The Potential of the Lead Dioxide–Lead Sulfate Electrode at Various Temperatures[1]

BY WALTER J. HAMER[1]

Owing to the industrial importance of the lead dioxide–lead sulfate electrode, an accurate value of its molal potential is desired. Although many attempts have been made to determine this potential, the value is not known with precision. Gerke[2] obtained 1.7 ± 0.1 v. at 25° from the measurements of Kendrick.[3] More recently, Vosburgh and Craig[4] obtained 1.681 ± 0.001 v. at 25° from measurements with a mercury–mercurous sulfate reference electrode. These values and others[5] show a diversity of ±0.1 v. Part of this discrepancy is due to the use of various reference electrodes, the potentials of which are not well known, and to the direct use of battery plates which may have been prepared by different methods and subjected to various treatments. In this contribution, measurements of the cell

$$H_2 \mid H_2SO_4(m) \mid PbSO_4 \mid PbO_2 \mid Pt^+$$
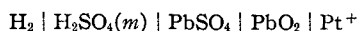
will be employed to determine the potentials of the lead dioxide–lead sulfate electrode.

This cell also has additional interest as a means of determining the thermodynamic properties of aqueous sulfuric acid solutions. In order to make a thorough study of this subject, the measurements have been extended over a concentration range of 0.0005 to 7.0 M and throughout a temperature range of from 0 to 60°.

Experimental Procedure

Sulfuric Acid.—Dilute solutions of sulfuric acid were prepared from a high grade of sulfuric acid (sp. gr. 1.8365) and conductivity water. This solution was analyzed gravimetrically and the analysis was checked by titration with solutions of standard carbonate-free sodium hydroxide. Phenolphthalein was employed as an indicator. The more concentrated solutions were prepared from sulfuric acid (sp. gr. 1.8365) by weight and analysis was obtained both by titration and by density determinations. These solutions were diluted to the desired strength with conductivity water. The concentrations of the solutions were known with an accuracy of ±0.1%. The solutions were boiled in vacuo and kept under hydrogen until de-

livered into the cells. The stock solution was tested for sulfite and was found to be free of this impurity, hence distillation was not considered necessary.

Hydrogen.—Tank hydrogen purified by passing over copper heated to 700° was employed.

Hydrogen Electrodes.—Platinum foil electrodes were used. These were plated in a chloroplatinic acid solution for three minutes at a current density of 400 milliamperes. A somewhat shorter electrolysis was employed for plating the electrodes which were used in the very dilute solutions.

Cells and Bubble Tubes.—The apparatus described by Hamer[6] was employed for these measurements. In this experiment the three way stopcock was essential to prevent hydrogen from coming into contact with the lead dioxide. Although lead dioxide is reduced by hydrogen gas at temperatures above 140°, its reduction in solution may take place at much lower temperatures.[7]

Potentiometer.—A Type K Leeds and Northrup potentiometer was employed. Measurements of voltages above 1.6 v. were made by the method suggested in the Leeds and Northrup pamphlet.

Lead Nitrate.—Lead nitrate to be used in subsequent preparations was crystallized twice from a hot concentrated solution of high grade lead nitrate by the addition of a concentrated solution of nitric acid. In the second crystallization redistilled nitric acid was employed.

Lead Sulfate.—500 cc. of 0.5 M lead nitrate and 500 cc. of 0.5 M sulfuric acid were added drop by drop to 2 liters of boiling 0.1 M sulfuric acid. The solution was stirred constantly by a current of dry carbonate-free air during the precipitation. The lead sulfate was well washed and digested for twenty-four hours on a steam-bath under 2 M sulfuric acid. The final preparation was kept under 0.1% sulfuric acid until used.

Lead Dioxide.—In order to find the kind of lead dioxide most suitable for use in the cells, seven samples were prepared.

(1) Dilute lead nitrate solution was added drop by drop to a dilute solution of sodium hydroxide. The lead hydroxide formed was washed well and then dissolved in a sodium hydroxide solution. The resulting sodium plumbite solution was heated to 93°, and while mechanically stirred bromine was added slowly until the precipitate turned dark brown.

