, an examination of the charge and discharge charts will usually show the reason for the change. Perhaps the station has been called on for heavier loads during a period of two weeks or so. A prime power unit may have been out of commission in the station. The old booster may not be large enough for the work to be done. It usually turns out that the battery has given a net discharge, or else the necessary net overcharge cannot be given in the time that remains after the hard work of the day. Some such cause will usually be found.

122. A few years ago I had hundreds of plates sent to me for chemical analysis from batteries where troubles of this kind appeared. The plates and the electrolyte were in all cases as pure as possible, but in most cases investigation showed that the battery was being charged at too low a rate and not fully charged at that; the plates had buckled and turned in color. In every case where investigation was possible operating conditions were responsible, but it

sometimes took careful examination and even diplomacy to bring out this truth. A good starting point in cases like this is the maxim "Look at the rates under which the battery is working." If a comparatively new battery, once healthy and lively, turns weak and sickly, and plates begin to buckle and shed, do not suspect "impurities." Suspect operating conditions. See that the battery is charged. See that it is overcharged, and the chances are large that all the troubles will disappear.

These directions are sometimes overdone, but not very often in my experience. It is, of course, quite possible to overcharge Planté plates until almost all the active material is blown off the positive plates by continued gassing. But few superintendents will allow their battery men to waste current in this way. Oftener they are obliged to beg for enough charging current to keep the battery in good condition.

A well-made large surface plate seems to love work. No battery looks so healthy (to me at least) as one which has stripped itself for service, at, say, the 20-min. rate or better. The plates look lean, but their color is good. They do not gas very much except at the very end of charge. The current which can be drawn from such a battery, especially when it is installed in a warm place, is astonishing. In earlier days the 8-hr. rate was "normal." In present-day service the 5-min. rate is more nearly the

rate at which the battery is most useful. There is a good reason for this. Suppose our battery can give 100 amperes for 8 hr. So can a 10 KW. 110-volt generator. This battery can give 3000 amperes for a minute or so. It would take fifteen or twenty generators to safely handle such a peak.

123. After the catalogue of ills just recited it might seem that the lead battery must be given up as a bad job. But we have been acting in the rôle of the pathologist in this case, and as a matter of fact the lead cell is a pretty healthy and lively machine, if it is well treated. Even under rather adverse conditions it often shows surprising powers of resistance. In our own laboratory we have cells in use which are over twelve years old. This battery has had occasional periods of a few months each of hard service, with long rests between. The rests have probably been harder on the plates than the work, for it has sometimes been left pretty well discharged, and the results have shown themselves in disintegration of the negative plates.

In easy service the life of positive plates should certainly reach six years, and that of negatives is much longer. In stand-by service positives may last ten years and negatives twelve or fifteen. In hard regulation work the positive life is three to five years and negative life five to eight.

Paste plates in service are much shorter lived.

Probably about 300 to 350 cycles for the positives and about 400 to 500 for the negatives may be taken as the average life. In stand-by service there seems to be no reason why the life should not be nearly as long as for Planté plates. Local action is much less effective, and the battery is kept well charged.

124. It is possible to give some general rules for the operation of batteries. For Planté plates:—

1. Keep the battery charged.
2. Charge at a fairly high rate. Usually this means at the 8-hr. rate or a little higher.
3. Inspect frequently and remove all possible short circuits immediately.
4. Keep acid density at the proper point.
5. Keep the acid above the top of the plates.
6. If plates buckle, straighten them as soon as possible.
7. Do not let the temperature reach too high a point. (100° F. is a safe limit.)

Discharge at almost any rate does not harm good Planté plates provided they are charged immediately after the discharge is finished.

For paste plates:—

1. Charge at a low rate, 12 hr. or lower.
2. Overcharge occasionally by 10 % or so. Once a week is often enough for the overcharge if the battery is in daily service.

3. Use an ampere-hour meter and regulate charge and discharge by that.

4. Try to give a nearly complete discharge before recharging. If the discharge is extended over two or three days, no harm is done.

5. Watch temperature carefully. High temperature is much more destructive to paste plates than to Planté types.

6. Test each cell frequently and inspect at the least sign of trouble.

The most usual trouble arises from continued net undercharge, especially in private installations.

CHAPTER XVII

SOME COMMERCIAL TYPES

125. The most important services performed by storage batteries are in regulation of large station loads and as "stand-by" batteries. The work performed in these two applications is wholly different, and there is a very evident movement toward the use of quite different types of plates in the two kinds of service.

Regulation (Trolley Service, Large Factory Service, etc.). — The battery is used in conjunction with a large power plant and often with a "booster." The charge and discharge rate vary from five minutes to twenty seconds or so. This is the hardest and most wearing service that a battery can be called on to perform, and it is the most important from the point of view of economy. High service Planté plates are eminently fitted for the work, and paste plates are quite out of their element.

A very large number of patents have been taken out on plates of the Planté type, and most of them have dealt with the methods of increasing the surface of the plate or with the method of forming it. Not

many of the really marked variations have met with commercial success, and gradually practice has left

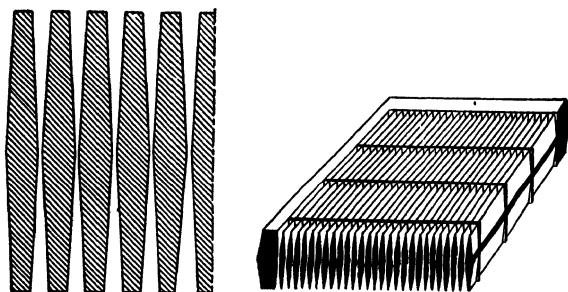


FIG. 81. — Cross section and sectional view of a "Tudor" plate.

only a very few really fundamental Planté plate types.

The fundamental intention is to increase the active surface of the plate by forming ribs. This development of the surface is carried out before formation with a rapid forming agent. The Tudor plate may be taken as type (Figures 80 and 81). It is made by casting pure lead in a mold of proper shape, and is probably the best known and most generally used of all European plates.

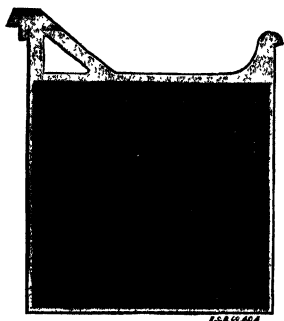


FIG. 82. — "Tudor" positive plate.

