U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1598

Part of Journal of Research of the National Bureau of Standards, Volume 33, August 1944

A COMPARISON OF PLATINUM AND PALLADIUM HYDROGEN-ELECTRODES IN AQUEOUS SOLUTIONS OF ACID POTASSIUM PHTHALATE

By Walter J. Hamer and S. F. Acree

ABSTRACT

A study was made of the reproducibility of hydrogen electrodes of various types and of silver-silver-chloride electrodes of the thermal-electrolytic type in aqueous solutions of phthalates, in order to learn whether phthalates are reduced to hexahydrophthalic acid and the electromotive force thereby changed. If so, glass electrodes would have to be used to determine the pH values of solutions of phthalates. This type of study is necessary for all reducible materials. Electromotive-force measurements of the electrode combinations were made for various periods of time. The potentials of hydrogen electrodes prepared with platinum sponge under a variety of conditions constantly increased with time and frequently were erratic, whereas those made with palladium sponge under different conditions remained remarkably constant for periods of 35 hours. Even after 75 hours, the potentials increased only 0.3 mv—which corresponds to an increase of only 0.005 in pH. Palladium or platinum electrodes having the same type of coating but of different ages agreed in potential after 2 hours in phthalate solutions. The rate and the magnitude of the increase in potential for the platinum electrodes after approximately 2 hours depend mainly upon the thickness of the metallic sponge. The characteristics of the palladium electrodes were practically independent of the thickness of the metallic sponge; of the current density used in the electrolysis; of the concentration, composition, acidity, and conductance of the plating solution; and of the concentration, composition, pH, and buffer capacity of the phthalate solutions in which the electrodes were used. The difference in the behavior of platinum and palladium hydrogen-electrodes may be caused by their different catalytic activity.

CONTENTS

Page
I. Introduction 87
II. Experimental procedures 90
  1. Materials and solutions 90
  2. Preparation of the electrodes 91
  3. Apparatus 93
III. Behavior of hydrogen electrodes in aqueous solutions of phthalates 93
IV. Conclusions 102
V. References 103

I. INTRODUCTION

Acid potassium phthalate is commonly used in the preparation of aqueous buffer solutions of known pH values. These are used in the calibration of various types of pH assemblies, especially those composed of glass and calomel electrodes. The pH values of these solutions have been determined from the measurements of the emf of galvanic cells comprised of the solution and hydrogen and calomel electrodes. The calomel electrode entails the use of a liquid junction whose potential cannot be determined on a thermodynamic basis. The present pH scale is based upon emf measurements of galvanic cells of this type for a series of pure and stable buffer solutions.[1] For the measurements to have significance, the cells must necessarily be reproducible, the emf must be independent of time, the electrodes must exhibit no temperature or pressure hysteresis, and the buffers must undergo no chemical reactions of any type, such as oxidation or reduction. For measurements with acid potassium phthalate there is considerable doubt as to whether these conditions can be attained.

Merrill [1][2], Oakes and Salisbury [2], Draves and Tartar [3], Kolthoff and Tekelenburg [4], Hitchcock and Taylor [5], and most recently MacInnes, Belcher, and Shedlovsky [6] stated that the emf obtained with solutions of acid potassium phthalate are not independent of time but show a gradual increase. This change, if not preventable, would exclude acid potassium phthalate as a possible pH standard. Draves and Tartar found that the hydrogen electrode completely reduced within 122 hours a 0.2-*M* solution of acid potassium phthalate to the salt of hexahydrophthalic acid.[3] The emf rose during reduction because the ionization constant of hexahydrophthalic acid is lower than that for *o*-phthalic acid. These authors suggested that the potassium hexahydrophthalate would make a better pH standard than the acid potassium phthalate because of its stability (completely reduced state). MacInnes, Belcher, and Shedlovsky found that the increase in the emf was more pronounced at 40° than at 25° C and atttrbuted this to an increase in the rate of reduction of the phthalate. Because of the uncertainty in their measurements with hydrogen electrodes, they obtained the pH value of a 0.05-*M* solution of acid potassium phthalate by means of a calibrated glass electrode. On the other hand, Acree and Knight [7] with acid sodium phthalate, and Clark and Lubs [8], Wood and Murdick [9], Russell and Stauffer [10], and Bacon, Hensley, and Vaughn [11] with acid potassium phthalate found that the emf was practically independent of time. Causes for these differences in observations still remain unexplained.

Draves and Tartar stated that the extent of the drifts in the emf depends on the thickness of the metallic sponge used in the preparation of the hydrogen electrodes. Oakes and Salisbury, and Hitchcock and Taylor believed that certain impurities catalyzed the reduction of the phthalate at the surface of the hydrogen electrodes. Oakes and Salisbury found that drifting potentials were obtained even after repeated recrystallizations of the buffer from water, whereas Hitchcock and Taylor reported satisfactory results after three recrystallizations. Clark [12] believed that the extent of the

---

[1] Work is now in progress at this Bureau on a pH scale based upon emf measurements of galvanic cells without liquid junctions. See W. J. Hamer and S. F. Acree, J. Research NBS **23**, 647 (1939) RP1261, and W. J. Hamer, J. O. Burton, and S. F. Acree, J. Research NBS **24**, 269 (1940) RP1284 for descriptions of the method, and R. G. Bates, W. J. Hamer, G. G. Manov, and S. F. Acree, J. Research NBS **29**, 183 (1942) RP1495 for buffer solutions fixing the pH scale from approximately 2 to 12.

[2] Figures in brackets indicate the literature references at the end of this paper.

[3] No attempts were made in this investigation to isolate the hexahydrophthalic acid in view of the fact that Draves and Tartar recovered this acid from the solutions by acidification with hydrochloric acid. They found that the dry acid and its anhydride melted at 192° and 31.5° C, respectively, in agreement with the melting points for these compounds found by Baeyer, Liebigs Ann. Chem. **258**, 219 (1890). Also Willstätter and Bequet, Ber. deut. chem. Ges. **51**, 767 (1918), reduced free phthalic acid in glacial acetic acid by hydrogen gas in the presence of platinum black.

drifts in the emf may have been due to the type of material used in the construction of the hydrogen electrodes. To investigate this possibility he compared an iridium electrode contained in one vessel with a platinum and a palladium electrode in another vessel. He found that these functioned similarly and that the potentials increased about 1 mv in 24 hours. However, since the platinum and palladium electrodes were used in the same vessel, no independent comparison of them was obtained. If the platinum electrode had catalyzed the reduction of acid potassium phthalate, thereby causing a change in the hydrogen-ion concentration of the solution, the potential would increase in accordance with the Nernst equation to correspond with the change in hydrgoen-ion concentration. The statement by Beans and Hammett [13], that if two or more hydrogen electrodes in the same solution agree in potential, their common potential is a measure of the true hydrogen-ion concentration, is true only if the electrodes have not been exposed to air and exhibit no drifts in potential with time. Acree and associates have shown [14] that electrodes prepared of platinum, palladium, iridium, and tin behave quite differently, especially in solutions which may be easily reduced at the surface of hydrogen electrodes, such as dimethylaniline hydrochloride and hydroxylamine. Slagle and Acree stated that palladium is to be preferred for use in solutions which may undergo reductions. Until now, however, no exact comparison of the various types of hydrogen electrodes has been made.