(2) This preparation was the same as (1) except that a stream of chlorine gas was bubbled into the sodium plumbite solution instead of bromine. The chlorine was generated by the action of concentrated hydrochloric acid on potassium permanganate and was washed by bubbling through water.

(3) This sample was prepared by the oxidation of sodium plumbite solution with hydrogen peroxide.

(4) 100 grams of lead nitrate and 400 cc. of concentrated nitric acid in a total volume of 3 liters was electrolyzed at

(1) This contribution is part of an investigation of the thermodynamic properties of the electrodes and electrolyte of the lead accumulator. The work was made possible by a grant from the Naval Research Laboratory, Anacostia Station, Washington, D. C., and is published with permission of the Secretary of the Navy.

(2) Gerke, Chem. Reviews, 1, 390 (1925).

(3) Kendrick, Z. Elektrochem., 7, 53 (1900).

(4) Vosburgh and Craig, THIS JOURNAL, 51, 2009 (1929).

(5) Cumming, Trans. Faraday Soc., 2, 209 (1907); Glasstone, J. Chem. Soc., 121, 1469 (1922).

(6) Hamer, THIS JOURNAL, 56, 860 (1934).

(7) Wright and Luff, J. Chem. Soc., 33, 532 (1878).

93°. The anode was a platinum gauze and the cathode a platinum wire sealed into glass and surrounded by a porous cup. The current density was maintained at 2.5 amperes per square centimeter of anode and a current of dry carbonate-free air was used to stir the solution.

(5) A small quantity of electrolytically prepared lead dioxide was dissolved with hot concentrated carbonate-free sodium hydroxide solution under an atmosphere of nitrogen. The solution was filtered and added drop by drop to a large volume of conductivity water kept at 93° and constantly stirred.

(6) This sample was the same as (5) except that precipitated lead dioxide (1) was used in place of electrolytically prepared lead dioxide.

(7) Two different samples of commercial lead dioxide were digested for two weeks with 3 M sulfuric acid, filtered, and redigested for several days. A small portion of each was treated by method (5) before digesting.

Digestion of Lead Dioxide.—All of the above preparations were digested separately under 3 M sulfuric acid on a steam-plate for a week. This digestion brings the dioxide into a more stable state and also converts any monoxide into lead sulfate. Since lead sulfate is added later its formation is not undesirable. Preparations which preclude this digestion were not employed since they were found to be unsatisfactory by Vosburgh and Craig.[8] The lead dioxide was kept under 0.1% sulfuric acid until used.

Lead Dioxide–Lead Sulfate Electrodes.—Lead dioxide was quickly sucked dry in a Gooch crucible, the bottom of which was covered with filter paper. It was then transferred to a glass-stoppered flask containing sulfuric acid at the concentration to be used in the cell. Lead sulfate dried in like manner was then added and the flask was shaken from fifteen to thirty minutes. This paste was placed in the cell compartment over a sealed-in platinum wire and sulfuric acid was introduced into the evacuated cell. The relative amounts of lead dioxide and lead sulfate could be varied but it is better to have approximately the same amounts of each. Unsatisfactory results are obtained if only traces of one or the other are used.

Preliminary Measurements.—Measurements were made with each of the lead dioxide preparations to determine which gave the most consistent and reproducible results. All electrodes were constructed as described above. In Table I the electromotive forces at 25° of the cell designated containing the various preparations of lead dioxide are compiled. Two series are given for each kind at the same concentration. All these measurements were made with boiled solutions and the cells were filled *in vacuo*. All samples came to equilibrium within two hours except at 0°, at which temperature three to four hours were required. After equilibrium has been reached at one temperature a much shorter time is required for equilibrium when the temperature is changed.

(8) Vosburgh and Craig, THIS JOURNAL, **51**, 2009 (1929); see also Glasstone. *J. Chem. Soc.*, **121**, 1469 (1922).