Other means than casting are also used to produce

the same increase of surface. The Gould plate (Figures 83 and 84) is made from pure sheet lead

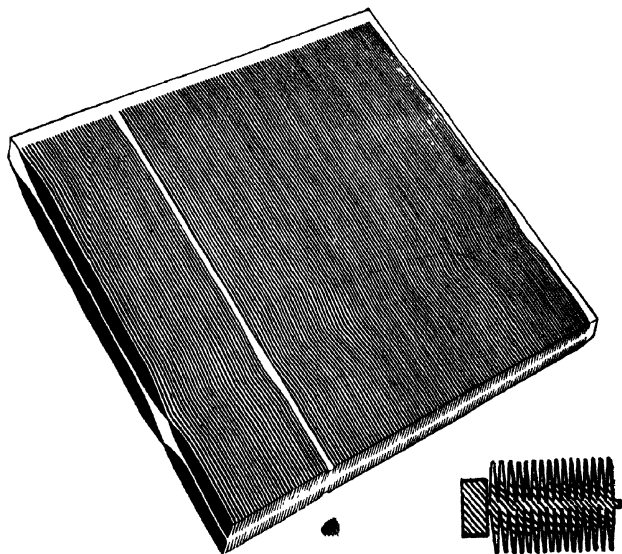


FIG. 83.—Section and cross section of "Gould" plate.

by a process of "spinning." The sheet of lead is fed back and forth between rapidly rotating mandrels

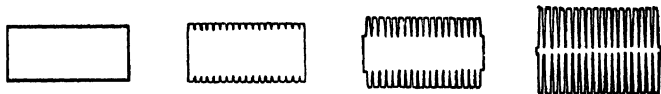


FIG. 84.—Steps in the spinning of a "Gould" plate.

filled with steel disks spaced far enough apart to give the right strength of rib for any particular service.

The National plate (Figure 86) looks much like the Tudor, but is made by **swaging** ribs and webs from a sheet of pure lead instead of by casting. Other plates very similar in final appearance are made by plowing, by pressing sheet lead through a die under great pressure, and in various other ways.

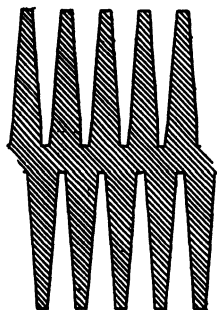


FIG. 85. — Cross section of "Gould" plate [drawn to scale].

One of the variations, and one of the oldest and most generally used, is the "Manchester" positive, shown in Figure 87 and already frequently mentioned in the more theoretical part of this book. This is not a very high surface plate, but it has shown itself well fitted for almost every kind of work. As will be seen from the cut, the active material is formed from "rosettes" of lead ribbon, and

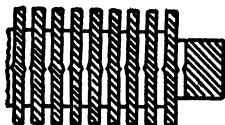


FIG. 86. — Longitudinal and cross sections of a "National" plate.



these are pressed into a cast frame of antimony lead before formation. The frame is so stiff that buck-

ling should not take place except under extreme ill treatment, and the surface is sufficient for any except the very highest rates. It is perhaps not quite so efficient at high rates as the plates with larger developed

Fig. 88. — Section showing dimensions of ribs, etc., in "Gould" positive.



surface (Tudor, Gould, National), but the latter demand rather more care in operation. The Gould plate (Figure 88) has the longest ribs of any of the types and its surface is very large

in proportion to its area. This is without question the plate most responsive in high-rate work, and most efficient in the hardest service, but the greater surface and longer rib mean greater inherent danger from local action and greater probability of buckling unless operating conditions are closely watched.

It is perfectly feasible to operate any of these high-surface batteries at astonishing rates, and in modern installations it is usually the booster which limits the

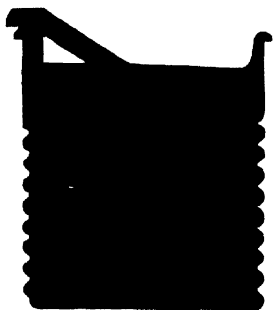


Fig. 87. — "Manchester" positive.

battery discharge. Most manufacturers are quite willing to send their batteries out to work at the 5-min. or even the 1-min. rate of discharge. A glance at the table will show what sort of an "overload" this is, if the term has any application to a storage battery.

"Normal rate"	1 for 8 hr.
×	2 for 3 hr.
×	4 for 1 hr.
×	8 for 20 min.
×	16 for 5 min.
×	32 for 1 min.

Of course the term "normal" as applied to the 8-hr. rate has lost significance, since the most important work of the battery is nowadays performed at a very much higher rate, and batteries of large size are not often put in for service at this rate except for stand-by or insurance purposes. The 20-min. rate is more nearly "normal" in modern battery practice.

In regulation work, batteries are usually operated in conjunction with a large power plant. The cells have each seventy-five to a hundred plates about 15×31 in., or 18×18 in. (See Figure 89.) Each 15×31 in. positive plate gives 40 amperes for 8 hr., and from this the capacity of the battery at various rates can easily be calculated. Suppose each cell has 101 plates.

50 positives $\times$ 40 = 2000 amperes for 8 hr.
or 4000 amperes for 3 hr.
or 8000 amperes for 1 hr.
or 16,000 amperes for 20 min.
or 32,000 amperes for 5 min.

If the battery is working in conjunction with a 500-volt power circuit, it will consist of about 260

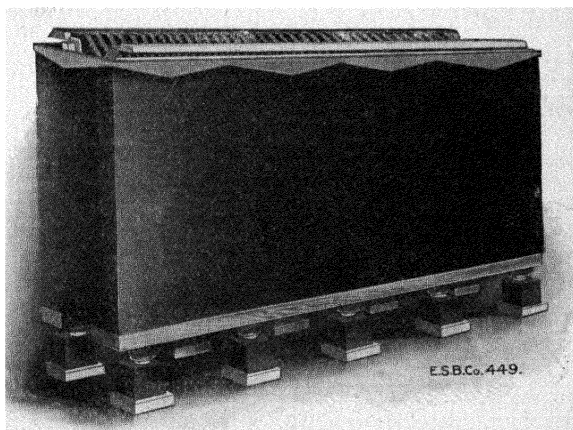


FIG. 89. — One cell of a large regulating battery.

cells. The power obtainable from the battery is therefore

2000 amperes at 500 volts =
1000 KW. for 8 hr.

and from this on up to

32,000 amperes at about 400 volts =
12,000 KW. for 5 min.

Such a battery would only be used in connection with a very large power plant—say of 5000 KW. or more.

It will be quite evident how such a battery should be used. Its little 1000 KW. would hardly be felt at the 8-hr. rate, but its 12,000 KW. can give regulation of enormous short peaks. For momentary peaks, lasting only a fraction of a minute at their maximum, this battery could furnish up to 25,000 KW.

As a matter of fact the total quantity of energy furnished by a single discharge of this battery is not very large, as measured by modern requirements. It can give

$$1000 \times 8 = 8000 \text{ KW.H.}$$

if discharged at the 8-hr. rate, and

$$12,000 \times \frac{1}{12} = 1000 \text{ KW.H.}$$

if discharged at the 5-min. rate.