Certain experimenters have attributed the drifts in the emf to a constantly changing potential at the junction between the solutions of acid potassium phthalate and the potassium chloride of the calomel half-cell. However, it has been shown for other materials that no drifts occur when properly constructed liquid junctions are used [15 to 21]. Russell and Stauffer have recently shown that this is also true for solutions of acid potassium phthalate. The design of the cell is therefore a factor that must be considered. Another possibility that may account for the lack of constancy of the emf [15] is the age of the hydrogen and calomel electrodes. It has been shown [18, 19, 20, 21] that if these electrodes are not sufficiently aged, they will give different potentials in solutions of the same composition. Smith and Taylor [22] have likewise shown that if silver–silver-chloride electrodes are not sufficiently aged, new electrodes will act as cathodes toward aged ones when immersed in a chloride solution and that periods as long as 1 week may be required for attainment of a common potential. Consequently, drifts in the emf will occur for this duration unless some means is found to eliminate the cause.

In view of these conflicting opinions and data, solutions of acid potassium phthalate cannot be certified as pH standards nor can a thermodynamic study be made of mixtures of *o*-phthalic acid and potassium hydroxide until it is established that precise measurements can be made with hydrogen electrodes. This paper presents the results of a systematic study of the behavior of hydrogen electrodes in acid potassium phthalate in which the various factors mentioned above have been investigated. Measurements were made at temperatures other than 25° C in order to ascertain the effects of such changes. Measurements were also made with acid potassium phthalate mixed with *o*-phthalic acid and with potassium hydroxide in order to determine whether the drifts in the emf observed with acid potassium phthalate could be caused by its relatively low buffer capacity [13]. Measurements were made by means of cells without liquid junction and with pure materials, thus eliminating two of the causes of the uncertainties mentioned above.

II. EXPERIMENTAL PROCEDURES

1. MATERIALS AND SOLUTIONS

All the tests were made with acid potassium phthalate, National Bureau of Standards Standard Sample 84a, of a certified purity of 100.00 percent determined by titration. It was prepared for use according to the directions given in the Bureau certificate.

Solutions containing various amounts of acid potassium phthalate and *o*-phthalic acid were prepared from known weights of the dry salt, dry acid, and conductivity water. The *o*-phthalic acid was prepared from resublimed phthalic anhydride that gave less than 0.002 percent of ash when ignited. The phthalic anhydride was boiled with distilled water after the manner of Van de Stadt [23]. The acid was then recrystallized three times from distilled water and extracted with benzene in a Soxhlet extractor. After removal of the benzene, the acid was boiled with distilled water to remove any traces of anhydride that may have been formed and was finally recrystallized from water. After air-drying, the crystals were lightly ground in an agate mortar and dried in vacuum at room temperature over anhydrous magnesium perchlorate. Two lots of the acid were prepared, and the purity of each was checked by weight titration in an atmosphere free of carbon dioxide, using CO_2-free sodium hydroxide, standardized against acid potassium phthalate, National Bureau of Standards Standard Sample 84a. Phenolphthalein solution was used as the indicator. The purity of one lot of the acid as indicated by the titrations was 100 percent, and that of the other was 99.85 percent. However, when samples of the second lot were carefully ground and redried the calculated purity rose to 100 percent. Hence it was assumed that the impurity was water entrapped in the crystals, and allowance was made for it in the preparation of the solutions.

Solutions containing acid potassium phthalate and dipotassium phthalate were prepared from the requisite amounts of dry acid potassium phthalate and standardized potassium hydroxide, since dipotassium phthalate is extremely hygroscopic. The standardized solution of potassium hydroxide was prepared by dilution with known weights of conductivity water of a 50-percent solution of potassium hydroxide from which the carbonate was removed by the dropwise addition of a saturated solution of barium hydroxide until no more precipitate of barium carbonate was formed. It was standardized against benzoic acid, National Bureau of Standards Standard Sample 39e, using phenolphthalein solution as the indicator. Results of 5 titrations agreed within 0.02 percent.

Potassium chloride was recrystallized twice from conductivity water and then thrice recrystallized from 95-percent ethanol by the method of Hahn [24], to remove the last traces of bromide. It was dried for at least 10 hours at 110° C and allowed to cool in a desiccator, using concentrated sulfuric acid as the desiccant.

After the solutions were prepared, they were deaerated by means of hydrogen gas, corrections being made for loss of water from the solutions and the differences between the densities of hydrogen and air. The specific conductance of the water used for these studies was 1.0×10^{-6} mho, and sometimes was as low as 0.6×10^{-6} mho.

2. PREPARATION OF THE ELECTRODES

Silver–silver-chloride electrodes of the thermal-electrolytic type were prepared from pure materials, as described by Hamer and Acree [25]. They were aged in distilled water in an attempt to bring them to a stable state. Some were stored in distilled water for 10 to 12 hours, some for 1 month, and a few for 3 months. All were preliminarily tested in 0.05–*N* hydrochloric acid and they usually agreed within 0.10 mv.

In order to test the effects of the nature and thickness of the metallic sponge on the performance of hydrogen electrodes, several types were studied. They may be grouped into two main categories—those made of platinum and those made of palladium. The platinum electrodes were constructed of platinum foil, 10 by 15 by 0.2 mm, welded to a platinum wire sealed in the end of a glass tube. The foil was cleaned for about 3 minutes in aqua regia diluted with an equal volume of distilled water, and then washed thoroughly in distilled water. The foil was then plated with platinum black in a chloroplatinic acid solution, designated as solution Pt_A, composed of 3 g of platinum in 100 ml of 0.25–*N* hydrochloric acid and 1 ml of a 5-percent solution of lead acetate. In every case the addition of lead acetate was found necessary. This solution had a specific conductance of 0.163 mho and a pH of 0.84 at 30° C. A current of 250 ma or 400 ma was used for a definite period of time. Electrodes designated $Pt_{1A(.08)}$, $Pt_{3A(.08)}$, and $Pt_{5A(.08)}$ were plated, respectively, for 1.0, 3.0, and 5.0 minutes at 250 ma or at a current density of 0.08 amp/cm^2. Here and elsewhere in the text, in the subscript describing the hydrogen electrode the first numeral refers to the number of minutes the electrode was plated, the capital letter refers to the type of plating solution used, and the numbers in parenthesis refer to the current density at which the electrode was plated. Those designated $Pt_{1A(.13)}$ and $Pt_{5A(.13)}$ were plated for 1.0 and 5.0 minutes at 400 ma, or at a current density of 0.13 amp/cm^2. Making a conservative estimate of a current efficiency of 50 percent, electrodes $Pt_{1A(.08)}$, $Pt_{3A(.08)}$, $Pt_{5A(.08)}$, $Pt_{1A(.13)}$, and $Pt_{5A(.13)}$ were covered, respectively, with 0.016, 0.046, 0.076, 0.021, and 0.122 g of platinum. Assuming uniform distribution of platinum on the surface of the foil, the thickness of the sponge (calculated as solid metal) was approximately 2, 6.9, 11, 3.2, and 17 microns, respectively.[4] In all cases, the sponge was finely divided and was jet black in appearance.

A few platinum electrodes, designated as $Pt_{1B(.08)}$, $Pt_{3B(.08)}$, $Pt_{5B(.08)}$, $Pt_{1B(.13)}$, and $Pt_{5B(.13)}$, were prepared from 50 ml of the solution Pt_A of chloroplatinic acid, diluted with 50 ml of conductivity water. This solution, designated Pt_B, had a conductivity of 0.089 mho and a pH of 1.18 at 30° C, and it was therefore less acidic and more resistant to current flow than the former. Solution Pt_B also yielded finely divided sponge, jet black in appearance.

---

[4] Studies of the capacitance and surface characteristics of the metals of the platinum group are being made that will give more information of the effective thickness and surface area of these electrodes.