TABLE I

THE ELECTROMOTIVE FORCES AT 25° OF THE CELL, H₂ | H₂SO₄(m) | PbSO₄ | PbO₂ | Pt⁺, CONTAINING VARIOUS PREPARATIONS OF PbO₂[a]

PbO₂ prep.[b]	0.01945 M	0.04945 M	0.09798 M	0.9967 M
1	1.51937	1.54391	1.56133	1.62288
	1.51952	.....	1.56092	.....
2	1.51984	1.54452	1.56127	.....
	1.51963	1.54471	1.56163	.....
3	1.51997	1.54400	1.56177	.....
	1.51948	.....	1.56151	.....
4	1.52069	1.54535	1.56258	1.62467
	1.52073	1.54538	1.56257	1.62458
5	1.52079	1.54538	.....	1.62456
	1.52061	1.54521	.....	.....
6	1.52039	1.54522	1.56240	.....
	1.52042	1.54543	1.56227	.....
7[c]	1.52827	.....	1.57011	.....
	1.52904	.....	1.56937	.....
7'[c]	1.51674	.....	1.55937	.....
	1.51770	.....	1.55825	.....

[a] The same relative differences persist at other temperatures. [b] The numbers refer to methods of preparation of PbO₂. [c] Neither of these gave consistent results when subjected to the treatment employed in preparing (5). (7) Refers to Baker's 96.4% "analyzed" lead peroxide. (7') Refers to Coleman and Bell's lead peroxide (Mn free).

A study of Table I shows that preparations (4), (5) and (6) are the most desirable and gave measurements consistent to within ±0.1 mv. The commercial samples evidently could not be sufficiently purified. The low results obtained by the first two methods are probably due to the tendency of lead dioxide to occlude the impurities, sodium bromide and chloride, which are formed in their preparation and which resist all effort of removal. The third preparation probably gives low results for the same reason or due to a possible colloidal condition. All the preparations are amorphous lead dioxide except (4) which is a fine crystalline preparation. Cumming[9] and Glasstone[10] found that crystalline lead dioxide gives a higher potential than the amorphous variety. The results of (5) and (6) indicate that this is true. but that the differences amount to only a few tenths of a millivolt, and that the low values of (1), (2) and (3) are due to other additional effects.

Lead dioxide prepared by electrolysis gave the most consistent results, which were reproducible to better than ±0.1 mv. Consequently, all subsequent measurements were made with preparation (4). Preparations (5) and (6) may also be

(9) Cumming, *Trans. Faraday Soc.*, **2**, 209 (1907).
(10) Glasstone, *J. Chem. Soc.*, **121**, 1469 (1922).

used but they require a longer time to prepare and only small quantities are obtained readily.

Electromotive Forces of the Cells H₂ | H₂SO₄(m) | PbSO₄ | PbO₂ | Pt⁺.—Three series of measurements were made. In series A. new lead dioxide–lead sulfate electrodes were prepared for each run from a new supply of the mixed paste. In series B the paste was kept after each run, retreated and then re-used. In series C a new electrolytic preparation of lead dioxide was employed and the procedure of series B was followed. The three series checked well and a paste of lead dioxide–lead sulfate can be used repeatedly with good results. In fact this procedure is to be recommended since an electrode of constant composition is used for all measurements. These measurements were made at five-degree temperature intervals from 0 to 60°. All electromotive forces were corrected to one atmosphere hydrogen pressure by employing the combined vapor pressures of aqueous sulfuric acid of Grollman and Frazer,[11] Brönsted[12] and Collins.[13] The corrections for 0° were obtained by extrapolation of above data.

Since the original data involved measurements at so many temperatures and concentrations, and since three complete series of results were obtained tables of these data were considered too bulky for publication. In the calculations of the molal electrode potential, the original results were used and will be shown on the graphs in the figures. In place of these data, we have compiled in Table III the constants of the equation which expresses the mean electromotive forces at round concentrations to within ±0.05 mv., namely

$$E = E_1 + at + bt^2 \qquad (1)$$

These were obtained from a large plot of $(E - RT/2F \ln m_{\mathrm{H}}{}^2 m_{\mathrm{SO}_4})$ against $(m_{\pm}/4^{1/3})^{1/2}$. At concentrations below 0.01 M it is necessary to correct for the solubility of lead sulfate in sulfuric acid. The molalities of the sulfate ion at 20, 25 and 30° due to this solubility were taken from the average values obtained by graphical interpolation of solubility measurements made by Pleissner[14] at 18°, by Huybrechts and Ramelot[15] at 18 and 30°, and by Purdum and Rutherford[16] at 20°. The