Its main importance lies in its power to absorb and give up very large quantities of energy in very short times without danger to itself or trouble to any one about the station.

“Stand-by” or Insurance Batteries. — The most important of all the applications of the storage battery is, strange to say, the one in which it is called upon to do the least actual work. This is as a mere reserve of power, to be used only in case of emergency.

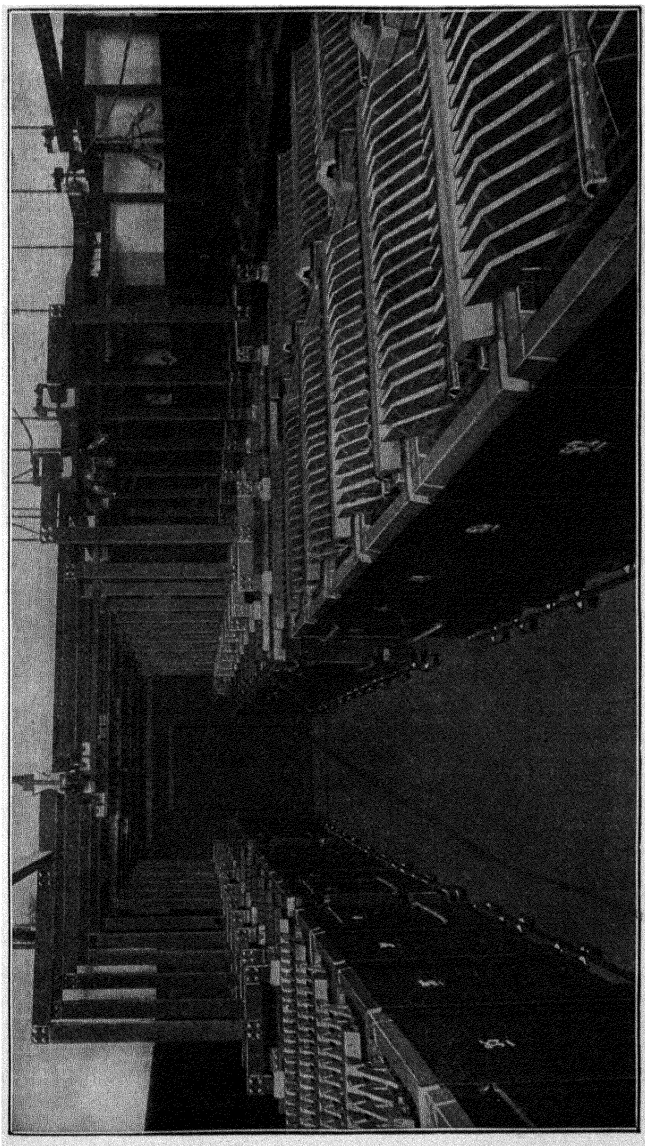


FIG. 90.

It is of the utmost importance that the supply of light and power, in a city or in any large service, should be continuous. The central power stations of a city supply thousands of consumers in every possible application of electric power. Lights, heat, machinery of every description, elevators, — all depend on the continuous service given by the power company. Any accident which resulted in stopping the supply of energy, even for a few minutes, would do a lot of damage and inconvenience many people. The stopping of all the generators in one of the New York stations would leave thousands of people in the dark, without elevator service, with no work to do because all the machinery in the factory was dead.

The great supply companies, like the various Edison Companies of the country, take every precaution to prevent such a stoppage in service. Engines, turbines, generators, — all are installed in separate units, each of which has only a fraction of the work of the station. Enough extra sets are provided to allow for all necessary repairs and replacements without interruption of service. At the bottom of all these precautions, the power house has connected with it a huge storage battery, which is kept constantly charged and which is called on for active service only in case of the utmost need.

The engineer in charge of the station has taken every precaution and has provided for every possible

emergency. But if anything should happen which puts the power house out of action for a time, the battery is big enough to carry the whole station load for a few minutes—long enough to get aid from neighboring stations or to make rapid repairs and changes. The battery is the only source of power which is wholly reliable. There are no moving parts, and there are no high pressures to cause trouble.

One of these stand-by batteries may cost \$200,000 and be called on for only two or three real discharges a year. Interest and depreciation is perhaps \$25,000 a year, and so these discharges cost \$12,000 apiece,—a couple of dollars per kilowatt-hour; but quite worth the price, for the station was able to continue uninterrupted service. The battery pays for itself in “good will” alone.

For this particular class of service the manufacturers are beginning to use a new class of plate. As far as life and capacity under high rate is concerned, the large surface Planté plate is of course the best, and many stand-by batteries of this type are in use. But they are expensive to make. Local action is considerable, and this may be especially true at the very low charging rate at which it is often necessary to charge such a battery. Paste plates can do this work quite as well as the more expensive Planté battery. They hold a charge longer, and work best on low

charge rates. The life of a paste plate battery is quite sufficient and its efficiency is good.

Figure 90 shows a large stand-by battery of paste plates. The experience of European manufacturers has shown that such batteries are economical, and we have finally come round to using paste plates for this work, but about ten years behind the practice in Europe.

126. Negative Plates. — Only a few manufacturers use the true Planté type of negative plate for any service whatever. The Gould plates are the only pure Planté negatives in general use in this country. The negative differs from the positive in having thinner ribs, and a thinner center web, and in having a much larger percentage of the whole weight in the form of active material. It is made by formation as positive first, and the rapid forming process is carried on until the lead of the original blank is nearly all changed to peroxide, just enough being left to hold the plate together. There is no danger of the plate ever getting any weaker after it goes into service, for once it has been reversed to the negative condition there will never be any further action on the lead of the support plate.

Paste Negatives. — The commonest type of negative plate for general service is a paste plate. It differs from the negatives used in electric automobiles only in being more heavily constructed. The grids for

these plates are usually made with the dovetails of the strips expanding outward to give the active material, which contracts in service, an opportunity to keep in good contact with the grid. I am not at all sure that this is anything more than an inherited idea, but it seems to be followed universally by manufacturers of paste negatives.

