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[CONTRIBUTION FROM THE UNIVERSITY OF NEBRASKA]

THE OXIDATION POTENTIAL OF THE LEAD DIOXIDE ELECTRODE IN PERCHLORIC ACID SOLUTION

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A great amount of work has been done on the lead dioxide electrode by those who used lead dioxide storage cell plates and sulfuric acid. A few used nitric acid. The concentrations were almost always high. Abegg,[1] based on these early results, gave the value +1.44 for the "normal potential." Glasstone,[2] the only more recent worker, concluded that "a mean value of 1.75 volts at 25° is indicated." The minimum concentration of acid used by Gladstone was 0.487 molar. Gerke[3] apparently considered none of the data suitable for the calculation of a value to include in his summary.

In our work the cell arrangement was

$$\mathrm{Pt, PbO_2 \mid Pb(ClO_4)_2, HClO_4 \mid H_2, Pt}$$

The reaction of the cell is

$$\mathrm{PbO_2 + 2H^+ + H_2(g) = Pb^{++} + 2H_2O(l)}$$

The free energy change for this reaction is

$$\Delta F = -NFE_c = -NFE_c - RT\ln\frac{a_{\mathrm{Pb^{++}}} \times a_{\mathrm{H_2O}}}{a^2_{\mathrm{H^+}}}$$

in which E_c is the voltage after correcting for the pressure of the hydrogen and it is assumed that the activity of the PbO_2 is unity. The oxidation potential at unit activity is

$$E_0 = E_c + \frac{RT}{2F}\ln\frac{a_{\mathrm{Pb^{++}}} \times a_{\mathrm{H_2O}}}{a^2_{\mathrm{H^+}}}$$

$$= E_c + \frac{RT}{2F}\ln\frac{\gamma m_{\mathrm{Pb(ClO_4)_2}} \times a_{\mathrm{H_2O}}}{(\gamma m_{\mathrm{HClO_4}})^2}$$

In the first series of measurements (Table I) the concentrations of the perchloric acid and lead perchlorate were equimolecular and the same throughout the cell, then

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[1] Abegg, Auerbach and Luther, "Messungen electromotorischer Krafte galvanischer Ketten," **207**, 70–77, 168–169 (1911).

[2] Glasstone, *J. Chem. Soc.*, **121**, 1469–1480 (1922).

[3] Gerke, *Chemical Reviews*, **1**, 390–391 (1924).

$$E_0 = E_c - \frac{RT}{2F} \ln m + \frac{RT}{2F} \ln \frac{\gamma_{Pb(ClO_4)_2} \times a_{H_2O}}{\gamma^2_{HClO_4}}$$

from the observed values $E' = E_c - RT/2F \ln m$ was calculated and extrapolated to zero concentration. If we assume that

$$\frac{RT}{2F} \ln \frac{\gamma_{Pb(ClO_4)_2} \times a_{H_2O}}{\gamma^2_{HClO_4}} \doteq 0$$

on dilution, this extrapolated value is E_c.

In the second series (Table II) the concentration of the perchloric acid was kept constant throughout the cell and the concentration of the lead perchlorate was varied in the lead dioxide electrode. Since the concentrations of the lead perchlorate were relatively low, the liquid junction potentials were negligible.[4] The oxidation potential, E_0, was calculated assuming that the activity of perchloric acid[5] is the same as that of hydrochloric acid as determined by Randall and Young,[6] that the activity of water was unity and that the activity of the lead perchlorate was the same as that of barium chloride.[7] This second series was made as a check on the first. The first is the basis for the determination of the oxidation potential.

Experimental Part

Doubly distilled water was used in the preparation of all solutions. Perchloric acid was obtained by dilution of the 60% C. P. acid and standardized against sodium carbonate. Lead perchlorate was prepared by the action of this acid on purified lead carbonate from C. P. lead nitrate. The concentration of this solution was determined with dichromate according to the method of Brown and Moss.[8]

Two hydrogen electrode vessels of the Ostwald type and triplicate or quadruplicate hydrogen electrodes prepared by a modification of the method of Ellis[9] were used in each measurement. Hydrogen was prepared by electrolysis of 15% sodium hydroxide and passed successively through glass wool, 20% perchloric acid, *M* perchloric acid, and a washer containing the electrode solution. The purity of this hydrogen was established[10] by checking an electrode for which it was used against another which obtained hydrogen from the action of C. P. hydrochloric acid on C. P. zinc. It is known that a solution of lead acetate has a depressing effect on the hydrogen electrode and on the adsorption of hydrogen by

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[4] Linhart, THIS JOURNAL, **38**, 2356 (1916).

[5] Schumann, *ibid.*, **46**, 58 (1924).

[6] Randall and Young, *ibid.*, **50**, 995 (1928).

[7] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 362.

[8] Unpublished material.

[9] Ellis, THIS JOURNAL, **38**, 737 (1916).