solubility of lead sulfate in water[17] was also employed in this graphical interpolation and extrapolation. To obtain the molalities of the sulfate ion at other temperatures the above values were plotted against $1/T$ and the best straight line was drawn and extrapolated to 0 and 60°. Values obtained in this manner are given in Table II. In the third and fourth columns of this table the values of r and s in the equation $S = S_0 + rt + st^2$ are given, where S and S_0 represent the solubility of lead sulfate in sulfuric acid at temperatures t and 0°, respectively. The constants r and s were obtained by the graphical method of Harned and Nims.[18]

TABLE II

SOLUBILITY OF LEAD SULFATE IN SULFURIC ACID FROM 0 TO 60°[a]

$m(\mathrm{H}_2\mathrm{SO}_4)$	$S_0 \times 10^5$	$r \times 10^8$	$s \times 10^{10}$
0.0004	34.0	80.6	3.0
.0005	32.3	76.0	2.5
.0007	28.5	66.6	2.2
.001	23.0	60.0	2.0
.002	16.0	40.0	1.6
.003	11.0	25.0	1.4
.005	9.0	20.0	1.0
.007	8.0	10.0	0.7
.01	7.0	5.0	.5

[a] These values are expressed in moles per 1000 g. of water.

These values were incorporated in the smoothing process by calculating the change in the potentials produced by the slight increase in the sulfate-ion concentration or more simply by substituting the total sulfate-ion concentration in the formula given above for smoothing. Dolezalek and Finckh[19] and Glasstone[20] found the solubility of lead dioxide in sulfuric acid to be extremely small in dilute solutions and no corrections for its solubility were necessary.

The values of the electromotive forces read from the curve at round concentrations were expressed by the equation (1) and the constants a and b were obtained by the method of least squares. The values of the electromotive forces at 0° and of these constants are given in Table III. This procedure is usually adopted in the calculation of thermodynamic data from electromotive force measurements in order to distribute the experimental error more evenly.

(11) Grollman and Frazer, THIS JOURNAL, 47, 712 (1925).

(12) Brönsted, Z. physik. Chem., 68, 693 (1910).

(13) Collins, J. Phys. Chem., 37, 1191 (1933).

(14) Pleissner, Arb. Kaiser Ges. Amt., 26, 419 (1907).

(15) Huybrechts and Ramelot, Bull. soc. chim. Belg., 36, 239 (1927).

(16) Purdum and Rutherford, THIS JOURNAL, 55, 3221 (1933).

(17) Böttger, Z. physik. Chem., 46, 604 (1903); Kohlrausch, Z. ibid., 64, 129 (1908); Huybrechts and de Langeron, Bull. soc. chim. Belg., 39, 43 (1930).

(18) Harned and Nims, THIS JOURNAL, 54, 423 (1932).

(19) Dolezalek and Finckh, Z. anorg. Chem., 51, 323 (1906).

(20) Glasstone, J. Chem. Soc., 121, 1469 (1922), gives the solubility product of (Pb)(OH)₄ as 3.25 × 10⁻⁶⁶.

TABLE III

THE ELECTROMOTIVE FORCES OF THE CELL H_2 | $H_2SO_4(m)$ | PbSO$_4$ | PbO$_2$ | Pt$^+$ AT ROUND CONCENTRATIONS AT 0° AND CONSTANTS OF EQUATION (1), $E = E_0' + at + bt^2$