Box Negative. — The Planté negative is peculiar in its ways, and not always easy to control. The paste negative has not the extremely tough constitution necessary for some of the modern high-rate regulation work. As a mean between the two, and with the intention of avoiding, if possible, the troubles of both the other types, what is called the “box” negative has been developed, and put into active service both in Europe and in this country. It is shown in Figure 91, and it consists of a frame of antimony lead into which are put the blocks of active material. A front and back cover, both full of fine perforations, complete the plate. The active material is prepared in the form of blocks which fit the openings in the frame. Some manufacturers have sent them out into service without any preliminary

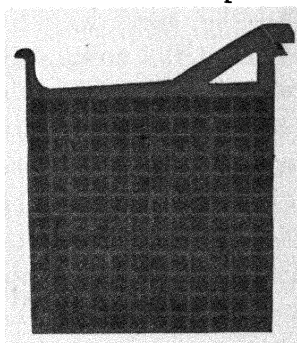


FIG. 91. — “Box” negative plate.

formation, the charge necessary for the development of the positives being just about sufficient to form the very porous active material of the negative. It is usually considered better to form them before sending them out.

At first sight it seems like a decided step backward to place active material inside a box, forcing diffusion to take place through small openings. But the much more difficult diffusion through the fine pores of the material inside the perforated cover completely overshadows any effect of the outside cover. Furthermore, the presence of the cover permits the maker to use a very porous active material indeed. It need have no coherence in the mechanical sense as long as it has conductivity, and the latter property is aided by adding finely divided carbon to the prepared block. The increased porosity which can be attained in this way more than makes up for the longer diffusion path through the perforations in the plate.

127. Submarine Cells. — Next in order of size after the central station and regulating batteries come the ones used in submarine boats. Here the design is most exacting, for both space and weight are sharply limited, especially the former, and a very large amount of power must be furnished over a considerable time. Paste plates are the rule, and the average size is about 15×24 in., and from 21 to 35 plates to the cell. The containing tanks are of hard

rubber, — much like giant vehicle cells, — and they are fitted with arrangement for disposal of all gases formed during operation. The mixture of hydrogen and oxygen which is produced in the cell is about as sharply explosive as anything possibly could be, and serious accidents have resulted from faulty gas disposal and ventilation. The best way seems to be to fit each cell with its own tight cover and with escape pipe, rather than to shut up the cells in a gas-tight compartment, which is freed from gas by a fan.

The plates for this service are made to have a capacity as high as is compatible with a reasonable life. Tests include not only capacity at various rates of discharge, but also tests for mechanical strength, and a discharge while the cell is being rocked rather violently through an angle of about 30°.

Of course the boat is dependent wholly on its batteries for power while submerged. Sixty cells must give about 5000 ampere-hours at the 3- or 4-hr. rate. Even this only means

$$\frac{110 \times 5000}{3 \times 746} = \text{about } 250 \text{ H.P.},$$

which is not a very large amount of power to drive a boat as large as a modern submarine.

128. Train-lighting and Car-lighting Service. — In Denmark cars have been carrying batteries for lighting service for more than twenty years, and they have

found this application a valuable one. This branch of storage battery engineering has been of increasing importance in this country in the past few years. Some day before long it will be statutory that every railroad train shall do all its lighting by electricity.

The simplest system is "straight battery." The charged battery is taken on at one terminal, discharged at a rather low rate during the trip, — at the 24–48 hr. rate — and removed at another point, a freshly charged battery taking its place. There is much of this practice in the United States. The regular cell for this work can give about 250 to 350 ampere-hours. Sixty cells in a battery give an average of 110 volts, and will run 60 16-candle-power lamps for 24 hr.

Car-lighting Systems. — Often an axle-driven dynamo is added, which can furnish somewhat more than power enough to run all the lamps when the train is moving at a speed greater than thirty miles per hour. The excess energy is absorbed by the battery when the train is running at higher speeds than this, and the battery must run the lights while the train is standing still. Usually a complete system of regulation is provided, so that the battery acts just as a large regulating battery would in a power plant — absorbing energy whenever an excess is being turned out by the dynamo and giving it out again at the times when the speed is low or the car is standing still.

Train-lighting Systems. — In through trains which make a run of many hours without change in make-up, the generator for the whole train is sometimes installed on the locomotive and driven by a steam turbine. A regular "booster" outfit is installed either on the tender or in the baggage car, and this attends to regulation of all load variations. The battery installed in each car is sufficient in capacity to run its own lights for a time, and the train can therefore be made up and broken up without interruption in service. As soon as the train has been made up, the generator takes the load and the batteries are kept nearly fully charged. They then have to care only for the regulation and to serve as reserve.

In all of these different kinds of lighting service, the pure Planté plates have done well, and most of the companies who do this work make special Planté type plates for it.

129. Vehicle Service. — A rapidly growing field of usefulness for the storage battery is in vehicle service. At first glance it seems a poor substitute for the light and efficient internal combustion engines of modern times. To drive a pleasure vehicle at a reasonable speed over average streets and good roads requires about 1.5 KW. If the battery has 32 cells, its average voltage during discharge will be 60, and each cell must be able to give 25 amperes for four or five hours. Such a bat-

tery will cost about \$250, and will weigh not far from 750 lb. complete.

But this electric vehicle has many important advantages. It is clean and neat, it is simple to operate, and it is almost absolutely certain to go if there

is a charge in the battery.

Where a central charging station can arrange to charge many batteries each night, the whole arrangement is efficient and economical. It is rather strange to see how the heavy truck, driven by electricity and doing its hard work day after day, has been the best of arguments with which to convince the doubter of the economy of the electric vehicle in light work and for pleasure.

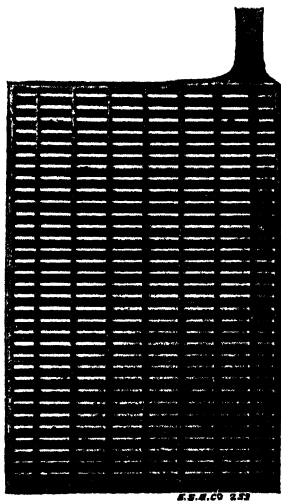


FIG. 92. — Paste vehicle grid.

The plates used in vehicle work are legion in name and varied as to fame. Paste plates are now almost universally used over the world. European practice runs toward thinner and lighter plates, cheaply made and with a limited but well understood life. In this country we make heavier and stronger plates of lower weight capacity, but having longer life.

WEIGHT EFFICIENCY OF PASTE BATTERIES

American Standard Plates	7½–8½ watt-hours per pound
American Light, high capacity,	10½ watt-hours per pound
Edison	12½ watt-hours per pound
Medium European	11 watt-hours per pound
Light European	14 watt-hours per pound

Figures 93 and 94 show one of the commonest types of grids used in making vehicle plates. Most positive grids are so made as to give support from outside to the rather loose and noncoherent peroxide. This support is supposed to be given by making the ribs of the cross-section shown in Figure 76. The negative grid is made with its dovetail in the opposite sense, as already explained. Many complicated forms of grid have been patented and used, but gradually the majority of manufacturers have settled down to the similar types. The old original ideas are sure to recur at fairly regular intervals, sometimes because the cause of trouble has been removed, and sometimes because it has been forgotten.