The palladium electrodes were constructed of platinum foil, 10 by 15 by 0.2 mm, welded to a platinum wire sealed in the end of a glass tube. They were cleaned as above or in dilute hydrochloric acid and thoroughly washed in distilled water. The foil was then plated with palladium black in four different solutions, described below, by passing a current of 250 or 400 ma for a definite period of time. Electrodes designated as $Pd_{1(.08)}$, $Pd_{3(.08)}$, and $Pd_{5(.08)}$ were plated, respectively, for 1.0, 3.0, and 5.0 minutes at 250 ma, or at a current density of 0.08 amp/cm². Electrodes designated $Pd_{1(.13)}$ and $Pd_{5(.13)}$ were plated for 1.0 and 5.0 minutes at 400 ma or at a current density of 0.13 amp/cm². Making a conservative estimate of a current efficiency of 50-percent, electrodes $Pd_{1(.08)}$, $Pd_{3(.08)}$, $Pd_{5(.08)}$, $Pd_{1(.13)}$, and $Pd_{5(.13)}$, were covered, respectively, with 0.008, 0.025, 0.042, 0.011, and 0.067 g of palladium. Assuming uniform distribution of palladium on the surface of the foil, the thickness of the coats (calculated as solid metal) of these five electrodes was approximately 2.4, 7.1, 11.8, 3.8, and 18.9 microns, respectively, or approximately the same thickness as the coats on the platinum electrodes. A few electrodes prepared of palladium foil, 5 by 10 by 0.2 mm, were also tested. These electrodes, designated respectively by the symbols $Pd'_{1B(.25)}$ and $Pd'_{5B(.25)}$ were plated with palladium black by electrolysis in palladium solution Pd_B (see below), using 250 ma for 1 and 5 minutes.

One solution used for the electrolysis was prepared by the dilution of 50 ml of H_2PdCl_4 solution with 40 ml of distilled water and 5 ml of 1.0-N hydrochloric acid. This solution, designated Pd_A, had a palladium content of 5.05 percent, a pH of 1.31, and a specific conductance of 0.4 mho. Electrodes prepared with its use were designated by the subscript A. A second solution was prepared by the dilution of 38 ml of Pd_A solution with 152 ml of distilled water and 10 ml of 1.0-N hydrochloric acid, to which 0.053 g of lead acetate was added. This solution, designated as Pd_B solution, contained 1.04 percent of palladium, had a specific conductance of 0.384 mho and a pH of 1.23. A solution of Na_2PdCl_4 containing 1 g of palladium per liter was tried. No palladium black could be obtained from this solution, even upon the addition of 1 ml of 5-percent lead acetate solution. However, upon the addition of 10 ml of 1.0-N hydrochloric acid to 100 ml of this solution, a finely divided deposit of palladium black was readily obtained by electrolysis. This solution, designated as Pd_C solution, contained 0.09 percent of palladium, had a pH of 1.04, and a specific conductance of 0.3 mho. A fourth solution was prepared from 30 ml of Pd_C solution by the addition of 10 ml of concentrated hydrochloric acid. This solution, designated as Pd_D solution, contained 0.068 percent of palladium, had a pH of 0.52, and a specific conductance of 0.155 mho. Solutions Pd_A and Pd_C gave fine deposits that were grayish brown in appearance, whereas solution Pd_D gave a very coarse or granular deposit that was likewise grayish brown. Solution Pd_B gave a very fine and smooth black deposit.

All the hydrogen electrodes were thoroughly rinsed in distilled water immediately after they were plated with sponge. Some were used immediately. Others were stored in distilled water for several days to several months. A few were stored in distilled water for a year before being used. Those in each age group were always checked against each other in 0.05–*N* hydrochloric acid before use. In all cases, the electrodes agreed within 0.1 mv after 1 hour and within 0.03 mv after 4 hours.

3. APPARATUS

The details of the apparatus used in these studies, including the cells, bubble tubes, electrodes, thermostat, and the emf recording instruments have been described by Hamer and Acree [25]. The cells consisted of two compartments, one for the hydrogen electrodes and one for the silver–silver-chloride electrodes. The volumes of the compartments for the hydrogen and silver–silver-chloride electrodes were 35 and 100 ml, respectively. The cells and bubble tubes were filled under reduced pressure, the temperature of the thermostat was controlled within 0.01° C at all the temperatures, and the emf was measured by means of a calibrated potentiometer with galvanometer and standard cell. The electromotive forces were corrected in the usual manner [26] to 1 atmosphere of hydrogen pressure. The hydrogen gas was purified for these studies by the method described by Hamer and Acree [25].

III. BEHAVIOR OF HYDROGEN ELECTRODES IN AQUEOUS SOLUTIONS OF PHTHALATES

All tests were made with galvanic cells without liquid junction, using hydrogen and silver–silver-chloride electrodes. Hydrogen electrodes consisting of platinum foil covered with platinum sponge were first studied at 25° C in solutions containing 0.05–*m* acid potassium phthalate and 0.05–*m* potassium chloride. The addition of the chloride is a prerequisite for the use of the silver–silver-chloride electrodes in such solutions.

The emf were measured at definite intervals of time after the flow of the hydrogen gas was started, and are recorded in table .1 The emf increased rapidly during the first hour, which is the time required for attainment of equilibrium. However, in all cases the emf continually increased, the rate of the increase being somewhat more marked for electrodes prepared with thicker coats of platinum black. The current density used in the formation of the platinum black seems not to be critical however, since electrodes $Pt_{1A(.08)}$ and $Pt_{1A(.13)}$ and electrodes $Pt_{5A(.08)}$ and $Pt_{5A(.13)}$ had coats of about the same thickness but were plated at different current densities, 0.08 amp/cm^2 for the former and 0.13 amp/cm^2 for the latter electrodes.

After 5 to 6 hours, electrodes prepared with the thicker coats behaved irregularly. This performance may be the result of a diffusion layer at the electrode surface. If the acid potassium phthalate in the vicinity of the electrode is rapidly reduced and is continually mixing with unreduced material, the solution near the electrode continually changes in composition, giving rise to erratic behavior. The "rocking type" of hydrogen electrode used by Clark [27] would eliminate this behavior, and the use of this electrode undoubtedly accounts for the fact that he did not observe fluctuations in the emf.

The electrodes were removed and replaced with thinly plated ones. Although the latter performed better, no constant value of the emf could be obtained with their use. However, the drifts were not very marked, amounting to a change of only 0.03 in pH in 24 hours for

TABLE 1.—*Results obtained with hydrogen electrodes made with platinum sponge*

Hydrogen electrodes were aged ½ hour; silver-silver-chloride electrodes were aged 12 hours. Electromotive forces of the galvanic cell Pt, $H_2(g)$/KHPh (0.05 *M*), KCl (0.05 *M*)/AgCl(s)/Ag(s) at 25° C for definite intervals of time after the flow of hydrogen gas was started.]