$m(H_2SO_4)$	E_0'	$-a \times 10^6$	$b \times 10^8$
0.0005	1.42151	684.79	91.11
.0007	1.43276	659.06	90.28
.001	1.44458	636.80	92.22
.002	1.46706	603.96	90.28
.003	1.47976	588.96	90.77
.005	1.49529	581.72	89.94
.007	1.50503	574.54	91.11
.01	1.51541	566.82	92.06
.02	1.53429	536.35	91.27
.03	1.54467	514.16	90.63
.05	1.55738	488.53	90.50
.07	1.56555	477.66	89.22
.10	1.57407	465.59	88.40
.20	1.59055	423.31	86.60
.50	1.61275	355.57	86.81
1.00	1.63214	303.83	76.43
1.50	1.64681	270.21	73.57
2.00	1.65728	251.86	75.30
3.00	1.67936	240.97	70.10
4.00	1.70009	240.48	66.20
5.00	1.72003	245.47	62.65
6.00	1.73861	248.59	62.96
7.00	1.75608	253.32	58.60

Evaluation of the Molal Electrode Potential E_0 of the Lead Dioxide–Lead Sulfate Electrode.

—The chemical reaction represented by the cell in question is taken to be

$$H_2(1 \text{ atm.}) + PbO_2(s) + H_2SO_4(m) = PbSO_4(s) + 2H_2O \text{ (in } H_2SO_4 = m)$$
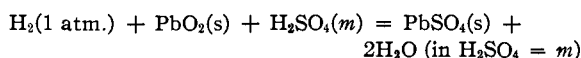
and the electromotive force is given by the equation

$$E = E_0 + (RT/2F) \ln m_H^2 m_{SO_4} + (RT/2F) \ln \gamma_H^2 \gamma_{SO_4} - (RT/2F) \ln a_w^2 \quad (2)$$

where E is the measured electromotive force of the cell at a molal concentration, m, E_0 is the molal electrode potential of the lead dioxide–lead sulfate electrode, and "m's" and "γ's" represent molalities and activity coefficients, respectively, of the ionic species denoted by subscripts. The activity of the water is represented by a_w.

We shall first employ the method of extrapolation of Lewis and Linhart.[21] Equation (2) may be rearranged in the form

$$E - (RT/2F) \ln m_H^2 m_{SO_4} = E_0 + (RT/2F) \ln \gamma_H^2 \gamma_{SO_4} - (RT/2F)\ln a_w^2 \quad (3)$$

and if the left side is plotted against the square root of the molality, a straight line may be obtained in the dilute solution range. At zero concentra-

tion this function equals E_0 since by definition the last two terms on the right vanish.

As a comparison with this extrapolation, the activity coefficients at 0° of Randall and Scott[22] obtained from freezing point determinations were used to evaluate the second term on the right of equation (4). The difference between this term and the left side of the same equation gives E_0, when a_w, a very small term, is neglected. The electromotive force measurements are parallel to their curve as found for other electrolytes by Randall and Young.[23] The extrapolations of the left side of equation (4) against $(m_\pm/4^{1/3})^{1/2}$ are given in Fig. 1 at 0, 25, 45 and 60° from 0.0005 to 0.01 M. The observed electromotive forces were employed. The three results at approximately the same concentration correspond to original series of results A, B, C, respectively. The smoothed values in Table III would fall on the curves as drawn. The lower curve is the one given by freezing point measurements. For clear comparison with electromotive force measurements 0.002 v. has been subtracted from the function computed from freezing point measurements. The freezing point curve has a slight "hump" below 0.002 M but this may be due to the somewhat arbitrary extrapolation by Randall and Scott of their "j" function in dilute solutions. Our points are not accurate enough to justify this slight "hump" and we have drawn a straight line. The same was done at the other temperatures. The normal potentials determined in this manner are given in the second column of Table IV. These were least squared to fit a quadratic equation, and the equation with numerical values is

$$E_0 = 1.67694 + 342.17 \times 10^{-6}t + 83.11 \times 10^{-8}t^2 \quad (4)$$

Values of E_0 calculated by this equation agree with the observed values to less than 0.1 mv.

Evaluation of the Molal Electrode Potential, E_0, of the Lead Dioxide–Lead Sulfate Electrode by a Method Employing the Ionization Constant of the Bisulfate Ion, K_2.

—In the above method for extrapolation we have employed stoichiometrical concentrations. Sulfuric acid is known to be a moderately strong electrolyte, the second step in its ionization being incomplete. This is shown to be true in Fig. 1.

