OXIDE FILM FORMATION ON THE SURFACE OF METALS IN AQUEOUS SOLUTIONS AND THE EVALUATION OF THEIR STANDARD POTENTIALS. II

THE MERCURY ELECTRODE

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In a previous investigation carried out by one of the present authors (21) on the copper electrode, it was found that metallic copper in aqueous solutions over a certain pH range is covered with an oxide film of cuprous oxide, as indicated by the fact that the copper electrode showed a potential varying linearly with the hydrogen-ion activity of the solution, with $\Delta E/\Delta pH$ and E_0 values practically coinciding with those for a copper-cuprous oxide electrode. The effect of this oxide film on the thermodynamic potential of the electrode was discussed, and a new technique was introduced for measuring the standard potential of copper out of contact with atmospheric oxygen so that no film exists.

The present investigation deals with metallic mercury, which has long been regarded as a standard and on which many different electrochemical investigations have been carried out. The study of the possible existence of an oxide film on the surface of the metal in aqueous solutions will be of importance not only in arriving at the conditions for the evaluation of its standard potential but also for any other study of metallic mercury which necessitates the absence of any oxide (19).

The probable existence of an oxide film on the surface of the metal in aqueous solution was gleaned by the method adopted in the case of copper (21), i.e., by studying the behavior of the mercury electrode in solutions of varying pH which were initially free from the metal ions. Gatty and Spooner (7) carried out some measurements on the mercury electrode in solutions containing no mercury ions, but these authors worked in a limited pH range and in nonbuffered solutions.

From a study of the behavior of the electrode in the presence of air and in the absence of air after applying a rigorous and special technique for removal of the oxide film from the surface of the metal, we were able to give the proper conditions under which a persistent oxide film is absent from the surface of metallic mercury in aqueous solutions. Only under these conditions can the true thermodynamic standard electrode potential as well as any other electrochemical property of metallic mercury be determined.

I. EXPERIMENTAL

The preparation of the electrodes and solutions for measurements in air

(1) Mercury electrodes

Two types of mercury electrodes were used, which we shall designate A and B. The results with these electrodes were also compared with the mercury-mercuric oxide electrode denoted as electrode C. These electrodes were prepared as follows:

Electrodes of type A: The purest British Drug Houses sample of mercury was sprayed three times into a long column of dilute nitric acid and the resulting mercury was then washed by spraying three times into a long column of conductivity water. The mercury after drying was then distilled three times under reduced pressure and filtered through a series of perforated filter papers. This pure mercury was introduced into an electrode vessel similar to Walpole's vessel (24) for the calomel electrode, in which sufficient mercury was used to cover a sealed-in platinum wire and deep enough to prevent the solution from reaching this contact on accidental shaking. Over the mercury layer was added the solution on which the measurements were to be made.

Electrodes of type B: These were prepared by electrolytic deposition of mercury from slightly acidified mercuric nitrate solution on platinum cathodes 1 cm. square, sealed into glass tubes with mercury contacts. The electrodes before use were washed several times with conductivity water and immediately before immersion with the solution to be used.

Electrodes of type C: These were similar to electrodes A with the addition of pure mercuric oxide, prepared as described later, over the surface of the mercury.

(2) Buffer solutions

In choosing our buffer mixtures care was taken to use solutions of such composition that the anions will not affect the probable presence of mercury oxide, i.e., in each solution the oxide of mercury is the least soluble component at the pH value of the solution.

From pH 3.62 to 5.61 we used the acetic acid-acetate mixtures prepared according to Cohn's system (2), having a constant ionic strength of 0.04. Buffer solutions varying from pH 6.77 to 9.11 were prepared according to Palitzsch (18) from 0.2 M boric acid and 0.2 M borax. For pH values 10.17, 10.55, and 11.04 the sodium carbonate-hydrochloric acid mixtures were used according to Kolthoff (11). For the extreme acid and alkaline ranges perchloric acid and sodium hydroxide solutions were made. All the solutions were prepared from highly purified materials and their pH values were carefully checked with the hydrogen electrode and when possible with the quinhydrone electrode.