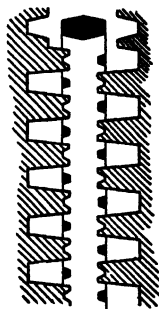


FIG. 93. — Cross-section of mold and grid casting.

About the only decided variation from the simple grid type now in evidence is the so-called “iron-clad” vehicle plate (Figure 95). The type is peculiar in depending on an insulating support grid or envelope of rubber, celluloid, porous biscuit ware,

wood, etc. This surrounds the active material and prevents shedding, and contact is made with a central lead strip or wire. There seems every reason to believe that the apparent security is not a very real one. It is quite possible for positive active material to lose coherence and capacity even though the material cannot get away and fall to the bottom of the cell, as it does in the ordinary case.

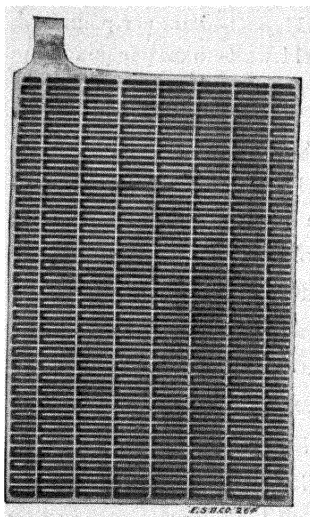


FIG. 94. — Type of grid for paste positive.

This particular plate has, however, been carefully tested by the makers, and may prove an exception to the rule.

The present status of the vehicle battery might be summarized as follows: There is not very much difference in standard plates by different makers. Grids differ but slightly. Formation and other treatment is becoming a well-known art. With proper operation the good American battery should give 250 to 400 cycles without much trouble. It must be cleaned once during this life, probably after 200 to 300 cycles.

If operating conditions are not right, the same battery may begin to give trouble after 100 discharges or less. I know of one company which manages to get nearly 450 cycles in hard service from any one of several of the standard American types.

A set of vehicle negative plates is usually assumed to outlast two sets of positives. This is usually conservative.

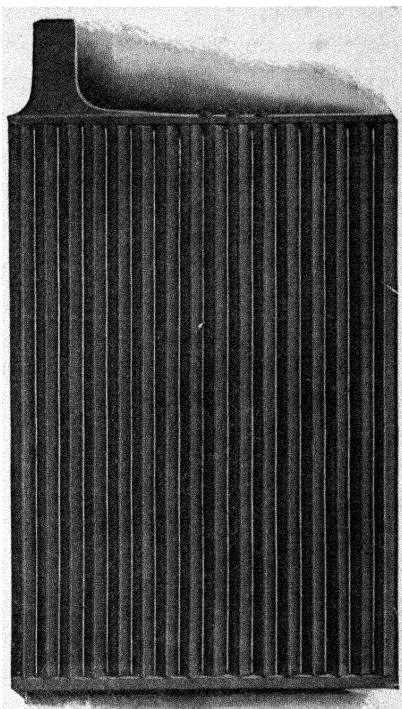


FIG. 95. — "Iron-clad" vehicle plate.

CHAPTER XVIII

ACCUMULATORS IN GENERAL

130. It is both strange and interesting that so few galvanic combinations have been found which are really fit for use as accumulators. Planté began his experiments in 1859, at a time when the whole scientific world was much interested in the subject of galvanic cells, and he worked for more than thirty years on the problem. During that time an immense number of combinations were suggested for use as primary cells, but hardly a new idea was brought forward for the improvement of secondary cell, with the exception of the Faure variation, which is mechanical rather than fundamental. The present Edison-Jungner iron-nickel-alkali accumulator is the first combination which seems to be a real rival of the lead cell. This rivalry seems to be confined to vehicle and traction work, and the alkaline battery can hardly be said to compete at all in the heavy work of the modern power plant.

It is hard to say just why progress has been so slow. Evidently the problem is a difficult one. Planté was exceedingly lucky in finding what seems

to be the best of all combinations, and the men who have developed the alkaline accumulator to its present mechanical perfection deserve all credit for that achievement.

Any categorical statement as to what can or cannot be done in any line of scientific or technical development is not likely to hold true very long. In the accumulator problem we seem to have made advances only in one direction, and it may be that there is some fundamental advantage in this direction. All our successful accumulators have plates which are very slightly soluble in the electrolyte used with them. There is a host of other possibilities. The electrolyte might be called upon to furnish a large part or all of the cell energy. Soluble plates might be used. The charge might be made by chemical means, in which case the cell would cease to be an accumulator in the usual sense of the word.

131. As far as our experience goes we can describe the ideal accumulator as follows : —

The active material is very slightly soluble in the electrolyte.

Current is carried through the main body of the cell by ions different from those which pass back and forth at the electrodes.

These two conditions seem to us at present to be necessary ones because we have found no other evident way of insuring *mechanical reversibility*. Even

lead sulphate has almost too great solubility in sulphuric acid, for negative plates lose in capacity because of the increase in the size of lead grain. Lead peroxide is ideal in this respect.

A reaction must be selected which yields a large amount of energy per gram equivalent of material used. While the substances used in the lead cell are unfortunate by reason of their high equivalent weights, they are fortunate in another way. Energy is obtained not only from the anode reaction, where lead goes into solution, but also from the PbO_2 reaction. Lead peroxide is one of the electrodes which can furnish energy during reduction.

The cell must have a low internal resistance, otherwise its efficiency will be impaired. Again the lead cell is a fortunate choice, for hardly any electrolyte has a lower specific resistance than 30 % sulphuric acid, and both lead and lead peroxide are good conductors.

The chemical reaction must be perfectly reversible. The losses in the lead cell are almost wholly due to the production of gas.

132. The first efforts toward the discovery of a cell other than Planté's start from his work and from his point of view, as would be expected. Peroxide of lead has been tried with most of the metals replacing lead as the other plate. Zinc, cadmium, copper, bismuth, etc., were all given a trial, and no one of them has proven better than lead. Then, too, the

alkaline combinations, starting with the Lalande-Chapeyron type, were given a trial. The following may be mentioned:—

Copper/potassium hydroxide/silver peroxide.

Cadmium/potassium hydroxide/copper oxide.

Zinc/potassium hydroxide/copper oxide.

Iron oxide/potassium hydroxide/manganese dioxide.

Iron (?) /potassium hydroxide/nickel peroxide.

Cobalt/potassium hydroxide/nickel peroxide.

133. Until recent years the lead-sulphuric acid cell has had the commercial field to itself. A great many suggested combinations were tried, but no one of them has stood the test. Usually it has been the mechanical reversibility which has been at fault, even when the chemical reaction has been a favorable one and quite reversible.