Time	Pt$_{1A(.08)}$[a]	Time	Pt$_{3A(.08)}$	Time	Pt$_{5A(.08)}$	Time	Pt$_{1A(.13)}$	Time	Pt$_{5A(.13)}$	Time	Pt$_{1B(.08)}$	Time	Pt$_{5B(.13)}$
hr	*v*	*hr*	*v*	*hr*	*v*	*hr*	*v*	*hr*	*v*	*hr*	*v*	*hr*	*v*
0.25	0.53871	0.25	0.53831	0.25	0.53852	0.25	0.53817	0.25	0.53823	0.25	0.53867	0.25	0.53869
.50	.53938	.50	.53927	.50	.53947	.50	.53901	.50	.53899	.50	.53931	.50	.53922
.75	.53981	.75	.53992	.75	.53975	.75	.53990	.75	.53973	.75	.53985	.75	.53985
1.0	.53992	1.0	.53993	1.0	.53998	1.0	.53988	1.0	.53998	1.0	.53999	1.0	.54002
2.5	.53995	2.5	.54010	2.5	.53999	2.5	.53991	2.5	.54003	2.5	.53999	2.5	.54033
3.5	.53999	3.5	.54072	3.5	.54006	3.5	.53995	3.5	.54124	3.5	.54000	3.5	.54061
5.0	.54001	5.0	(b)	5.0	.54021	5.0	.53999	5.0	.54316	5.0	.54006	5.0	.54067
6.0	.54007			6.0	.54044	6.0	.54004	6.0	(b)	6.0	.54009	6.0	.54075
7.0	.54013		Pt$_{1A(.08)}$	7.0	(b)	7.0	.54009			7.0	.54018	7.0	.54079
9.0	.54023					9.0	.54019			9.0	.54021	9.0	.54092
10.0	.54035				Pt$_{1A(.08)}$	10.0	.54023		Pt$_{1A(.13)}$	10.0	.54022	10.0	.54093
11.0	.54047					11.0	.54029			11.0	.54027	11.0	.54101
12.0	.54061	1.0	0.54002			12.0	.54044			12.0	.54041	12.0	.54127
24.0	.54187	2.0	.54077			24.0	.54133	0.5	0.54004	24.0	.54153	24.0	.54265
		3.0	.54082	0.50	0.53991			1.5	.54019				
		4.0	.54082	1.5	.54042			2.5	.54021				
		5.0	.54091	2.5	.54051			3.5	.54021				
		6.0	.54099	3.5	.54057			4.5	.54033				
				4.5	.54063			5.5	.54037				
				12.5	.54109			13.5	.54113				

Cells drained of solution and refilled. Hydrogen electrodes aged 24 hours; silver–silver–chloride electrodes 36 hours

Time	Pt$_{1A(.08)}$	Time	Pt$_{3A(.08)}$	Time	Pt$_{5A(.08}$	Time	Pt$_{1A(.13)}$	Time	Pt$_{5A(.13)}$	Time	Pt$_{1B(.08)}$	Time	Pt$_{5B(.13)}$
hr	*v*	*hr*	*v*	*hr*	*v*	*hr*	*v*	*hr*	*v*	*hr*	*v*	*hr*	*v*
0.25	0.53844	0.25	0.53871	0.25	0.53889	0.25	0.53905	0.25	0.53897	0.25	0.53888	0.25	0.53897
.50	.53907	.50	.53966	.50	.53926	.50	.53971	.50	.53977	.50	.53981	.50	.53986
.75	.53986	.75	.53990	.75	.53981	.75	.53992	.75	.53994	.75	.53997	.75	.54000
1.0	.53979	1.0	.53993	1.0	.53988	1.0	.53992	1.0	.53999	1.0	.53997	1.0	.54002
2.0	.53988	2.0	.53995	2.0	.54002	2.0	.54001	2.0	.54007	2.0	.53998	2.0	.54011
3.0	.53999	3.0	.54042	3.0	.54010	3.0	.54007	3.0	.54023	3.0	.53999	3.0	.54029
4.0	.54001	4.0	.54056	4.0	.54051	4.0	.54007	4.0	.54016	4.0	.53999	4.0	.54044
5.0	.54001	5.0	.54059	5.0	.54029	5.0	.54006	5.0	.54091	5.0	.54003	5.0	.54057
6.0	.54004	6.0	.54064		([b])	6.0	.54014	6.0	([b])	6.0	.54007	6.0	.54061
7.0	.54011	7.0	.54069			7.0	.54018			7.0	.54012	7.0	.54077
8.0	.54013	8.0	.54077			8.0	.54021			8.0	.54016	8.0	.54090
9.0	.54017	9.0	.54083		Pt$_{5B(.08)}$	9.0	.54022		Pt$_{5B(.13)}$	9.0	.54023	9.0	.54108
10.0	.54018	10.0	.54091			10.0	.54022			10.0	.54030	10.0	.54123
20.0	.54044	20.0	.54220			20.0	.54067			20.0	.54071	20.0	.54198
				0.5	0.53886			0.5	0.53957				
				1.5	.53971			1.5	.53999				
				2.5	.53997			2.5	.54029				
				13.5	([c])			2.5	.54029				
								13.5	([c])				

[a] In the subscript describing the hydrogen electrode, the first numeral refers to the number of minutes the electrode was plated, the capital letter refers to the type of plating solution used, and the numbers in parentheses refer to the current density at which the electrode was plated. For example, the electrode Pt$_{1A(.08)}$ was made of platinum sponge and was plated for 1 minute, using solution Pt$_A$ at a current density of 0.08 amp/cm.^{2}

[b] Cell became erratic and hydrogen electrode was replaced by one of a different type.

[c] Cell became erratic; not replaced by a new electrode.

the thinly coated electrodes and to only 0.01 in pH after 3.5 hours for the heavier coated ones. The rate of increase was somewhat less than that found by Draves and Tartar. However, they employed only 15 ml of solution whereas in this work 35 ml was used, and 100 ml more was available in the silver–silver-chloride compartment for diffusion of the phthalate to the hydrogen electrode. This fact may account in part for the differences in data reported in the literature. The extent of the drifts in the emf depends upon the amount of solution used in the hydrogen electrode compartment and is less marked for large volumes of solution. Hence, design of the cell is one of the factors that must be considered in the use of hydrogen electrodes in phthalate solutions.

In view of the small drifts in the emf, it was considered possible that the electrodes may not have been in a stable state. Consequently, the cells were drained of solution and refilled. Hydrogen electrodes aged for 1 day and silver–silver-chloride electrodes aged for 36 hours were then used. Similar results were observed with the aged electrodes. The emf obtained with them also agreed almost perfectly with the emf obtained with new ones. Evidently, the small drifts in the observed emf cannot be explained by aging effects. Smith and Taylor have shown that the aging effects for silver–silver-chloride electrodes arise from concentration polarization. The process of filling the cells under reduced pressure used in these studies undoubtedly reduces substantially the differences in concentration of solution inside and outside the pores of the silver–silver-chloride electrodes, thus decreasing the cause of the aging effects. Data of table 3 for silver–silver-chloride electrodes aged 12 hours or a week likewise show that the age of the silver–silver-chloride electrodes is not responsible for the drifts in the emf.

The possibility that the composition of the solution of chloroplatinic acid used in the preparation of the platinum sponge may be responsible for electrode characteristics was next briefly investigated. Electrodes were plated with platinum sponge, using solution Pt_B. The data are recorded in the last two columns of table 1. The emf drifts and other characteristics were the same for these electrodes as were observed for those plated in solution Pt_A.

Hydrogen electrodes of platinum foil covered with palladium sponge were next studied under identical conditions. The results are given in table 2. The emf remained remarkably constant for all thicknesses of palladium sponge. Only after 34 hours were drifts observed, and even after 75 hours of continual use the increase in the emf corresponded to a change in pH of only 0.005. This is true of fine (solution A) and coarse (solution D) deposits and for sponges deposited at different current densities. For example, electrodes $Pt_{1A(.08)}$ and $Pd_{1D(.08)}$ were plated at a current density of 0.08 amp/cm^2, and $Pd_{5A(.13)}$ and $Pd_{5D(.13)}$ at a current density of 0.13 amp/cm^2. No significant differences were noted for electrodes prepared with platinum and palladium foil (compare columns 12 and 14 with other columns of table 2) or plated in solutions of different composition. The electrode characteristics are therefore determined primarily by the metal composing the spongy coating on the electrode.