(3) Mercuric oxide

The red and yellow forms of mercuric oxide are similar in every respect save particle size (1, 3, 16, 17, 20, 25). We prepared the red form, which possesses the larger particle size and thus has the normal solubility (22). For this preparation a method similar to that of Garrett and Hirschler (5) was followed. The purest sample of mercury was dissolved in thrice-redistilled nitric acid and the mercuric nitrate solution partially crystallized. The nitrate was then ignited for several days until the resulting oxide was nitrogen-free. The presence of nitrogen impurity due to still undecomposed nitrate was followed during the period of ignition with the micro-Kjeldahl method.

II. PREPARATION OF ELECTRODES AND SOLUTIONS FOR MEASUREMENTS OUT OF CONTACT WITH AIR

In order to perform the measurements without the effect of atmospheric oxygen on both the electrodes and solutions, a special device was constructed, the principal part of which is represented diagrammatically in figure 1. The purest sample of mercury was introduced into bulb 1 through the top tube, which was then sealed. The empty, well-cleaned electrode G was sealed to the other end of the device, which was connected to a high vacuum system at F. Evacuation was then commenced and when the pressure was below 10^{-6} mm. of mercury, as indicated with a McLeod gauge, pure hydrogen was introduced into the system and the mercury heated for 1 hr. at a temperature slightly below its boiling point



FIG. 1. Apparatus for measurements out of contact with air FIG. 2. Special cell

(about 300°C.). The pressure inside the apparatus was then reduced and the mercury allowed to distil over to the second bulb. After high vacuum was again attained, pure hydrogen was introduced and the mercury in the second bulb was again heated near its boiling point for 1 hr., after which the pressure inside the apparatus was again reduced to allow distillation of mercury to the third bulb. By repeating this process, the distillation of mercury was continued until at last it reached the electrode G, which was then sealed at the capillary constriction under high vacuum. The electrode was then fitted tightly into the electrode vessel shown in the right-hand side of figure 1, which contained the solution on which the measurements were to be made. Pure nitrogen was bubbled through this solution with the help of tap T_1 for about 15 min. to remove dissolved oxygen

before turning the joint T_2 around, thus breaking the capillary end of the electrode and allowing the solution to rush up and fill the evacuated space above the mercury.

The hydrogen used in this investigation was supplied in cylinders and was purified by first passing it through tubes heated electrically to about 450°C. and containing successively platinized asbestos and copper gauze, then through a series of three bubblers containing about 15 per cent potassium hydroxide and some lead monoxide. The pure hydrogen was then bubbled through another series of three bubblers containing conductivity water, dried by passing through tubes containing phosphorus pentoxide, and lastly allowed to pass through tubes packed with glass wool.

The nitrogen was purified by passing through tubes heated electrically to about 450°C. and containing copper filings, then through a series of bubblers containing successively dilute sulfuric acid, potassium hydroxide, silver nitrate, and concentrated sulfuric acid, and lastly through a long tube packed with glass wool.

III. PREPARATION OF ELECTRODES AND SOLUTIONS FOR THE EVALUATION OF THE STANDARD ELECTRODE POTENTIAL

In order to minimize the liquid-junction potential the cell used was of the following type:

H₂, HClO₄ (xM), HClO₄ (xM) + Hg₂(ClO₄)₂ (x'M), Hg

in which x' was made small as compared with x. Thus the two solutions became nearly identical and the liquid-junction potential was negligible. For measurements out of contact with atmospheric oxygen a special cell was used. This is shown in figure 2, where A is the hydrogen electrode and B is the mercury half-cell.

For each measurement the previously standardized mercurous perchlorate solution was diluted with an equal volume of perchloric acid, which was exactly twice as concentrated as the acid used in the hydrogen half-cell. For measurements out of contact with atmospheric oxygen, pure nitrogen was allowed to pass through the solution to remove the dissolved oxygen; joint T was then turned around, breaking the capillary tip of the electrode and allowing the solution to fill the evacuated space above the mercury.

