A STANDARD BATTERY.

BY G. A. HULETT.

IN working with a potentiometer considerable inconvenience was occasioned by the variations in the batteries used. Storage batteries gave a fairly constant current for certain portions of the discharge, but during long continued observations it was necessary to frequently refer to the standard cell and make the necessary change in the regulating resistance. This inconvenience has been obviated by the use of some batteries which have given an exceedingly constant current and have practically no temperature coefficient. Since these batteries may be of use in many lines of work, where a small but steady current is needed, it has seemed well to describe them.

In 1903 Mr. Edward Weston patented a combination — Cd amalgam cadmium sulphate solution $\text{Hg}_2\text{SO}_4\text{Hg}$ — which had an exceedingly small temperature coefficient and has been known as the Weston cell. This is a secondary standard and when calibrated served admirably as a laboratory instrument for giving a definite E.M.F. which was independent of ordinary temperature variations. This unsaturated cell, or the saturated cadmium standard cell, cannot be used as a battery, due partly to the form and dimensions given to it, but more particularly to the irregular cathode reactions. Considerable evidence has been obtained by the author,¹ showing that the cathode system of these cells ($\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$, Hg_2SO_4 , Hg solution) was in unstable equilibrium and it was concluded that the cathode was not a reversible electrode. In studying this system by the rotation experiments, it was found that the presence of a certain amount of sulphuric acid caused the system to come to equilibrium at once. It had been assumed that the neutral cadmium sulphate solution hydrolyzed the mercurous sulphate and formed a basic salt which was responsible for slow changes in the E.M.F. of the cell, it was therefore expected that the sulphuric acid would have the effect observed.

¹ PHYS. REV., 22, 321; 23, 166; 25, 16.

It seemed therefore that it was only necessary to add a certain amount of sulphuric acid to the cell to make it completely reversible, and when a special arrangement was devised by which large electrode areas were obtained it was found possible to construct batteries which were quite reproducible and especially was it found that the mercurous sulphate could be made in the battery after it was set up, that is, it could be charged and the troublesome manipu-

lations of preparing and washing the depolarizer entirely obviated. A great many forms have been tried, but for simplicity and effectiveness the form represented by Fig. 1 has given the best results.

Fig. 1.

A low form salt mouth bottle about 8 cm. in diameter with a neck diameter of 5 cm., was provided with a paraffined cork. The cork was perforated by two holes and served to hold the anode cup *A* and the tube *B* through which contact with the mercury cathode *K* was made. Resting on the mercury and surrounding the anode cup was a 50 per cent. solution of cadmium sulphate to which was added 1 per cent. of sulphuric acid. By passing a current in through the mercury electrode *K*, mercurous sulphate was formed and cadmium deposited in the amalgam in the anode cup. It was found advisable to keep the solution stirred while charging.

All the materials for these batteries were at hand except the anode cups and they were not very difficult to make. A thin-walled tube, 4 cm. in diameter, was closed at one end so that the bottom was flat (Fig. 2) and in the middle on the inside of this flat bottom was sealed the little tube *C*. Before this tube was sealed on a small platinum wire was stuck to its end so that after the seal was made the platinum wire extended from the inside of the tube out into the cup in order to make contact with the amalgam and a little mercury which was placed inside the tube for contact with the lead

Fig. 2.

wire. The large tube was now cut off at D , 3 or 4 mm. above the end, with a cracking coal. (Common watch glasses were found to be of the right shape and size for the anode cups, but in fusing on the glass tube for a holder it was found that these watch glasses were not soda glass. Recourse was had to fusing two of these glasses together at the ground edge and drawing them out into tubing which was used to fuse into other watch glasses and thus very serviceable cups were made.) These cups were filled with a 12½ per cent. amalgam and the stem fastened into the cork with wax so that the bottom of the cup was about 2 cm. above the bottom of the bottle when the cork was in place. With this arrangement the electrodes were close together and the cadmium sulphate formed at the anode readily diffused over into the solution and thus concentration changes were minimized.

The bottom of the bottle was covered with mercury to a depth of ½ cm. and on this was placed the electrolyte to a depth of 4 or 5 cm. This electrolyte was made by adding 10 c.c. of strong sulphuric acid (sp. gr. 1.84) to a liter of water and in this was dissolved an equal weight of cadmium sulphate crystals (ordinary c.p. $\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$). For example 200 grams of the crystals were powdered and dissolved in 200 c.c. of the dilute sulphuric acid solution which made 250 c.c. of the electrolyte, just enough for one battery. The rate of solution was very slow and a motor driven stirrer was generally used to bring the salt into solution. In forming the mercurous sulphate electrolytically in the battery there is some danger of forming a small amount of a basic salt at the mercury electrode unless the solution is stirred, the stirring was easily accomplished by giving the battery a rotary motion with the hand and then a current of one ampere to 50 cm.² mercury surface was used and in 20 minutes sufficient mercurous sulphate had formed. Due to the rapid deposition of cadmium there was a tendency for the amalgam to grow over the edge of the anode cup during the charging, this growth was carefully brought back into the cup. In some cases the charging was done before the anode cup was adjusted, a platinum spiral was hung in the electrolyte and a wire, protected from the electrolyte, made contact with the mercury, and then a motor-driven stirrer was used while the mer-

curous sulphate was being formed. These batteries have been charged from time to time as the surface of the mercury became exposed at any point, also occasional stirring kept the mercurous sulphate uniformly distributed over the mercury.