From these few measurements it would appear that palladium sponge is preferable to platinum sponge for use in solutions of acid potassium phthalate at 25° C. This is probably due to the lower catalytic

TABLE 2.—*Results obtained with hydrogen electrodes made with palladium sponge*

[Hydrogen electrodes were aged ½ hour; silver-silver-chloride electrodes were aged 12 hours. Electromotive forces of the galvanic cell Pd, H_2 (g)/KHPh (0.05 *M*), KCl (0.05 *M*)/AgCl (s)/Ag (s) at 25° C for definite intervals of time after the flow of hydrogen gas was started]

Time	[a] $Pd_{1A(.08)}$	Time	$Pd_{3A(.08)}$	Time	$Pd_{5A(.08)}$	Time	$Pd_{1A(.13)}$	Time	$Pd_{5A(.13)}$	Time	[b] $Pd'_{1B(.25)}$	Time	$Pd'_{5B(.25)}$
hr		*hr*		*hr*		*hr*		*hr*		*hr*		*hr*	
0.25	0.53861	0.25	0.53887	0.25	0.53862	0.25	0.53827	0.25	0.53892	0.25	0.53873	0.25	0.53900
.50	.53932	.50	.53951	.50	.53943	.50	.53909	.50	.53957	.50	.53949	.50	.53973
.75	.53968	.75	.53983	.75	.53980	.75	.53981	.75	.53990	.75	.53983	.75	.53994
1.0	.53979	1.0	.53991	1.0	.53984	1.0	.54000	1.0	.53993	1.0	.53997	1.0	.53995
2.5	.53992	2.5	.53993	2.5	.53996	2.5	.54002	2.5	.54000	2.5	.53997	2.5	.53996
3.5	.53993	3.5	.53995	3.5	.53997	3.5	.54000	3.5	.53999	3.5	.53998	3.5	.53996
5.0	.53990	5.0	.53997	5.0	.53997	5.0	.54000	5.0	.53998	5.0	.53999	5.0	.53996
6.0	.53991	6.0	.53996	6.0	.53997	6.0	.54004	6.0	.54000	6.0	.53997	6.0	.53997
7.0	.53992	7.0	.53997	7.0	.53999	7.0	.54002	7.0	.53998	7.0	.53997	7.0	.53996
9.0	.53995	9.0	.53999	9.0	.54001	9.0	.54001	9.0	.53998	9.0	.53999	9.0	.53997
10.0	.53994	10.0	.54000	10.0	.54000	10.0	.54000	10.0	.53996	10.0	.53999	10.0	.53997
	(c)	12.0	.54001		(c)		(c)	12.0	.53999		(c)		(c)
	$Pd_{1D(.08)}$	22.0	.54007		$Pd_{5D(.08)}$		$Pd_{5D(.13)}$	22.0	.54001		$Pd_{1B(.08)}$		$Pd_{5B(.08)}$
0.5	0.53927	34.0	.54001	0.5	0.53594	0.5	0.53807	34.0	.54004	0.5	0.53968	0.5	0.53980
1.5	.53990	51.0	.54007	1.5	.53998	1.5	.53996	51.0	.54017	1.5	.54003	1.5	.54007
12.5	.53988	55.5	.54016	12.5	.54001	12.5	.53999	55.5	.54023	12.5	.54000	12.5	.54008
24.5	.53997	75.0	.54022	24.5	.53996	24.5	.53994	75.0	.54032	24.5	.54006	24.5	.54011
41.0	.54003			41.0	.54007	41.0	.54000			41.0	.54009	41.0	.54017

[a] In the subscript describing the hydrogen electrode, the first numeral refers to the number of minutes the electrode was plated, the capital letter refers to the type of plating solution used, and the numbers in parentheses refer to the current density at which the electrodes were plated. For example, the electrode $Pd_{1A(.08)}$ was made of palladium sponge and was plated for 1 minute, using solution Pd_A at a current density of 0.08 amp./cm².

[b] Electrodes designated with a prime (columns 12 and 14) were made with palladium foil, whereas the others not primed were made of platinum foil.

[c] Hydrogen electrode was replaced by one of a different type.

activity of palladium. In studies of catalytic reduction, Lorch [28] found that palladium has a much lower activity than platinum or iridium. Although it is well known that palladium adsorbs more hydrogen than platinum of iridium, it is not the amount of hydrogen that is adsorbed but the catalytic activity that determines the effectiveness of a hydrogen electrode. Popoff, Kunz, and Snow [29] found that electrodes given a preliminary plating of gold, as recommended by Lewis, Brighton, and Sebastian [30] because gold is impervious to hydrogen and therefore should come to equilibrium more quickly, showed no differences from electrodes not plated with gold.

In order to determine whether the same characteristics prevail at other temperatures, similar measurements were made at 0°, 45°, and 60° C, using a new pair of hydrogen and silver–silver-chloride electrodes and a pair aged for 1 week. The data recorded in table 3 show that similar conclusions regarding the age of the electrodes and the relative behavior of platinum and palladium apply to these temperatures as well. A slight increase in the emf was noted at 60° C after 4 hours, which may indicate reduction of the phthalate. However, other results given in later tables show less drifting at 60° C. Two series of measurements were made at 0° C. In series A, the flow of hydrogen gas was started within 3 minutes after the temperature of the bath reached 0° C. In series B, the flow of hydrogen gas was started 3 hours later. For series A, the emf increased steadily during the first 4 hours, whereas for series B the equilibrium values were obtained within ½ to 1 hour. In series A, the initial increase in the emf was not due to reduction of the phthalate but to the time required to attain temperature equilibrium within the cell compartments. It was also observed in this series of experiments that electrodes which at first behaved erratically functioned properly when retained long enough in the solutions.

Most of the observations reported in the literature on the behavior of hydrogen electrodes are for aqueous solutions of phthalates alone, whereas the above observations were for 0.05–*m* acid potassium phthalate containing 0.05–*m* potassium chloride. In order to determine whether the presence of potassium chloride had any influence upon electrode behavior, a series of measurements were made at 25° C for solutions containing various amounts of potassium chloride. The results are given in table 4. Three equilibrium values obtained at 25° C with palladium electrodes are given as *a*, *b*, *c*. The first set of values was obtained after 5 hours of hydrogen flow, the second was taken 44 hours later, and the third 60 hours later. The first two sets agree within 0.05 mv, and the third set was about 0.1 mv higher than the second. After the third set of readings had been obtained at 25° C, the palladium electrodes were replaced by $\mathrm{Pt}_{5A(.08)}$ electrodes aged 1 month. With their use, the emf continually increased, again showing that platinum sponge catalyzes the reduction of acid potassium phthalate, the extent of which is not critically dependent upon the concentration of the potassium chloride. Hence, potassium chloride does not influence the performance characteristics of hydrogen electrodes in solutions of acid potassium phthalate. After 20 hours these were replaced by $\mathrm{Pd}_{5A(.08)}$ electrodes. At equilibrium the emf were slightly higher than the final ones obtained with platinum sponge, probably because of a slight dilution of the solutions by the insertion of the wet $Pd_{5A(.08)}$ electrodes and to hysteresis in the emf during reduction by the platinum electrodes, but remained at the same value for 24 hours. They were then replaced by $Pt_{1A(.08)}$ electrodes and again the emf continually increased, although not to as large an extent as for the $Pt_{5A(.08)}$ electrodes that were covered with thicker coats of sponge.