The pure nitrogen used, as well as the hydrogen of the hydrogen electrode, was saturated before use with water vapor at the vapor pressure of the solution. After each measurement the solution inside the electrode vessel was checked for its composition by analysis, as will be seen later.

Perchloric acid

The British Drug Houses analar perchloric acid was used, from which solutions of varying concentrations were prepared and accurately standardized against standard sodium carbonate solutions.

The mercurous perchlorate

Exactly equivalent amounts of pure mercuric oxide and perchloric acid were shaken together with an excess of pure mercury in the dark for a week, and the solution obtained was then filtered in the dark from excess mercury. The gram molarity of this stock solution was determined by two different methods: namely, the gravimetric estimation of mercurous mercury as mercurous chloride and the volumetric estimation of mercurous perchlorate by means of standard sodium chloride solution, using bromophenol blue as indicator (23). The two methods were found to agree with each other satisfactorily. From this stock solution several others were prepared by accurate volumetric dilution, and the concentrations of these diluted solutions were always checked by the two methods as stated before.

Electrical measurements

The measurements were always carried out in duplicate with differently prepared stock solutions. In the buffer solutions the measurements were performed using a saturated calomel electrode as the reference half-cell. Following the procedure suggested by Harned and Owen (9), the experimental E_0 pH value of our saturated calomel electrode, as determined in buffers with acids of known dissociation constants and involving all the necessary corrections, was taken as 0.2448 v. at 25°C. The cells were always kept in an air thermostat fixed at 25°C. \pm 0.02°C.

The E.M.F. measurements were carried out using a calibrated meter bridge on which accurate readings could be taken to 0.02 cm. A cadmium cell calibrated by the National Physical Laboratory and an Onwood mirror galvanometer having a sensitivity of 190 mm./microampere were used.

IV. RESULTS AND DISCUSSION

1. The behavior of the electrodes in solutions of varying pH and initially containing no mercury ions in air

Consideration of the variation of potential with time as well as with the pH of the solution for the three different types of electrodes revealed the following:

(1) In the case of electrodes of types A and B, the potential became fairly steady within about 45 min. of immersion in unstirred solutions with pH's in the range of 0.9 to 5.6. After 24 hr. it was noticed that there had been a slight drift towards the more negative side. The results in this pH region were fairly reproducible, although they were not so reproducible as in the more alkaline region. In the more alkaline solutions, the steady-state potentials were reached within a shorter period of time and remained quite constant for the next 24 hr. The steady-state potentials for both types of electrodes were approximately the same over the whole pH range.

(2) For electrodes of type C, the steady-state values were reached for pH's from 0.9 to 5.6 within about 30 min. and remained practically constant for the next 24 hr. In more alkaline solutions the steady-state values were attained in the first 15 min. after immersion and remained perfectly constant for the next 24 hr., which was the time limit of our experiments. The steady-state values for electrodes of type C were always higher than the corresponding values for A or B, although at the extreme alkaline side the values became approximately the same.

(3) By plotting the steady-state potential values against pH for the electrodes of types A and C, the two curves shown in figure 3 were obtained. These curves reveal the interesting fact that the potentials of the mercury electrode, as well as that of the mercury-mercuric oxide electrode, are linear functions of the pH of the solution from the extreme acid to the extreme alkaline solutions, but with a small break from about pH = 5 to the neutral point. The linearity of the mercury-mercuric oxide electrode is, of course, in accordance with the well-known principle of a true metal-metal oxide electrode. The question arises as to the reason for the linearity in the case of metallic mercury electrodes. If it is due to oxide film formation, then why does it not coincide with that of the mercury-mercuric oxide electrode?