[10] Smith, *ibid.*, **27**, 1287 (1905).

catalytic platinum. Denham and Allmand[11] and Maxted[12] showed that the amount of hydrogen adsorbed varied with the concentration of Pb^{++} ion. In our case it was discovered that hydrogen electrodes in 0.5 *M* perchloric acid and 0.5 *M* lead perchlorate did not show a definite equilibrium value, but fluctuated within a range of five millivolts, the value depending on the length of time hydrogen was furnished to the electrode. The same fluctuation occurred in the measurement employing 0.25 *M* lead perchlorate but to a less degree. At 0.1 *M* lead perchlorate concentration duplicate hydrogen electrodes checked within a maximum of 0.3 of a millivolt. In order to obtain further proof that the effect of lead perchlorate on the hydrogen electrode became negligible at 0.01 *M* or lower concentration of lead perchlorate duplicate hydrogen electrodes were set up one containing 0.01 *M* perchloric acid, and the other 0.01 *M* perchloric acid and approximately 0.01 *M* lead perchlorate. The potential difference was constant and of the order of 0.75 millivolt, no correction being made for ionic strength and consequent difference in activity of H^+. In order to make this activity difference negligible, the observations of potential were made with quadruplicate hydrogen electrodes, two in 0.25 *M* perchloric acid and two in 0.25 *M* perchloric acid and 0.01 *M* lead perchlorate solutions and although those in the solution containing lead perchlorate required a longer time to attain equilibrium, the maximum variation was 0.4 millivolt. This is less than the variation in the lead dioxide electrode and consequently would not introduce sufficient error to make it advisable to discard the method as unsuitable if the average value of triplicate[13] or quadruplicate hydrogen electrodes be employed as the reference electrode value, as was done in our case, and taking into consideration the fact that the variation caused by lead perchlorate decreases as the concentration of lead ion becomes smaller.

Electrolytic lead dioxide was deposited on platinized platinum which had been treated with a blast lamp flame to give a rough surface, by electrolysis of basic lead perchlorate or lead nitrate, nitric acid solutions. The best results were obtained by electrolysis of solutions containing 0.1 to 0.5% lead nitrate and 1.5 to 2.5 *N* in nitric acid. In every case the first electrode plated of a series failed to attain a stable value and the lead dioxide did not adhere very well to the platinum. Electrodes plated with a current density of 0.01 to 0.03 amps./cm.^{2} and a potential drop of 2.2 volts for twenty minutes usually attained a stable value in three to five days and remained constant from three to ten days or longer and then decreased in potential either[12] at a slow uniform rate or abruptly at first and then very slowly. The following are representative:

[11] Denham and Allmand, *J. Chem. Soc.*, **93**, 424 (1908).

[12] Maxted, *ibid.*, **117**, 1501 (1920).

[13] Glasstone, *ibid.*, **121**, 1456 (1922).

0.25 M $HClO_4$ and 0.01 M $Pb(ClO_4)_2$		
5/ 7/28	set up	1.50369
5/12/28		1.50175*
5/21/28		1.50133*
5/28/28		1.49790
5/29/28		1.49649

0.001 M $HClO_4$ and $PbClO_4$	
4/16/28	Set up
4/17/28	1.37904*
4/18/28	1.37604*
4/21/28	1.37621*
4/24/28	1.37197

The values within the range represented by the starred values were used. The values given in the table are the average of five or six such values which checked within the limits given there.

Glasstone[13] also investigated dioxide prepared in the above manner and suggested that the presence of a trace of higher oxide, possibly PbO_3, was the cause of the high initial value. However, since the best results were obtained by electrolysis of solutions containing small amounts of lead under conditions at which Smith[10] and also A. Fischer and Vossen[14] found that the electrolytic deposit from lead nitrate acid solutions approached and ultimately attained the formula PbO_2 with decreasing lead content and since no one has been able to demonstrate the presence of high oxides in the electrolytic lead dioxide deposit[15] we concluded that the high initial values are due to an excess of energy stored in physical strains such as observed by Nielsen[16] for electrolytically deposited copper.

The decrease in potential following the period of stability is in all probability due to the slow formation of Pb^{++}, which is to be expected due to the value of the oxidation potential of lead dioxide in relation to that for the oxygen electrode. The period of stability varied directly with the length of time used to plate the electrode. After various lengths of time the lead dioxide lost its property of adhering to roughened platinum and in several cases the formation of reddish brown spots in the deposit was observed. One electrode plated for eight hours at approximately 0.003 amp./cm.^{2} was used in four measurements and each time attained a constant value after three or four days which checked that of freshly prepared electrodes. In all, this electrode was used for two and one-half months and was lost by an accident.

Cumming,[17] who also used lead dioxide deposited on platinum from lead nitrate nitric acid solutions, saturated his electrolytic solution with solid lead dioxide before plating in order to obtain an adhering deposit and good results. Cumming also reported that an electrolytic lead dioxide electrode first gave a high initial value, fell to one that remained constant for various lengths of time and then slowly dropped off.

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[14] Fischer and Schleicher, "Electranalytische Schnellmethoden," zweite Auflage, **1926**, p. 243.