The straight lines labeled "L. L." are those predicted from the limiting law of Debye and Hückel for a completely dissociated electrolyte.

(21) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Company, New York, p. 334.

(22) Randall and Scott, THIS JOURNAL, 49, 647 (1927).

(23) Randall and Young, ibid., 50, 989 (1928).

The experimental slopes are greater than those required by theory, and due to this fact will be shown to require modification.[24]

The method of extrapolation employed in the last section possesses the advantage of simplicity but is subject to two major criticisms. Due to the fact that $m^{1/2}$ is plotted, the extrapolation from the last experimental point to zero concentration is long. Secondly, for an electrolyte which is partially dissociated, the straight line extrapolation does not conform to the law of Debye and Hückel at zero concentration. Another method which has the advantage of including the limiting law but possesses the disadvantage of being very complicated numerically will now be described.

If the value of the real concentration of the hydrogen ion given by the equation

$$K_2 = (m_H m_{SO_4} \gamma_H \gamma_{SO_4})/(m_{HSO_4}\gamma_{HSO_4}) \quad (5)$$

is substituted in equation (2), there results the equation

$$E = E_0 + (RT/2F) \ln$$
$$m_H m_{HSO_4} + (RT/2F) \ln$$
$$\gamma_H \gamma_{HSO_4} + (RT/2F) \ln$$
$$(K_2/a_w^2) \quad (6)$$

In making this step a number of considerations are involved. In the first place, the assumption that sulfuric acid dissociates completely into the hydrogen and bisulfate ion is made. In the second place, we regard the "m's" as representing the true concentrations of the species present, and not the stoichiometrical concentrations. This permits the substitution of the limiting law of Debye and Hückel for the activity coefficients. Upon substitution of this law with an additional term, $\beta'\mu'$, for the third member on the right of equation (6), the equation

$$E - (RT/2F) \ln m_H m_{HSO_4} + 2A\mu'^{1/2} - (RT/2F)$$
$$\ln K_2 = E_0 - (RT/2F) \ln a_w^2 + \beta'\mu' \quad (7)$$

results. Since at very low concentrations all quantities on the left side may be either obtained

(24) Hamer, THIS JOURNAL, 56, 860 (1934).

experimentally or evaluated, an extrapolation of the left side against μ' gives E_0 at zero concentration, since the second term on the right side vanishes by reason of its definition. The slope of the curve gives the value of β' which may or may not be constant with μ'. μ' is the ionic strength computed from the real concentrations of the ionic species.

The ionic concentrations of each of the ions (H^+, HSO_4^- and SO_4^-) were estimated from equation (5) and the logarithm of the activity coefficient ratio was obtained from the limiting
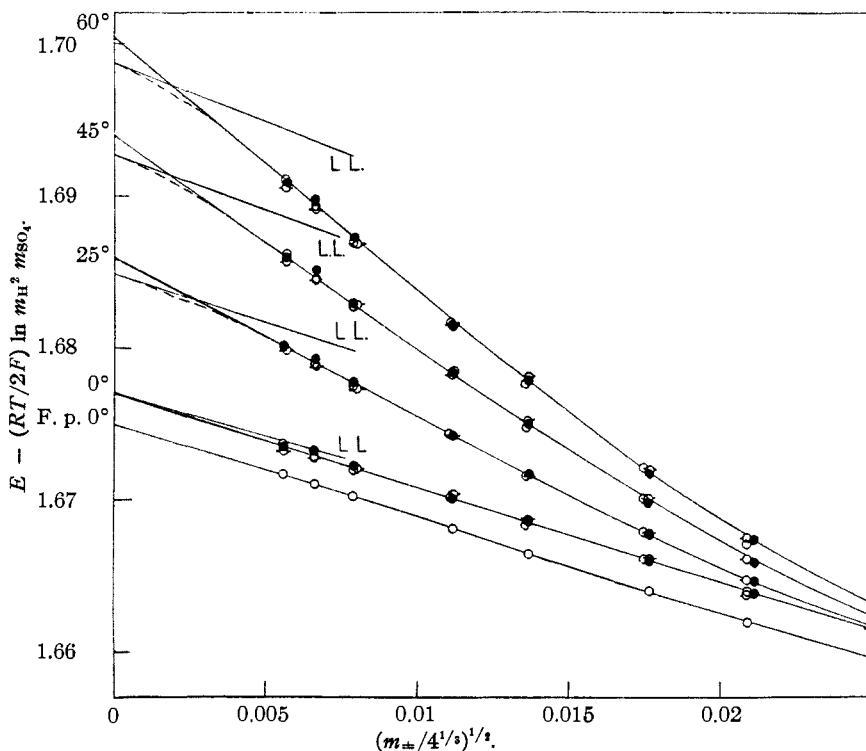