Gatty and Spooner (8) observed similar phenomena when comparing the potential of the mercury electrode in alkali hydroxide with those of the mercury-mercuric oxide electrode. The lower potential observed in the former case was given different explanations: thus, they stated that it may be due to a slow saturation of the interface with mercuric oxide, a conclusion which is, however, in marked contrast to the fact that the direct addition of mercuric oxide to the solution immediately raises the potential to the metal-metal oxide value. Also, the present authors found that when the buffer solutions studied were previously saturated with mercuric oxide, ultrafiltered from excess of solid mercuric oxide, and then the behavior of the mercury electrode studied, the results represented diagrammatically in figure 4 were obtained. In this diagram the potential of the mercury electrode in each solution is shown against the logarithm of the time in hours after which the measurements were taken. It may be seen that at first the potentials approximated to the mercury-mercuric oxide potentials but after a certain time (which varies from one solution to another) the potentials decreased towards the values obtained with metallic mercury. Gatty and Spooner also claimed the possibility of mercuriate formation, which prevented the interface from becoming saturated with mercuric oxide, but the mercuriate is expected to be more readily formed at pH values far removed from the isoelectric point of mercuric oxide. The isoelectric point of this oxide is expected to be at about the neutral point (5, 6) and consequently the mercuriate will be formed more readily in the more alkaline solutions. Figure 3 reveals, however, that the deviation from the mercury-mercuric oxide potential is more pronounced in the less alkaline solutions. Finally, Gatty and Spooner put forward a suggestion that initially a less soluble oxide is precipitated and that this oxide is slowly converted to mercuric oxide. There is no definite proof as far as the present authors are aware for the real existence of such a form of mercuric oxide.

When a metal is exposed to air, oxygen becomes adsorbed over the surface and the metal becomes covered with an oxide film. In aqueous solutions, oxide formation in air is usually attributed to the transfer of electrons to dissolved oxygen, transforming it into OH ions which are attracted to the metal lattice forming an oxide film. In the case of mercury we would expect the rate of this process to be very slow, since metallic mercury, when in thermodynamic equilibrium with its own ions in solution, possesses in general a comparatively high electropositive potential value. Now concerning the probable formation of mer-



FIG. 3. Plot of steady-state potential values against pH for electrodes of types A and C.

FIG. 4. Plot of the potential of the mercury electrode in each solution against the logarithm of the time after which the measurements were taken. Curve 1, pH = 3.6; curve 2, pH = 4.0; curve 3, pH = 4.6; curve 4, pH = 5.6; curve 5, pH = 7.1; curve 6, pH = 8.1; curve 7, pH = 9.1.

FIG. 5. Plot of equilibrium potentials against pH.



curous oxide, although its existence is still a subject of controversy (1, 4), yet by taking its heat of formation as -21,600 cal. (12), and an estimated value of about 32 cal. per degree for its entropy (12), the entropy of formation of mercurous

oxide will be -29.5 cal. per degree and its free energy of formation -12,800 cal. The potential of the couple:

$$2OH^{-} + 2Hg \rightleftharpoons Hg_2O + H_2O + 2e^{-}$$

will be, therefore, equal to 0.123 v. as compared with 0.098 v. for the mercurymercuric oxide electrode (12). This indicates that the mercury-mercurous oxide electrode would possess potentials more positive than the corresponding potentials of the mercury-mercuric oxide electrode. This fact, which is only based on calculations after certain estimations, is quite unusual, and the higher potential of mercury-mercurous oxide relative to mercury-mercuric oxide also indicates that the former will be unstable. From this, it can be concluded that the behavior of the mercury electrode cannot be attributed to mercurous oxide, and thus we are left with the possibility of the formation of mercuric oxide. Owing to the liquid nature of metallic mercury, its molecules are capable of movement throughout the bulk of the liquid and we should not expect an inhibitive oxide film to form over the surface, but rather that most of the surface should be the bare metal, especially in the less alkaline pH range where the solubility of the oxide is greater. Since this is the case, one must take into consideration the reaction $Hg^{++} + Hg \rightleftharpoons Hg_2^{++}$ and its equilibrium constant $[Hg_2^{++}]/[Hg^{++}] = 81$ (12). The following processes are expected, therefore, to be consecutively occurring at the surface of the electrode: (a) formation of mercuric oxide at the electrode surface; (b) dissolution of mercuric oxide in the layer of solution at the interface to give Hg^{++} and OH^{-} ions; (c) reaction of Hg^{++} ions with mercury to give Hg_2^{++} ions; (d) diffusion of Hg_2^{++} and Hg_2^{++} ions into the bulk of the solution.