[15] (a) MacInnes and Townsend, *J. Ind. Eng. Chem.*, **14**, 120 (1922); (b) MacInnes, Adler and Joubert, *Trans. Am. Electrochem. Soc.*, **37**, 641 (1920).

[16] Nielsen, THIS JOURNAL, **49**, 2423 (1927).

[17] Cumming, *Z. Electrochem.*, **13**, 19 (1907).

Chemical lead dioxide was prepared by adding bleaching powder, sodium hypochlorite and bromine water solutions to boiling solutions of lead acetate, washing repeatedly with water, hot dilute nitric acid, again with water and drying at 80 to 110°. The four best grades of lead dioxide obtainable were repurified by boiling with 10% sodium hydroxide and then digested with dilute nitric acid, washed and dried. All this work was done and the electrodes were set up by inserting a smooth platinum foil in a quantity of lead dioxide in the bottom of the electrode vessel in an atmosphere free from hydrogen. Only the repurified dioxide and that prepared with bleaching powder gave constant potential values and those only in solutions containing 0.025 *M* or higher concentrations of lead perchlorate, even after twenty-four hours rotation and repeated purification with dilute nitric acid or perchloric acid to remove divalent lead, which was tested for by shaking up lead dioxide with nitric acid of perchloric acid decanting, adjusting the acid concentration and adding potassium chromate. Negative tests were obtained immediately after purification. However, the lead dioxide gave a test for Pb^{++} upon standing dry in stoppered amber bottles in the dark for a week. From the energy relations involved it would be expected that lead dioxide is unstable in neutral or acid solution. However, it would not be expected to decompose when dry in the dark and protected from hydrogen. The potentials of the repurified lead dioxides were initially high or low depending on whether they were prepared by chemical oxidation or electrolytic methods. The equilibrium potential value of the chemical lead dioxide remained constant indefinitely and agreed within a millivolt or two with the average stable value of a number of electrolytic lead dioxide electrodes.[13,15b]

The experimental half cell consisted of a pyrex test-tube with a sealed-in side arm and closed by a one-holed rubber stopper through which a glass tube with a platinum foil sealed in the lower end was inserted. Contact was made to the potentiometer by filling the tube with mercury and inserting the potentiometer lead.

Liquid contact was established between the electrodes by allowing the side arms to dip in a vessel which contained the same solution as the electrodes in the first series of measurements and in the second series contained the same concentration of perchloric acid as the hydrogen electrode. This intermediate vessel was protected from evaporation by a layer of purified paraffin, which was found not to affect the measured values in any way.

Temperature was maintained constant at 25 ± 0.03°. The potential differences were measured with a Leeds and Northrup Type K potentiometer, and a new Weston Standard cell calibrated by the U. S. Bureau of Standards.

In the following tables E_c is the average first stable value of five or six electrolytic lead dioxide electrodes.

TABLE I

EXPERIMENTAL DATA

Mole $HClO_4$ = mole $Pb(ClO_4)_2$	E_c, mv.	E'
0.1	1.432 ± 3	1.461
.025	1.417 ± 3	1.464
.1	1.407 ± 3	1.466
.0025	1.389 ± 2	1.467
.001	1.378 ± 2	1.467
E_0 by extrapolation of E'		1.467

TABLE II

EXPERIMENTAL DATA

$HClO_4$, mole (per 1000 g.	$Pb(ClO_4)_2$, mole of H_2O)	E_c	E_0
0.25	0.01	1.501	1.475
.25	.001	1.523	1.467
.25	.0001	1.549	1.464
		E_0 average	1.469

Summary

1. The possible sources of error in the previous work on the lead dioxide electrode have been discussed.
2. The work of former investigators who found the first stable value of electrolytically prepared lead dioxide to agree within one or two millivolts with the potential of that obtained from chemical sources has been checked.
3. An attempt has been made to explain the high initial value and the final drop in potential of electrolytic lead dioxide. The factors involved in lengthening the stable period of this lead have also been studied.
4. The effect of lead perchlorate on the hydrogen electrode has been investigated and found to be proportional to the Pb^{++} concentration.
5. The standard oxidation potential of Pb^{++}–PbO_2 in molal H^+ has been measured by two methods and found to be 1.467 ± 0.003 volts.

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SOME OF THE THERMODYNAMIC PROPERTIES OF AMMONIA. I. THE COMPRESSIBILITY OF AND AN EQUATION OF STATE FOR GASEOUS AMMONIA. THE VAPOR PRESSURE OF LIQUID AMMONIA

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1. Introduction

The compressibility of gaseous ammonia is of interest because the curvature of the isometries is greater than for any other gas, except steam, for which there is a considerable body of data. The earlier measurements either do not extend over a very wide range, or the volumes were uncertain. Roth[1] studied the pressure–volume–temperature behavior of ammonia from 30 to 180°, but his volumes were not definitely determined;

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[1] Roth, *Wied. Ann.*, **11**, 1 (1880).