Lately one combination has been developed which bids fair to make a place for itself in practical service. It is already a success as far as all tests of reversibility, mechanical and chemical, are concerned. This is the iron/potassium hydroxide/nickel peroxide cell, as developed by Edison to mechanical perfection in this country. Figure 96 shows an assembled cell. The cell and support plates are made of nickel steel. The perforated hollow tubes of the positive plate (see Figure 97) contain a mixture of metallic nickel and nickel oxide before development. After development the active material is perhaps

NiO_2 , the peroxide of nickel. In the finely perforated flat boxes of the other plate (see Figure 98) is a mixture of iron, iron oxide, and lampblack. This

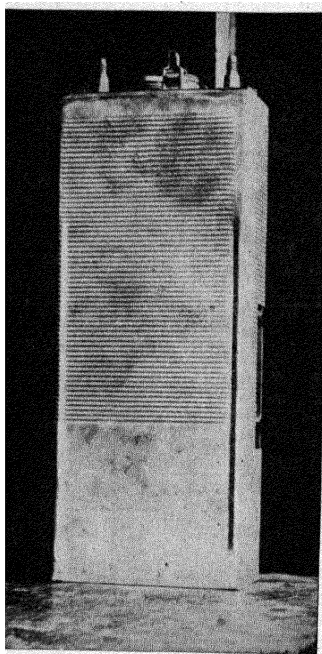
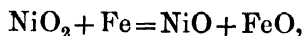


FIG. 96. — Edison cell.

is the negative plate, and on charge metallic iron seems to be formed in part. The electrolyte is concentrated caustic potash solution.

There is still much to be learned about the fundamental cell reaction. The simplest formula is



and this is a fairly close statement though not an accurate one. This formula indicates one interesting point. The electrolyte does not appear at all. And it is quite true that the change in

the density of the electrolyte, from complete charge to complete discharge, is small. There is a slight change of concentration, but not sufficient to be of service as an indication of the condition of the cell.

It is of course perfectly certain that there are changes of concentration of the electrolyte in the active part of the plates, and that these changes are proportional to the rate at which the cell is working. It is quite certain that the effect of diffusion, which has been called on so often in explanation of the course of charge and discharge curves of lead cells, plays just as important part in the Edison cell. Until we know just what the fundamental cell reaction is, we cannot foresee just how great the effect of change in the OH^- concentration will be.

There are many interesting things about the curves taken on this type of cell. Figure 99 shows discharge curve to a low voltage, much lower than would be reached in practice. The evident two stages in the curve, without any change in the distribution of active material to account for it, may mean a change in the cell reaction at that point.

This particular type of cell has the following characteristics at 25°C. :—

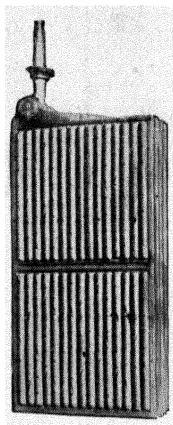


FIG. 97.—Group of Edison positive plates.

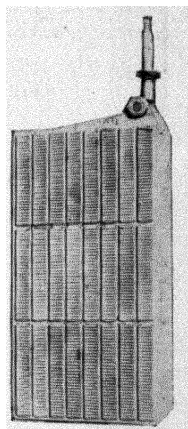


FIG. 98.—Group of Edison negative plates.

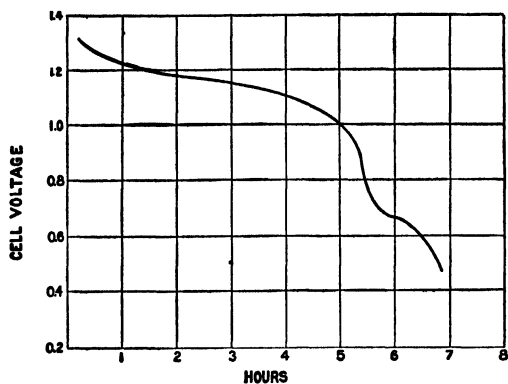


FIG. 99. — Discharge curve of Edison cell.

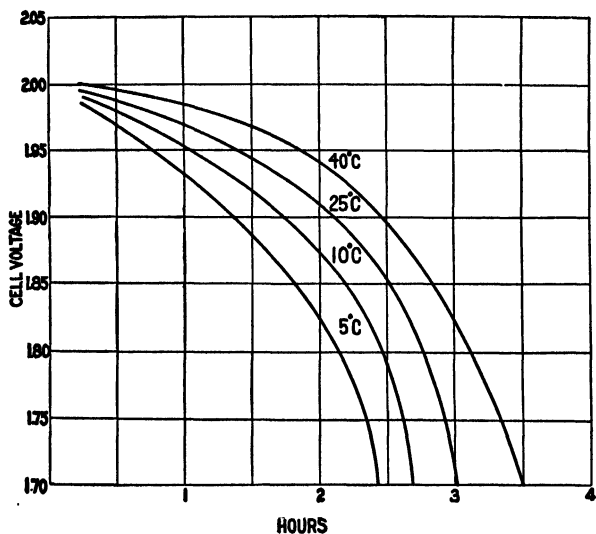


FIG. 100. — Discharge curves of standard American paste type at various temperatures.

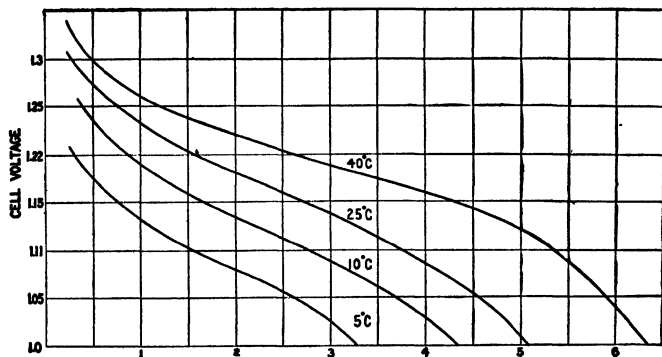


FIG. 101. — Discharge curves of Edison cell at various temperatures.

Weight of complete cell, 19.25 lbs.

Capacity $\left\{ \begin{array}{l} \text{ampere-hours, 225.} \\ \text{watt-hours, 248.} \end{array} \right.$

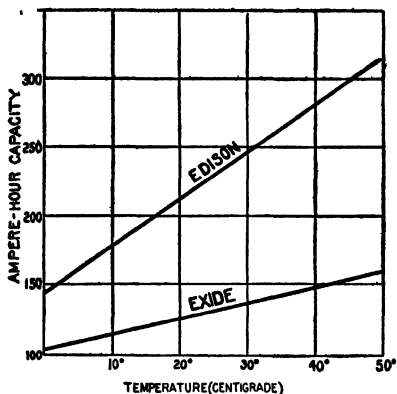


FIG. 102. — Summary showing change in ampere-hour capacity with temperature. [Exide and Edison.]