It may be suggested that since process (a) is slow, the concentration of Hg^{++} ions at the interface produced by process (b) will tend to, but may not, attain the value corresponding to a saturated solution of mercuric oxide and in strongly acid solutions, where the solubility of mercuric oxide is high, this difference is likely to be very marked, leading to a potential much lower than the mercurymercuric oxide value. At higher pH values, as the solubility of mercuric oxide decreases, the difference will be less, but will still be appreciable owing to the participation of reaction (c). Thus, if we suppose the rate of formation of mercuric oxide was just sufficient to maintain a saturated film of mercuric hydroxide at the electrode surface and then allowing for reduction, the potential under these conditions would be also a linear function of the pH value but about 0.05 v. lower than the mercury-mercuric oxide value. Only where the rate of formation of mercuric oxide exceeds the rate of removal of mercuric ions by diffusion outwards and reduction would the potential be expected to reach the mercurymercuric oxide value and this, as expected, is most nearly reached in alkaline solutions where the solubility of mercuric oxide is least.

Another view is that the mercuric oxide formed tends to saturate the double layer between the electrode and solution and at the same time, owing to reaction (c), reduction of Hg^{++} to Hg_2^{++} will take place according to the previous equation and governed by the corresponding equilibrium constant; then, in order to

establish the disturbed equilibrium, more mercuric oxide will dissolve and this will take place until finally we have the dynamic equilibrium:

$$HgO + H_2O \rightleftharpoons Hg^{++} + 2OH^{-}$$
$$+$$
$$Hg$$
$$\downarrow \uparrow$$
$$Hg_{2^{++}}^{++}$$

This increase in the solubility of the oxide, especially in the more acid solution, will lead to an increase in the pH value, at least within the double layer, and consequently the potential will be lower than expected from the original bulk pH of the solution. In a comparatively strong acid solution, for example of pH = 1, the $[Hg^{++}]$ as calculated from the solubility product of mercuric oxide $([Hg^{++}] \cdot [OH^{-}]^2 = 2.7 \times 10^{-26} (12))$ will be equal to 2.7 gram-ions/liter; the corresponding $[Hg_2^{++}]$ which must be present in equilibrium in the presence of metallic mercury will be equal to 218.7 gram-ions/liter, which is an enormous quantity and must affect the pH value of the solution to such an extent that this solubility cannot be reached.

Against the first view is the reproducibility of the results, and it can be shown also that the mercury ions present at any lower pH value, as determined from the measured potentials in these solutions, are enough to exceed saturation at higher pH values as expected from the solubility product of mercuric oxide. This is the case so long as there is no reason to consider that the rate of formation of mercuric oxide at higher pH values is less than at lower pH values.

The only difficulty with the second view is that in order to account for the discrepancy in potential, we must expect a local increase of pH amounting in some cases to some 1-2 pH units and, as we are working in a well-defined buffer solution, such change of pH may be looked upon to be unlikely as well as its long persistence at the electrode surface.

At this stage, therefore, although the experimental data suggest the existence of an oxide over the surface of metallic mercury electrodes in air, yet it is probably impossible to reach any certain conclusion as to the reason for the discrepancy between the potential of the mercury electrode in air and the mercury-mercuric oxide.¹

From the general trend of the potential-pH curves of both the mercury electrode and the mercury-mercuric oxide electrode it can be noticed that a break always occurs between pH 5 and about the neutral point. This break, which is similar to that obtained with the copper electrodes (21), can be explained upon the basis of the amphoteric character of mercuric oxide, which dissociates as a base below and as an acid above the isoelectric point. The isoelectric point of

¹Since the authors are at present in the University of Liverpool, working with Dr. A. Hickling, they intend to study the anodic behavior of metallic mercury in solutions of varying pH and to follow the new method introduced by Hickling, using the cathode-ray oscillograph (10). Such a study is expected to throw some light on this point.

mercuric oxide is expected to be slightly on the alkaline side of the neutral point (5, 6); its exact position was determined by the present authors and found to be at about pH 7.5. The method of determination as well as a detailed discussion of this point will be published later. The fact that the break in the potential-pH curves appeared to be slightly on the acid side is of course in accordance with our previous discussion, that the pH value of the solution at the interface is higher than the original pH value of the solution.

