TABLE I

WAVE LENGTHS OF ABSORPTION BANDS OF BENZENE DERIVATIVES

Derivative	Benzene	Toluene	*p*-Xylene	Mesitylene
$\lambda(\mu)$	1.1409	1.1442	1.1498	1.1539

BRYN MAWR, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE EFFECT OF AIR ON THE POTENTIAL OF THE MERCURY-MERCUROUS SULFATE ELECTRODE

BY MERLE RANDALL AND HENRY A. STONE

RECEIVED MARCH 13, 1929 PUBLISHED JUNE 5, 1929

Vosburgh[1] has shown that the potential of Weston standard cells with slight additions of basic mercuric sulfate to the mercury–mercurous sulfate electrode in neutral or slightly acid saturated cadmium sulfate solutions or prepared with the materials in contact with air is about 0.03 mv. higher than that of cells prepared out of contact with the air. Randall and Young[2] found relatively large errors of the order of 1.5 mv. in acid calomel electrodes prepared in the presence of air. We shall here study the effect of air on the hydrogen–mercurous sulfate–mercury cell.

The Reaction between Dilute Sulfuric Acid and Mercury.—Redistilled mercury and 0.1 *M* sulfuric acid were sealed in pyrex flasks[2] and rotated for twenty-four hours in a thermostat at 25°. In some of the flasks the air was displaced with a current of pure nitrogen and acid which had been freed from air by boiling in a current of pure nitrogen was used. There was no evidence of the formation of a precipitate but upon the addition of air-free dilute hydrochloric acid a precipitate of mercurous chloride appeared in the acid from the flasks in which no precautions had been taken to exclude air.

Materials.—The sulfuric acid was prepared and analyzed as described by Randall and Scott.[3] Nitrogen was prepared by passing commercial nitrogen over three feet of reduced copper turnings at a bright red heat, or by adding a small amount of hydrogen and passing the mixed gas over white-hot platinum wire. The dilute acids were prepared from the stock acid by dilution with conductivity water (weight burets, concentration in moles per 1000 g. of water in vacuum) and traces of air were removed by bubbling through pure nitrogen for eight hours. The acids were stored in quartz flasks.

Mercurous sulfate was prepared by precipitation in the dark from mercurous nitrate.[4] It was washed six to eight times with air-free acid in an atmosphere of nitrogen in the pipet (Fig. 1) and introduced into the cell by a slight adaptation of the method of Vosburgh.[1] Considerable care was taken to shield the mercurous sulfate from the light. We found that mercurous sulfate in contact with 0.1 *M* sulfuric acid

---

[1] Vosburgh, THIS JOURNAL, **47**, 1255 (1925).

[2] Randall and Young, *ibid.*, **50**, 989 (1928).

[3] Randall and Scott, *ibid.*, **49**, 636 (1927).

[4] Prepared by the method of Randall and Frandsen (unpublished); see ref. 2.

had turned yellowish-brown after two months' contact with mercury in the half-cells which had been submerged in the oil thermostat at 25° in a moderately lighted room.[5] In the experiment quoted here the outside of the half-cells was coated with black "Duco" lacquer.

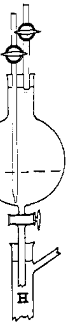

Fig. 1.—Pipet.

Cells.—The hydrogen electrode was the usual type.[2] The essential parts of the mercury–mercurous sulfate half-cell are shown in Fig. 2. To insure the absence of air a current of pure nitrogen was used to displace the air in the apparatus assembled as shown, with stopcocks A, B and C open and D and E closed. The stopper F of the half-cell H was then quickly withdrawn (with an increased current of nitrogen), the mercury introduced and then the pipet (Fig. 1) containing the air-free suspension of mercurous sulfate in the sulfuric acid replaced the stopper. The mixture of paste and acid then filled the cell to the level of the side arm, and while the current of nitrogen was continued the pipet was withdrawn and the cell again quickly sealed by the stopper F. (The pipet could have been left in the cell.) The stopcock A was now closed and acid introduced into the reservoir I and bubbled with pure nitrogen, the cell painted with black "Duco" and then transferred to the thermostat with the oil level as indicated by the dotted line. The current of nitrogen was replaced by a current of electrolytic hydrogen which had passed over a white-hot filament to remove traces of oxygen. After three days the sulfuric acid in the cell was replaced by flushing the cell by opening stopcock A. The intermediate vessel J was filled, stopcock C closed, the tube leading to D filled and this stopcock closed. The acid was then removed through C until flushing was complete. Contact with the hydrogen electrode was made through the greaseless stopcock E, the tube leading to J being filled with acid brought from the hydrogen electrode vessel. The stopcock B also connected to a second mercury–mercurous sulfate half-cell. The flushing was usually done in the evening and reading commenced on the following morning. The cells came to equilibrium in from twenty-four to forty-eight hours and were constant to less than a maximum difference of 0.03 mv.