Ampere-hours per pound of cell, 11.3.

Watt-hours per pound of cell, 12.4.

Ampere-hour efficiency, 82 %.

Watt-hour efficiency, 60 %.

An examination of the temperature effect shows the important part which diffusion plays in the cell activity.

The curves of Figures 100 and 101 show the relative temperature effects on a standard type of lead cell

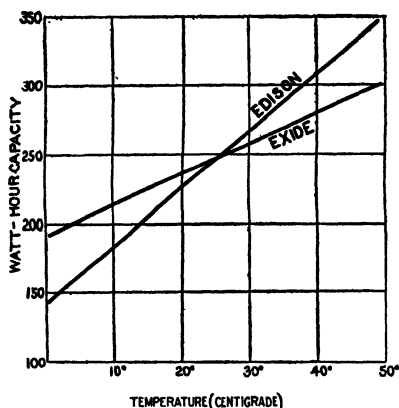


FIG. 103. — Change in watt-hour capacity with temperature. [Exide and Edison.]

and on an Edison cell, and these are summarized in the curves of Figures 102 and 103.

The factors which determine the practical success of such a cell are numerous. Without any intention of either criticizing or advertising, we can examine the general characteristics of some present-day types.

The following table gives data on three types—a rather heavy American plate, a rather light European type, and the regular Edison type of approximately the same watt-hour capacity.

	STANDARD AMERICAN	LIGHT EUROPEAN	EDISON
Watt-hours per pound . .	8	12	12.5
Life	1	$\frac{3}{4}$	3
Cost	1	$\frac{1}{2}$	2 $\frac{1}{4}$
Watt-hour efficiency . . .	75 %	80 %	60 %

APPENDIX

I

**The General Equation for the Electromotive Force of a Cell
in Terms of the Heat of the Chemical Reaction and the Tem-
perature Coefficient of the Electromotive Force**

Assume

1. The law of the conservation of energy.
2. The second law, in the form

$$\frac{\text{work done}}{\text{heat used in doing it}} = \frac{dT}{T}.$$

We send our cell through the following cycle : —

1. At temperature T , send 96,540 coulombs through at e volts. The work done is Fe joules.

Suppose the cell cool while it works. It will absorb W calories from its surroundings. $W = eF - Q$, Q being the chemical heat of reaction.

2. Raise the temperature of the cell to $T + dT$. This will take P calories. The electromotive force is changed to $e + de$.

3. Now send 96,540 coulombs through in the *opposite direction*, against $e + de$ volts. The work done is $F(e + de)$ joules. The cell heats when it works

in this direction. It gives out $W + dW$ calories.
 $W + dW = F(e + de) - [Q + dQ].$

4. Cool the cell back to T . We get back our P calories.

dW and dQ are vanishingly small. They can be neglected, since dT is an infinitesimal temperature difference.

The net result of this cycle is an amount of available work Fde . To produce this amount of available work, a quantity of heat $F e - Q$ changed its temperature from $T + dT$ to T .

Apply the second law.

$$\frac{Fde}{Fe - Q} = \frac{dT}{T}.$$

Transforming,

$$e = \frac{Q}{F} + T \frac{dQ}{dT}$$

II

Calculation of the Electromotive Force of a Cell in Terms of the Solution Pressure at the Electrodes and the Osmotic Pressure in the Solution

Assume the gas law to hold for osmotic pressures.

$$pv = RT.$$

p = osmotic pressure.

v = volume of a gram-molecule.

R = gas constant.

T = absolute temperature.

The work obtainable by a change in concentration from p_1 to p_2 at constant temperature is

$$\int_{p_1}^{p_2} RTv dp = RT \int_{p_1}^{p_2} \frac{dp}{p} = RT \ln_e \frac{p_1}{p_2}.$$

Solution pressure is continually balanced at the electrode by osmotic pressure and work done is osmotic work.

$$A = RT \ln_e \frac{P}{p} \text{ where } P \text{ is solution pressure, } p \text{ is}$$

osmotic pressure, and A is work done at the single electrode.

We are calculating in gram-molecules. For a univalent ion, 96,540 coulombs will pass the cell with a gram-molecule; and e , the electromotive force, will be a measure of A , the work done at the electrode.

For a univalent ion

$$e = \frac{RT}{F} \ln_e \frac{P}{p}.$$

If the ion which maintains equilibrium is bivalent, only half as much of it need pass the electrode to carry the 96,540 coulombs, and if it is n -valent, $\frac{1}{n\text{th}}$ as much will be enough.

For an n -valent ion we have

$$e = \frac{RT}{nF} \ln_e \frac{P}{p}.$$

At the other electrode we have a precisely similar equation to express the action, but here the ion passes the electrode in the opposite direction and e has the opposite sign. The electromotive force of the whole cell will be the difference of the two single electromotive forces.

$$e_1 - e_2 = \frac{RT}{nF} \ln_e \frac{P_1}{p_1} + \frac{RT}{nF} \ln_e \frac{P_2}{p_2}.$$

$\frac{RT}{F}$ is constant at constant temperature. Its numerical value at 17° C. is

$$\frac{8.31 \times 290 \times 2.303}{96,540} = 0.0575.$$

We have introduced the factor 2.303 which changes natural logarithms to common. The equation as usually applied is

$$e = \frac{0.0575}{n} \log_{10} \frac{P_1 \cdot P_2}{p_1 \cdot p_2}.$$

III

Calculation of the Concentration of the Active Ions in the Lead Accumulator

(1) *The concentration of Pb⁺⁺ ion.*

The solubility of lead sulphate in pure water is 1.4×10^{-4} gm.-mol. per liter. Assuming complete

dissociation and that the mass law holds for ionic equilibrium, we have

$$\text{Pb}^{++} \cdot \text{SO}_4^{--} = (1.4 \times 10^{-4})^2 = 1.96 \times 10^{-8}.$$

Accumulator acid is about 2 *N* but is only about 50 % dissociated. In this acid SO_4^{--} is therefore 1.0 *N*, and in the cell

$$\text{Pb}^{++} = 2 \times 10^{-8} \text{ gm.-mol. per liter.}$$

(2) *The concentration of H^+ ion.*

As stated above, 2 *N* H_2SO_4 is about 50 % dissociated, the concentration of H^+ is therefore about 2 gm.-mol. per liter.