Fig. 1.—Plot of the left side of equation (3) against $(m_\pm/4^{1/3})^{1/2}$: Series A, ●; Series B, ○; Series C, -○-.

law of Debye and Hückel. In equation (5) $m_H = M + m_{H'}$, $m_{SO_4} = m_H + S$ and $m_{HSO_4} = M - m_{H'}$ where M is the stoichiometrical concentration and $m_{H'}$ is the concentration of the sulfate or hydrogen ion produced in the ionization of the bisulfate ion. The ionic strength is equal to $M + (M + 2m_{H'} + 2S)$. The values of $m_{H'}$ and the ionic strength were obtained by successive approximations. In these calculations, the experimental values of K_2 obtained by Hamer were employed.[24] The A values at the various temperatures are those from Table VII of the compilation of Harned and Ehlers multiplied by $d^{1/2}$ where d is the density.[25]

(25) Harned and Ehlers, ibid., 55, 2179 (1933).

The values of the concentrations obtained by this method are only approximations in solutions of appreciable ionic strength but in the limit at zero concentration they approach the correct values and should yield a correct extrapolation.

Fig. 2.—Plot of the left side of equation (7) against μ': Series A, O; Series B, △; Series C, ✕.

Because of the extended nature of these calculations, we shall not include the tables of numerical results but simply illustrate the extrapolation by Fig. 2 in which the left side of equation (7) is plotted against μ'. The final results are given in the third column of Table IV. These results may be computed by the equation

$$E = 1.67699 + 0.000285\,t + 1.2467 \times 10^{-6}\,t^2 \quad (8)$$

which was obtained from them by the method of least squares. The fourth column contains the differences between these values and those obtained by the first method of extrapolation.

In Fig. 2 the second extrapolation is shown at all temperatures. At 0° the plots have a slight curvature but at higher temperatures they are straight lines and it is a comparatively simple

matter to make the short extrapolation, indeed much simpler than the purely empirical extrapolation shown in Fig. 1.