The first batteries were made in April, 1906, the electrolyte was *neutral* cadmium sulphate and the mercurous sulphate was made and washed in the usual way. Two of these batteries were used in series on the potentiometer, but in a few months they began to show a rapidly decreasing E.M.F. and could no longer be used, although there was still plenty of mercurous sulphate on the mercury cathodes. The electrolyte was then made acid, with sulphuric acid, and the batteries soon regained their normal value and have now been in use on the potentiometer circuit for about two years and have required very little attention. They are compact, clean and easily insulated, so are particularly convenient for the potentiometer installation suggested by Walter P. White.¹

The first attempt to make the mercurous sulphate in the batteries was in the case of batteries Nos. III., IV. and V., which were made in small bottles with a cathode area of 20 cm.², No. III. was charged with a current of .185 amp. for 20 minutes and shortly after breaking the circuit it showed 1.02205 volts.

In 30 minutes	1.02222 volts.
2 hours	1.02226 "
6 hours	1.02214 "
2 days	1.02212 "
3 days	1.02215 "

These observations were taken as the battery stood in the laboratory subjected to ordinary temperature changes. On closing this battery over a resistance of 100,000 ohms, it immediately took up the value of 1.02200 and remained perfectly constant for 20 minutes when the resistance was lowered to 50,000 ohms and then the voltage at the battery terminals very soon dropped to 1.02187, over 40,000 ohms the voltage was 1.02180, over 30,000 1.02170, over 20,000 1.02151 and over 10,000 ohms it showed 1.02100 volts. When left on this last resistance for an hour the voltage showed a change of only 4 in the fifth place decimal as it slowly

¹PHYS. REV., 25, 342.

decreased to 1.02096 volts. On increasing the resistance, reversing the order just given, the voltages assumed their steady values for each resistance even more rapidly than on decreasing the resistances and there was very little hysteresis as the constant values observed were only slightly lower than those just given. The internal resistance of this battery was 6.2 ohms, so there was some slight polarization. For accurate and long continued work it has been found most satisfactory to use 100 cm.² cathode surface to 10,000 ohms; of course very much less resistance may be used, but then a very slow drift is noticed. No harm was done one of these batteries by directly short-circuiting the terminals for some time, for it soon regained its E.M.F. when the circuit was broken, and had only lost some mercurous sulphate which was easily restored.

Some very large batteries of this type have been made by Mr. B. J. Spence for the purpose of obtaining a steady current for a bolometer in infra-red radiation measurements. Large battery jars which allowed a mercury surface of 340 cm.² were used. The wooden cover of the jar supported the four anode cups, each of 5 cm. diameter. One and a half liters of the acid cadmium sulphate solution and about 150 gr. of mercurous sulphate were put into each of these batteries, later they have been charged at a low current density without stirring. The cover of these batteries should also be provided with an "L" shaped stirrer so arranged that the arm would pass close to the surface of the mercury and with stirring the charging could be done in a short time with no danger of forming the basic salt. The first battery made by Mr. Spence showed a voltage of 1.02206, with an internal resistance of less than one ohm, when closed over resistances the electrode potential

dropped to	1.01691	for 100	ohms.
	1.01535	" 90	"
	1.01451	" 80	"
	1.01196	" 60	"
	1.00690	" 40	"
	1.99196	" 20	"

When left on the 20 ohms for one half an hour the p.d. was .99190. Four of these large batteries have been made and, joined in parallel have been furnishing a current of .150 amp. for bolometer work and have shown a constancy that was entirely unattainable with storage batteries.

The following observations have been made on three of the small batteries :

	No. III.	No. IV.	No. V.
February 12	1.02194	1.02190	
“ 16	1.02187	1.02177	1.02198
“ 23	1.02180	1.02150	1.02148
March 6	1.02155	1.02118	1.02122

During this period these batteries had been used for various purposes, where a small current was needed, and they were subjected to ordinary temperature variations, but had not been charged except when made. It would seem from the experience so far gained that the value of these batteries was the same whether the mercurous sulphate was made and washed in the usual way or made electrolytically in the batteries. They are reproducible to better than one part in 1,000, regardless of ordinary temperature changes, and the E.M.F. is 1.022 volts (Clark cell at $15^{\circ} = 1.4330$ v.). When calibrated they have served for exact measurements of E.M.F. or for furnishing a small current. With a bridge of known resistance and a large regulating resistance, small electromotive forces may be accurately measured by the null method and with simple apparatus.

PRINCETON UNIVERSITY,

April, 1908.