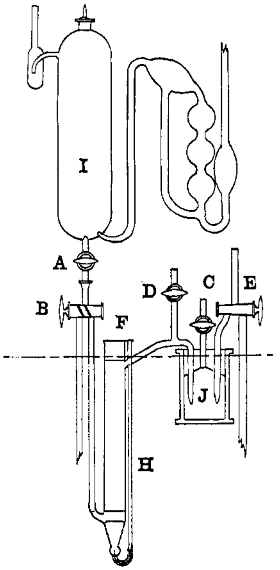

Fig. 2.—Half cell.

---

[5] Similar discolorations have been noted by (a) Hulett, *Phys. Rev.*, **32**, 262 (1911); (b) Obata, *Proc. Phys. Math. Soc., Japan*, (3) **2**, 79, 223 (1920) and (c) Horsch, THIS JOURNAL, **41**, 1787 (1919), who stated that the discoloration (in the presence of zinc sulfate) would not take place if a small concentration of hydrogen ion was present.

Potential Measurements.—After three days moist air was introduced at the surface of the mercury, at first only a few bubbles and later as much as a liter. Initial values from 0.2 mv. to 0.4 mv. lower were obtained but in fifteen minutes the cells would be back to their normal voltage and remained constant as before for thirty days. Replacing the electrolyte produced no change in the potential.

The following values of the hydrogen–mercury–mercurous sulfate cell are shown in Table I.

TABLE I

VALUES OF THE HYDROGEN–MERCURY–MERCUROUS SULFATE CELL

Molality of sulfuric acid	0.1000	0.2101
Exptl. e.m.f., volts	0.73694	0.71858
Interp. e.m.f. (R. and C.)[6]	0.73697	0.71852

Summary

Mercury is dissolved by dilute sulfuric acid containing air.

The effect of air upon the potential of the mercury–mercurous sulfate electrode in moderately concentrated acid solution is negligible when the electrodes are prepared in the usual manner.

BERKELEY, CALIFORNIA

NOTE

Sodium Maleate—A Buffer for the *P*H Region of 5.2 to 6.8.—In the course of a research on autoxidation the author has found that the buffering range of sodium hydrogen maleate–sodium hydroxide mixtures extends from a *P*H of 5.2 to 6.8, giving maximum buffering power in the region where phthalate and phosphate buffers have the least. The lower valence of the ions results in a smaller salt effect than is the case with citrate buffers.

Sodium hydrogen maleate is easily prepared in pure form as $NaHC_4H_2O_4 \cdot 3H_2O$.[1] The following method was found convenient. A liter of aqueous solution containing 250 g. of maleic acid was exactly halved. To the first half was added 6 *N* sodium hydroxide until the precipitate first formed had redissolved, then normal sodium hydroxide to the neutral point. The two halves were mixed, cooled in an ice-bath and the crystallized salt was filtered off. Recrystallization is very easy. One recrystallization was found sufficient for a product made from Kahlbaum acid. When dried in a warm place in the open room, the salt conforms exactly to the trihydrate formula and may be weighed as such. Preliminary tests indicated that it might even be used as a primary standard in acidimetry.

---

[6] Randall and Cushman, THIS JOURNAL, **40**, 393 (1918).

[1] Büchner, *Ann.*, **49**, 64 (1844); Weiss and Downs, THIS JOURNAL, **45**, 2342 (1923).