In tables 5 and 6, similar data are given for platinum and palladium electrodes in solutions containing dipotassium phthalate, acid potassium phthalate, and potassium chloride of pH 4.92 to 5.33 and in solutions containing *o*-phthalic acid, acid potassium phthalate, and potassium chloride of pH 2.73 to 3.16. Each type of electrode

TABLE 3.—*Electromotive forces of the galvanic cell* Pd *or* Pt, $H_2(g)/KHPh(0.05\ M)$, $KCl\ (0.05\ M)/AgCl\ (s)/Ag(s)$ *at 0°, 45°, and 60° C for definite intervals of time after the flow of hydrogen gas was started*

Temperature	Series A at 0° C [a]		Series B at 0° C [b]		45° C		60° C	
Cell number	1	2	1	2	1	2	1	2
H_2 electrodes	$Pd_{3A(.08)}$ [c]	$Pd_{3C(.08)}$	$Pd_{3A(.08)}$	$Pd_{3C(.08)}$	$Pd_{3A(.08)}$	$Pd_{3C(.08)}$	$Pd_{3A(.08)}$	$Pd_{3C(.08)}$
Aged	12 hr	1 week	0.5 hr	1 week	12 hr	1 week	12 hr	1 week
Ag-Ag Cl electrodes, aged	12 hr	1 week	12 hr	1 week	12 hr	1 week	12 hr	1 week
Time	Electromotive force							
hr	*v*	*v*	*v*	*v*	*v*	*v*	*v*	*v*
0.25	-----	-----	0.52703	0.52706	0.55005	0.55002	0.55761	0.55752
.50	0.52628	0.52637	.52713	.52714	.55008	.55009	.55770	.55772
.75	-----	-----	-----	-----	.55009	.55008	.55773	.55775
1.00	.52660	.52666	.52714	.52718	.55011	.55008	.55773	.55775
1.25	-----	-----	-----	-----	.55010	.55008	.55770	.55771
1.50	.52673	.52677	.52714	.52818	.55008	.55009	.55773	.55774
1.75	-----	-----	-----	-----	-----	-----	.55774	.55777
2.00	.52688	.52695	.52717	.52719	.55012	.55011	.55774	.55779
2.50	-----	-----	-----	-----	.55008	.55009	.55774	.55776
3.00	.52702	.52707	.52717	.52719	.55011	.55011	.55773	.55774
3.50	-----	-----	-----	-----	.55012	.55013	.55779	.55776
4.00	.52714	.52720	.52716	.52719	.55009	.55011	.55781	.55780
5.00	.52711	.52719	-----	-----	.55011	.55012	.55786	.55783
6.00	.52717	.52722	.52718	.52719	.55014	.55013	.55797	.55791
7.00	.52712	.52719	.52719	.52721	-----	-----	-----	-----
8.00	.52717	.52719	-----	-----	-----	-----	-----	-----
9.00	.52719	.52721	-----	-----	-----	-----	-----	-----
10.00	.52725	.52729	-----	-----	-----	-----	-----	-----
14.00	.52717	.52721	-----	-----	-----	-----	-----	-----
Palladium-sponge hydrogen electrodes replaced by platinum-sponge hydrogen electrodes aged 1 week								
H_2 electrodes	$Pt_{1A(.08)}$	$Pt_{5A(.08)}$	$Pt_{1B(.08)}$	$Pt_{5B(.08)}$	$Pt_{1A(.08)}$	$Pt_{5A(.08)}$	$Pt_{1A(.08)}$	$Pt_{5A(.08)}$
hr								
1.0	0.52725	0.52729	0.52733	0.52729	0.55030	0.55021	([d])	0.558
2.0	.52718	([d])	.52718	.52721	.55021	.55027	([d])	([d])
3.0	.52725	.52743	.52725	.52733	([d])	([d])	0.558	.558
5.0	.52732	.52792	.52731	([d])	.55019	([d])	([d])	([d])
6.0	.52729	.52812	.52733	.52809	.55035	.55100	.55849	.55961
7.0	.52737	.52827	.52733	.52777	.55039	.55209	.55871	.55973
8.0	.52739	.52841	.52741	.52868	.55041	.55224	.55886	-----
10.0	.52746	.52851	.52739	.52888	.55051	.55248	-----	-----

[a] Flow of hydrogen gas was started within 3 minutes after the temperature of the bath reached 0° C.

[b] Flow of hydrogen gas was started within 3 hours after the temperature of the bath reached 0° C.

[c] In the subscript describing the hydrogen electrode, the first numeral refers to the number of minutes the electrode was plated, the capital letter refers to the type of plating solution used, and the numbers in parentheses refer to the current density at which the electrode was plated. For example, the electrode $Pt_{3A(.08)}$ was made of palladium sponge and was plated for 3 minutes, using solution Pd_A at a current density of 0.08 amp/cm².

[d] Cell behaved erratically.

behaves in these solutions substantially as in solutions containing only acid potassium phthalate and potassium chloride. Their behavior therefore is not dependent upon pH, composition, concentration, or buffer capacity of the solution. Some hydrogen electrodes that had been aged for as long as a year were also used in these solutions. They behave in a manner similar to unaged electrodes. These observations as well as those for the ones aged only a month do not substantiate the statement of Andrews [31], that palladium electrodes deteriorate on standing for long periods in water, and that

TABLE 4.—*Electromotive forces of the galvanic cell* Pd *or* Pt, $H_2(g)/KHPh$ (0.05 *M*), KCl (*m*)/AgCl(s)/Ag(s) *at 25° C for definite intervals of time after the flow of hydrogen gas was started*

[Hydrogen electrodes were aged for 2 hours; silver-silver-chloride electrodes were aged for 12 hours]

Molality of potassium chloride	0.05 *m*	0.03 *m*	0.02 *m*	0.01 *m*	0.007 *m*	0.005 *m*	0.003 *m*	0.002 *m*	0.001 *m*
H_2 electrode	$Pd_{1A(.08)}$ [a]	$Pd_{1A(.08)}$	$Pd_{1A(.08)}$	$Pd_{1A(.08)}$	$Pd_{1A(.08)}$	$Pd_{1A(.08)}$	$Pd_{1A(.08)}$	$Pd_{1A(.08)}$	$Pd_{1A(.08)}$
Time	Electromotive force								
hr	*v*	*v*	*v*	*v*	*v*	*v*	*v*	*v*	*v*
([b])	0.53999	0.55363	0.56440	0.58255	0.59173	0.60040	0.61354	0.62396	0.64186
([c])	.53998	.55364	.56435	.58257	.59174	.60042	.61356	.62393	.64190
([d])	.54002	.55369	.56438	.58270	.59184	.60045	.61368	.62403	.64201
	Palladium electrodes replaced by $Pt_{5A(.08)}$ electrodes—aged 1 month								
1.0	0.54001	0.55358	0.56427	0.58249	([e])	0.60028	0.61355	0.62392	0.64196
2.0	.54063	.55438	([e])	.58322	0.59240	.60086	.61397	.62459	([e])
3.0	([e])	.55461	.56531	.58363	.59279	.60132	.61470	([e])	.64210
6.0	.54131	.55501	.56620	.58400	.59354	.60225	.61537	([e])	.64265
7.0	.54167	.55513	.56633	.58439	.59372	.60239	.61554	.62591	.64288
19.0	.54283	.55663	.56686	.58522	.59466	.60323	.61633	.62674	.64375
20.0	.54290	.55667	.56706	.58534	.59464	.60333	.61642	.62683	.64373
	Platinum electrodes replaced by $Pd_{5A(.08)}$ electrodes—aged 1 month								
1.0	0.54233	0.55593	0.56693	0.58526	0.59426	0.60277	0.61520	0.62614	0.64352
2.0	.54279	.55654	.56708	.58537	.59444	.60287	.61625	.62647	.64371
4.0	.54295	.55669	.56704	.58536	.59472	.60345	.61654	.62697	.64375
5.0	.54298	.55663	.56704	.58536	.59472	.60337	.61653	.62695	.64386
6.0	.54297	.55666	.56707	.58536	.59473	.60339	.61650	.62696	.64388
7.0	.54298	.55669	.56709	.58537	.59466	.60341	.61652	.62698	.64384
10.0	.54301	.55671	.56706	.58537	.59468	.60345	.61650	.62700	.64391
23.0	.54292	.55663	.56709	.58530	.59463	.60349	.61666	.62695	.64388
24.0	.54292	.55662	.56709	.58530	.59464	.60351	.61669	.62695	.64388
	Palladium electrodes replaced by $Pt_{1A(.08)}$ electrodes—aged 1 month								
1.0	0.54221	0.55593	0.56703	0.58530	0.59434	0.60310	0.61620	0.62673	0.64335
2.0	.54295	.55617	.56713	.58537	.59457	.60347	.61645	.62710	.64365
4.0	.54298	.55681	.56713	.58538	.59563	.60355	.61645	.62714	.64385
5.0	.54301	.55680	.56717	.58538	.59464	.60355	.61655	.62716	.64387
6.0	.54299	.55687	.56721	.58541	.59466	.60363	.61653	.62730	.64381
10.0	.54313	.55701	.56718	.58550	.59575	.60371	.61659	.62761	.64434
23.0	.54330	.55760	.56747	.58564	.59477	.60385	.61690	.62794	.64474
24.0	.54330	.55755	.56748	.58565	.59477	.60385	.61689	.62797	.64482