(3) *The concentration of PbO_2^{--} ion.*

From the mass law : —

$$\text{PbO}_2^{--} = \text{Pb}^{++} \cdot (\text{O}^{--})^2$$

and $(\text{H}^+)^2 \cdot \text{O}^{--} = \text{constant.}$

Therefore,

$$\text{PbO}_2^{--} = \text{constant} \frac{\text{Pb}^{++}}{(\text{H}^+)^4}.$$

The value of the constant can be calculated by measurements of the solubility of lead hydroxide in sodium hydroxide solution, and these measurements are within the range of analytical attack. In Dolazalek's determination the sodium hydroxide was 0.066 normal, and it dissolved Na_2PbO_2 to a concentration of 0.00305 gm.-mol. per liter. In this

solution PbO_2^{--} was therefore about .003 *N* and the remanent alkali contained 0.054 gm.-mol. OH^- per liter.

The concentration of H^+ in this solution we can calculate with the aid of the mass law. We have

$$\text{H}^+ \cdot \text{OH}^{--} = 1.1 \times 10^{-14}$$

from measurements on water, gas cells, etc.

In our alkali solution, OH^- is about .05 normal.

H^+ is therefore about 2×10^{-13} *N*.

The lead ion concentration in the alkali we need also. In pure water, lead hydroxide dissolves to about 4×10^{-4} gm.-mol. per liter.

We have

$$\text{Pb}^{++} \cdot (\text{OH}^-)^2 = (4 \times 10^{-4})^3 = 6 \times 10^{-11},$$

and for our .05 *N* alkali

$$\text{Pb}^{++} = \frac{6 \times 10^{-11}}{(.05)^2} = 2 \times 10^{-8}.$$

Now we can calculate our constant

$$K = \frac{\text{PbO}_2^{--} \cdot (\text{H}^+)^4}{\text{Pb}^{++}}.$$

$$K = \frac{(3 \times 10^{-3}) \cdot (1.6 \times 10^{-13})^4}{2 \times 10^{-8}}.$$

$$K = 3 \times 10^{-46}.$$

From this, for 2 *N* acid

$$\text{PbO}_2^{--} = 3 \times 10^{-46} \cdot \frac{\text{Pb}^{++}}{(\text{H}^+)^4}.$$

From (1) $\text{Pb}^{++} = 2 \times 10^{-8}$.

From (2) $\text{H}^+ = 2$.

$$(\text{H}^+)^4 = 16.$$

$$\text{Finally } \text{PbO}_2^{--} = \frac{3 \times 10^{-46} \cdot 2 \times 10^{-8}}{16}.$$

$$\text{PbO}_2^{--} = 4 \times 10^{-53}.$$

This is the concentration of the PbO_2^{--} ion in the ordinary lead cell, using as electrolyte 2 *N* acid.

IV

Variation in Capacity with Volume of Electrolyte

An important factor in the design of a storage cell is the permissible volume of the electrolyte. It is

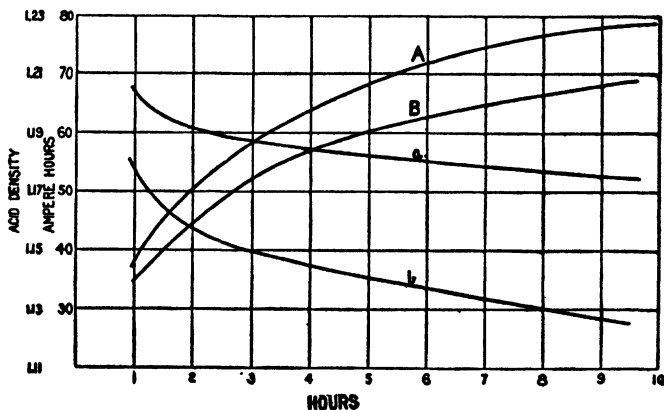


FIG. 104. — Variation in capacity with volume of electrolyte.

A, capacity with 2000 cu. cm. of electrolyte, at various rates.

a, density of electrolyte corresponding to A.

B, capacity with 1100 cu. cm. of electrolyte.

b, density corresponding to B.

quite evident from general considerations that in a cell containing many plates and little electrolyte, the latter may limit capacity by becoming so dilute that the useful working voltage is soon passed.

Figure 104 shows the capacity of a cell and the change in the density of the cell electrolyte at different rates of discharge and with different volumes of electrolyte in the cell.

V

The Gas given off from the Lead Cell

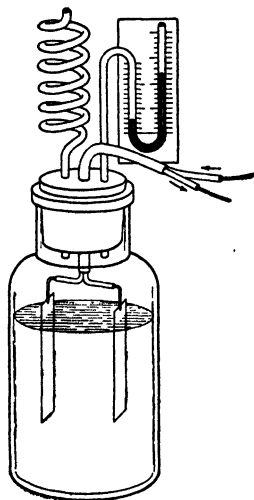


FIG. 105. — Ampere-manometer for measuring rate of evolution of gas.

A mixture of oxygen and hydrogen is given off from a lead accumulator during the latter part of charge. This is a very explosive gas mixture, and in submarines and other places where batteries are closely confined, ventilation must be very carefully looked out for.

Figure 105 gives a diagrammatic picture of apparatus which can be used to measure the rate at which gas is evolved during charge and discharge. The gas escapes through the narrow capillary, and the gas pressure is measured by the small mercury manometer.

Figure 106 gives curves of a test on the rate of gassing of paste and Planté negative plates during charge at the 8-hr. rate.

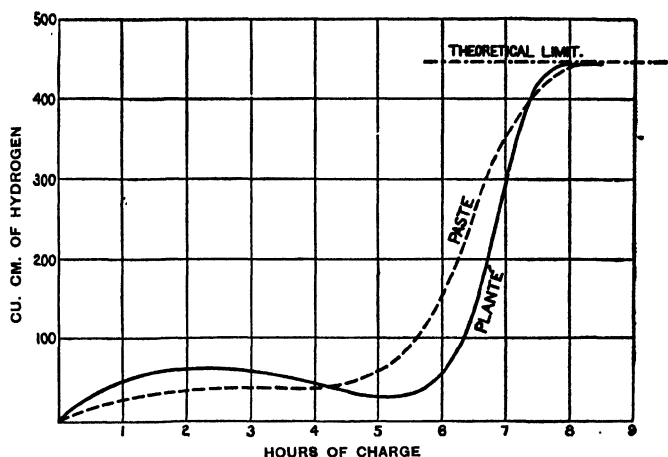


FIG. 106.—Curves showing evolution of hydrogen from paste and Planté negative plates during charge.

VI

Specific Resistance

Aluminium	3×10^{-6}
Lead	2×10^{-5}
Copper	1.7×10^{-6}
Graphite (about)	5×10^{-3}
Quartz	3×10^{10}
30 % H_2SO_4	1.4
31 % HNO_3	1.3
20 % HCl	1.3

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