2. The behavior of the electrodes in solutions of varying pH and initially containing no mercury ions out of contact with air

Mercury electrodes prepared after subjecting the metal near its boiling point for four times to the action of hydrogen, then distillation, and lastly to high vacuum when examined in oxygen-free solutions revealed the following: (1) In the unstirred solutions the potentials became nearly steady in almost all solutions within 1 to 1.5 hr. of immersion and remained practically constant for the next 24 hr. (2) By plotting the attained equilibrium potentials against pH the curve shown in figure 5 was obtained, which reveals more or less constancy in the potential of the mercury electrode up to about pH 5. Throughout this range the potential of the mercury electrode in complete absence of oxygen was about 0.54 v. The reproducibility of the results within this pH range was only of the order of 1.5 centivolts.

Above pH 5 the protected electrode also began to show potentials which were a linear function of the pH. In a similar manner as in Section I, it can be shown that the linearity in the potential of the mercury electrode with pH was due to the formation of mercuric oxide and to the mercuric-mercurous equilibrium in the presence of metallic mercury. The state of affairs occurring on the surface of a metallic mercury electrode under these conditions can be explained as follows: When a pure metal is dipped into an aqueous solution containing no ions of this metal and also in the absence of dissolved oxygen, which may act as electron acceptor, the potential of this metal in the comparatively acid solutions is expected to be extremely negative, leading to dissolution of the metal and the discharge of hydrogen ions. The potential observed in this case is expected to be governed by the potential of the hydrogen electrode at the corresponding pressure and the pH prevailing within the double layer, and also with the hydrogen overpotential on the particular metal. In more alkaline solutions, owing to the increased [OH⁻], a state is expected to be reached where the [OH⁻] together with the metal ions present will be enough to saturate the interphase with the metal hydroxide; hence the metal will again start functioning as a metal-metal oxide electrode.

3. The evaluation of the standard potential of mercury

From the previous study it is clear that in air an oxide film persists on the surface of metallic mercury in aqueous solutions from extreme acid to extreme alkaline solutions, while out of contact with atmospheric oxygen and after subjecting the mercury four times to the reducing action of hydrogen and distillation, such an oxide only appears at pH values above 5. Measurements of the mercury electrode potential in mercurous salt solutions under these latter conditions will be expected to give the exact standard potential of the metal. For this determination and in order to overcome the liquid-junction potential the cell of the type:

H₂, HClO₄ (xM), HClO₄ (xM) + Hg₂(ClO₄)₂ (x'M), Hg

was constructed, as stated before, in such a way as to allow the measurements to be taken out cf contact with air (figure 2). For comparison, the same cell was also studied without the rigorous protection from atmospheric oxygen. In table 1 are given the results of the equilibrium values of one set of measurements for both the protected and the unprotected electrodes. For the protected electrodes the equilibrium was found to be attained within the first 30 min. and to remain

CONCENTRATION OF HClO4	CONCENTRATION OF Hg2(ClO4)3	É.M.F. IN AIR	E.M.F. OUT OF CONTACT WITH AIR	E0 IN AIR	E0 OUT OF CONTACT WITH AIR
М	M	volts	volts	volts	volts
0.1012	0.00568	0.7820	0.7803	0.7989	0.7972
	0.00284	0.7731	0.7715	0.7989	0.7973
	0.00142	0.7647	0.7627	0.7991	0.7971
0.0500	0.00142	0.7839	0.7822	0.7987	0.7970
	0.000766	0.7760	0.7743	0.7987	0.7970
	0.000369	0.7671		0.7991	
0.0100	0.000738	0.8198	0.8182	0.7985	0.7969
	0.000341	0.8097	0.8085	0.7984	0.7972
	0.000170	0.8010	0.7997	0.7986	0.7973
Mean				0.7988	0.7971

TABLE 1

Equilibrium values of one set of measurements for both protected and unprotected electrodes

constant for several hours. In the unprotected electrode the equilibrium was attained after 1 hr. and remained constant for a few hours, after which a drift was noticed.