[a] In the subscript describing the hydrogen electrode, the first numeral refers to the number of minutes the electrode was plated, the capital letter refers to the type of plating solution used, and the numbers in parentheses refer to the current density at which the electrode was plated. For example, the electrode $Pd_{1A(.08)}$ was made of palladium sponge and was plated for 1 minute, using solution Pd_A at a current density of 0.08 amp/cm.^{2}

[b] First recorded emf 5 hours after the flow of hydrogen gas was started.

[c] Second recorded emf 44 hours later, after measurements at temperatures from 0° to 20° C.

[d] Third recorded emf 105 hours later, after measurements at temperatures from 0° to 60° C.

[e] Erratic.

ones which had stood for 3 days never attain a state of equilibrium within any reasonable length of time. Although it is well known that surface characteristics of electrodes, such as grain size, may change on standing in air or in various solutions, it does not seem likely that distilled water alone should alter the characteristics of palladium or platinum sponge, and the results obtained in this investigation indicate that it does not.

TABLE 5.—*Electromotive forces of the galvanic cell* Pd *or* Pt, $H_2(g)/KHPh(m_1)$, $K_2Ph(m_2)$, $KCl(m_3)/AgCl(s)/Ag(s)$ *at 25°C for definite intervals of time after the flow of hydrogen gas was started*

[Hy drogen electrodes were $Pd_{1B(.08)}$ [a] aged 3 months; silver-silver-chloride electrodes were aged 2 months]

	Molalities and pH values of the solutions									
$m_1 \times 10^5$	7.6605	16.690	23.505	49.454	69.349	95.161	183.81	263.58	415.27	629.63
$m_2 \times 10^4$	7.7041	16.788	23.639	49.736	69.744	95.703	184.86	265.08	417.64	633.21
$m_3 \times 10^4$	7.6712	16.714	23.538	49.524	69.447	98.295	184.07	263.95	415.86	630.51
pH	5.33	5.29	5.27	5.18	5.15	5.08	5.07	5.04	4.99	4.92
Time	Electromotive forces of the solutions									
hr	*v*	*v*	*v*	*v*	*v*	*v*	*v*	*v*	*v*	*v*
([b])	0.72333	0.70180	0.69223	0.67082	0.66100	0.65171	0.63190	0.62093	0.60705	0.57800
([c])	.72336	.70181	.69223	.67084	.66101	.65174	.63187	.62097	.60705	.57807
([d])	.72343	.70185	.69230	.67086	.66107	.65174	.63190	.62099	.60716	.57815
	Palladium electrodes replaced by $Pt_{1A(.08)}$ electrodes—aged 3 months									
1.0	0.72331	0.70180	0.69227	0.67083	0.66097	0.65168	0.63182	0.62098	0.60663	0.57734
2.0	.72361	.70195	.69237	.67103	.66111	.65176	.63199	.62119	.60724	.57812
5.0	.72388	.70221	.69266	.67125	.66132	.65208	.63214	.62148	.60761	.57841
6.0	.72391	.70223	.69271	.67137	.66140	.65217	.63233	.62149	.60761	.57843
7.0	.72395	.70227	.69277	.67137	.66136	.65215	.63237	.62153	.60767	.57848
19.0	.72449	.70298	.69340	.67196	.66199	.65291	.63288	.62197	.60821	.57905
20.0	.72453	.70296	.69347	.67203	.66199	.65290	.63297	.62212	.60837	.57907
	Platinum electrodes replaced by $Pt_{5A(.13)}$ electrodes—aged ½ to 1 hour									
1.0	0.72358	0.70173	([e])	([e])	([e])	([e])	0.63171	0.62099	0.60711	0.57800
2.0	.72467	.70297	0.69332	0.67200	0.66193	([e])	.63303	.62223	.60822	.57915
5.0	.72499	.70382	.69430	.67275	.66282	0.65382	.63399	.62299	.60911	.57998
6.0	.72520	([e])	.69449	.67307	.66171	([e])	.63423	.62329	.60932	.58002

[a] In the subscript describing the hydrogen electrode, the first numeral refers to the number of minutes the electrode was plated, the capital letter refers to the type of plating solution used, and the numbers in parentheses refer to the current density at which the electrode was plated. For example, the electrode $Pd_{1B(.08)}$ was made of palladium sponge and was plated for 1 minute, using solution Pd_B at a current density of 0.08 amp/cm².

[b] First recorded emf 6 to 7 hours after the flow of hydrogen gas was started.

[c] Second recorded emf 52 hours later, after measurements at 0° to 20°C.

[d] Third recorded emf 107 hours later, after measurements at 0° to 60°C.

[e] Cell behaved erratically.

TABLE 6.—*Electromotive forces of the galvanic cell* Pd *or* Pt, $H_2(g)/H_2Ph(m)$, $KHPh(m_2)$, $KCl(m_3)/AgCl(s)Ag(s)$ *at 25° C for definite intervals of time after the flow of hydrogen gas was started*

[The hydrogen and the silver—silver-chloride electrodes were aged 3 months. Hydrogen electrodes were $Pd_{1B(.08)}$.][a]

	Molalities and pH values of the solutions									
$m_1\times10^4$	16.373	28.010	29.096	47.034	49.281	62.049	73.487	100.00	143.56	180.00
$m_2\times10^4$	8.1865	14.005	14.548	23.517	24.641	31.025	36.743	50.00	71.782	90.00
$m_3\times10^4$	8.1865	14.005	14.548	23.517	24.641	31.025	36.743	50.00	71.782	90.00
pH	3.16	3.03	3.02	2.93	2.92	2.88	2.86	2.81	2.76	2.73
Time	Electromotive forces of the solutions									
hr	*v*	*v*	*v*	*v*	*v*	*v*	*v*	*v*	*v*	*v*
(b)	0.59284	0.57227	0.57085	0.55334	0.55170	0.54357	0.53779	0.52745	0.51565	0.50847
(c	.59287	.57228	.57082	.55333	.55170	.54359	.53783	.57242	.51563	.50844
(d)	.59294	.57233	.57091	.55337	.55172	.54360	.53783	.52746	.51569	.50852
Palladium electrodes replaced by Pt $_{1A(.08)}$ electrodes—aged 3 months; last four, aged over a year										
1.0	0.59261	0.57207	0.57109	0.55345	0.55127	0.54378	0.53766	0.52730	0.51544	0.50839
2.0	.53000	.57251	.57109	.55382	.55175	.54360	.53788	.52754	.51574	.50853
5.0	.53018	.57272	.57124	.55404	.55194	.54374	.53800	.52772	.51595	.50866
6.0	.53022	.57273	.57133	.55406	.55199	.54378	.53800	.52776	.51596	.50873
7.0	.53029	.57283	.57139	.55415	.55202	.54380	.53813	.52777	.51595	.50878
19.0	.53091	.57339	.57180	.55481	.55279	.54445	.53866	.52856	.51650	.50922
20.0	.53098	.57351	.57197	.55481	.55281	.54447	.53877	.52856	.51658	.50927
Platinum electrodes replaced by Pt $_{5A(.13)}$ electrodes—aged from ½ to 1 hour										
1.0	0.53072	0.57334	0.57199	0.55488	0.55287	0.54423	0.53875	0.52856	0.51663	0.50900
2.0	.53161	.57422	.57276	.55545	.55332	.54513	.53970	.52900	.51699	.50998
5.0	.53263	.57508	.57360	.55627	.55422	.54600	.54056	.53007	.51784	.51061
6.0	.53267	.57517	.57371	.55631	.55428	.54622	.54067	.53008	.51788	.51086

[a] In the subscript describing the hydrogen electrode, the first numeral refers to the number of minutes the electrode was plated, the capital letter refers to the type of plating solution used, and the numbers in parentheses refer to the current density at which the electrode was plated. For example, the electrode $Pd_{1B(.08)}$ was made of palladium sponge and was plated for 1 minute, using solution Pd_B at a current density of 0.08 amp/cm^2.

[b] First recorded emf 4 to 5 hours after the flow of hydrogen gas was started.

[c] Second recorded emf 47 hours later, after measurements at temperatures from 0° to 20° C.

[d] Third recorded emf 99 hours later, after measurements at temperatures from 0° to 60° C.

IV. CONCLUSIONS

Reliable measurements can be made with hydrogen electrodes in aqueous solutions of acid potassium phthalate and phthalate solutions of pH ranging from 2.73 to 5.33 and for temperatures from 0° to 60° C.

The inconsistencies regarding the behavior of hydrogen electrodes in phthalate solutions reported in the literature are due to the type of hydrogen electrode used and not to the design of the cell, or to variations in the potential of the liquid junction formed between the solutions of phthalates and the potassium chloride of the calomel electrode, or to the unstable state or unaged condition of the electrodes, or to increased reduction of the phthalates at the hydrogen electrode because of impurities.

It has been found that the potentials of hydrogen electrodes prepared with palladium sponge of various thicknesses remain constant for 35 hours and increase only 0.3 mv after more than 100 hours of operation. Their characteristics are independent of the current density used in the electrolysis; of the concentration, composition, pH, and conductivity of the plating solution; and of the concentration, composition, pH, and buffer capacity of the phthalate solutions in which they are used.

On the other hand, the potentials of hydrogen electrodes prepared with platinum sponge increase steadily with time, and the rate of increase depends upon the thickness of the sponge. Frequently, such electrodes exhibit erratic behavior because of reduction of the phthalates at the electrode surface. Equilibrium values of the potential may be obtained at times if a very thin coat of platinum sponge is used and a large volume of solution is employed in the hydrogen-electrode compartment. However, the former condition cannot always be reproduced. The different behavior of platinum and palladium hydrogen-electrodes may be accounted for by the difference in their catalytic activity.

The authors are indebted to C. G. Malmberg for the measurements of the conductivities of the plating solutions used in these studies and to W. W. Walton for the purification of the *o*-phthalic acid.

V. REFERENCES

[1] A. R. T. Merrill, J. Am. Chem. Soc. **43**, 2690 (1921).
[2] E. T. Oakes and H. M. Salisbury, J. Am. Chem. Soc. **44**, 948 (1922).
[3] C. Z. Draves and H. V. Tartar, J. Am. Chem. Soc. **47**, 1226 (1925).
[4] I. M. Kolthoff and F. Tekelenburg, Rev. trav. chim. Pays-Bas **46**, 33 (1927).
[5] D. I. Hitchcock and A. C. Taylor, J. Am. Chem. Soc. **59**, 1812 (1937).
[6] D. A. MacInnes, D. Belcher, and T. Shedlovsky, J. Am. Chem. Soc. **60**, 1094 (1938).
[7] S. F. Acree and N. G. Knight, Science **61**, 498 (1925).
[8] W. M. Clark and H. A. Lubs, J. Biol. Chem. **25**, 479 (1916).
[9] C. J. Wood and P. P. Murdick, J. Am. Chem. Soc. **44**, 2008 (1922).
[10] J. Russell and R. E. Stauffer, J. Am. Chem. Soc. **60**, 2820 (1938).
[11] L. R. Bacon, J. W. Hensley, and T. H. Vaughn, Ind. Eng. Chem. **33**, 723 (1941).
[12] W. M. Clark, J. Am. Chem. Soc. **44**, 1072 (1922).
[13] H. T. Beans and L. P. Hammett, J. Am. Chem. Soc. **47**, 1215 (1925).
[14] S. F. Acree and E. A. Slagle, Abs. Bact. **5**, 5 (1921) E. H. Fawcett and S. F. Acree, Ind. Eng. Chem. **2**, 78 (1930); J. O. Burton, W. J. Hamer, and S. F. Acree, J. Research NBS **16**, 575 (1936) RP895; J. G. Wangler, E. W. Geniesse, A. W. Wells, G. M. Kline, and S. F. Acree, Dissertations, George Washington Univ., Washington, D. C. (unpublished); C. N. Myers and S. F. Acree, Am. Chem. J. **50**, 396 (1913); L. J. Desha and S. F. Acree, Am. Chem. J. **46**, 638 (1911).
[15] S. F. Acree and E. A. Slagle, Abstracts Bact. **5**, 5 (1921).
[16] G. M. Kline, M. R. Meacham, and S. F. Acree, BS J. Research **8**, 101 (1932) RP403.
[17] J. O. Burton, W. J. Hamer, and S. F. Acree, J. Research NBS **16**, 575 (1936) RP895.
[18] N. E. Loomis and S. F. Acree, Am. Chem. J. **46**, 585 (1911).
[19] W. F. Clarke, C. N. Myers, and S. F. Acree, J. Phys. Chem. **20**, 243 (1916).
[20] C. N. Murray and S. F. Acree, BS J. Research **7**, 713 (1931).
[21] C. N. Myers and S. F. Acree, Am. Chem. J. **50**, 396 (1913).
[22] E. R. Smith and J. K. Taylor, J. Research NBS **20**, 837 (1938) RP1108.
[23] E. Van de Stadt, Z. physik Chem. **31**, 250 (1899); **41**, 353 (1902).
[24] F. L. Hahn, J. Am. Chem. Soc. **57**, 2537 (1935).
[25] W. J. Hamer and S. F. Acree, J. Research NBS **23**, 647 (1939) RP1261.
[26] N. E. Loomis and S. F. Acree, J. Am. Chem. Soc. **38**, 2391 (1916).
[27] W. M. Clark, The Determination of Hydrogen Ions, 3d ed. (The Williams & Wilkins Co., Baltimore, Md.).
[28] A. E. Lorch, Ind. Eng. Chem., Anal. Ed. **6**, 164 (1934).
[29] S. Popoff, A. H. Kunz, and R. D. Snow, J. Phys. Chem. **32**, 1056 (1928).
[30] G. N. Lewis, T. B. Brighton, and R. L. Sebastian, J. Am. Chem. Soc. **39**, 2245 (1917).
[31] J. C. Andrews, J. Biol. Chem. **59**, 479 (1924).

WASHINGTON, April 13, 1944.