The reaction taking place in the cell can be represented as follows:

$$H_2 + Hg_2^{++} = 2Hg + 2H^+$$

Therefore

$$E = E_0 - \frac{RT}{2F} \ln \frac{a_{\mathbf{H}e}^2 \cdot a_{\mathbf{H}^+}}{a_{\mathbf{H}e} \cdot a_{\mathbf{H}e}^{*+}}$$
(1)

Since mercury and hydrogen are at their standard states, equation 1 at 25°C. reduces to:

$$E = E_0 - \frac{0.05915}{2} \log \frac{a_{\rm H}^2}{a_{\rm Hg_2}^2}$$

It is, therefore, only necessary for calculating the standard electrode potential to determine the activity of hydrogen ion in the hydrogen half-cell and that of mercurous ion in the mercury-mercurous perchlorate half-cell. Following the procedure of Lewis and Randall (13) for calculation of the activity coefficient at various ionic strengths, the E_0 values in the case of the unprotected and the protected electrodes were calculated and given in the last two columns of table 1. The measurements obtained in air, as can be seen from the table, gave a mean E_0 value of 0.7988 v., which agrees with that obtained by Linhart (15) after being corrected by Lewis and Randall (14). Out of contact of air the mean E_0 value is 0.7971 v., which is the true standard potential of mercury. As in the case of the copper electrode (20), the maximum error in our measurements is 0.0004 v.

V. SUMMARY

1. The behavior of the mercury electrode in solutions of varying pH and initially free from mercury ions was examined from the extreme acid to the extreme alkaline range and the probable existence of an oxide film on the surface of the metal was discussed.

2. A new apparatus and technique were described for measuring the potential of mercury out of contact with air. By comparing the results obtained in and out of contact with air in the solutions of different pH values and initially free from mercury ions a set of conditions was chosen leading to the evaluation of the true standard electrode potential.

3. The standard electrode potential of mercury was determined using this new technique and found to be 0.7971, v. at 25° C., as compared with the value of 0.7988 v. at 25° C. in air.

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COMMUNICATIONS TO THE EDITOR

THE ROLE OF THE UNPAIRED ELECTRON IN CARCINOGENESIS

Homolytic organic reactions resulting from single-electron transfer processes have been intensively studied only during the last ten years. A consequence of such reactions is the formation of a chemical molecule with an unshared valence electron. A molecule of this kind is endowed with many peculiar properties. The magnetic moment of the odd electron is not compensated by the magnetic moment of an electron with antiparallel spin. Therefore, the molecule is paramagnetic and it possesses the ability to initiate a multitude of very strange chemical reactions. These reactions usually occur with a low energy of activation, so that, like the reactions of enzymes, they may occur with great facility at the temperature of the human body. One of these reactions is especially interesting. A molecule with an unpaired electron (a so-called free radical) is able to initiate a chemical chain reaction. A single odd-electron molecule may initiate a reaction chain involving thousands of molecules of substrate. Chain reactions of this sort may be accompanied by an enormous evolution of energy. For example, chemical explosions and the combustion of inflammable materials are chain reactions, initiated by molecules with an unshared electron.

It has been experimentally established that azo compounds, complex hydrocarbons, organic amines and their derivatives, actinic radiation, x-rays, and the radiation from radioactive materials are able to form free radicals (W. A. Waters: *The Chemistry of Free Radicals*, University Press, Oxford (1946)). It has also been experimentally established that azo dyes, complex hydrocarbons,