We are now in a position to compare the two methods of extrapolation. In Fig. 1, we have drawn lines (L. L.) to the values of E_0 obtained by the second method of extrapolation which show the requirement of the limiting law of Debye and Hückel. First, it is to be noticed that at zero degrees the slope of the Lewis and Linhart extrapolation happens to be nearly the same as that required by the limiting law. Consequently, at this temperature both methods of extrapolation give the same values of E_0. At the higher temperatures, most noticeable at 60°, the slope of the Lewis and Linhart graph is greater than that required by theory. It is obvious that if we do not abandon the theory, the values of E_0 must be lower than those obtained by the first method. Such conformity with theory is represented by the dotted lines drawn to the values of E_0 obtained by the second
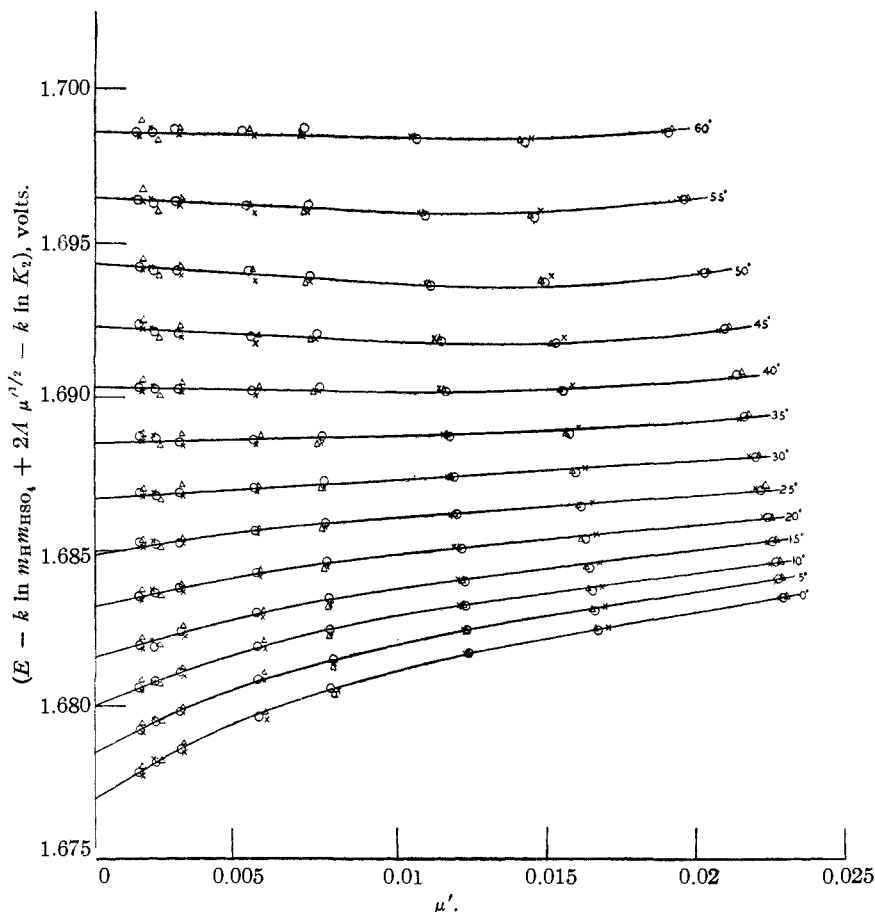
TABLE IV

THE MOLAL ELECTRODE POTENTIAL OF THE | PbSO₄ | PbO₂ | Pt ELECTRODE FROM 0 TO 60°

t, °C.	E_0 (Eq. 3)	E_0 (Eq. 7)	Δ (mv.)
0	1.67694	1.67694	0
5	1.67870	1.67846	0.24
10	1.68045	1.67998	.47
15	1.68228	1.68159	.69
20	1.68411	1.68322	.89
25	1.68597	1.68488	1.09
30	1.68800	1.68671	1.29
35	1.68991	1.68847	1.45
40	1.69196	1.69036	1.60
45	1.69396	1.69231	1.65
50	1.69616	1.69436	1.80
55	1.69831	1.69649	1.82
60	1.70044	1.69861	1.83

method. Somewhere in the region of concentration below 0.0005 M the results should show a curvature, and the slopes of experimental graphs should approach the limiting slopes. Although the present results show no tendency to approach the limiting law, we think that this is simply due to the fact that reliable experiments cannot be obtained from the cells in question at such extreme dilutions.

In view of this well established theoretical requirement there is no doubt that the values of E_0 obtained by the second method of extrapolation are the better.

The writer takes this opportunity to express his appreciation to Professor Herbert S. Harned for his advice and help during the progress of this work.

Summary

1. A study of the lead dioxide–lead sulfate–platinum electrode has been made. Crystalline lead dioxide prepared by electrolysis was found to give most consistent results. The reproducibility was within ± 0.1 mv.

2. Measurements of the cell

$$H_2 \mid H_2SO_4(m) \mid PbSO_4 \mid PbO_2 \mid Pt^+$$
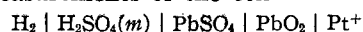
have been made over a concentration range of 0.0005 to 7.0 M and at temperatures from 0 to 60° at 5° intervals.

3. Values of the molal electrode potentials of the lead sulfate–lead dioxide–platinum electrode have been computed from 0 to 60°. Results by two methods of extrapolation have been discussed.

Activities and the Hydrolysis of Sucrose with Concentrated Acids

BY VERNON K. KRIEBLE

The influence of the common acids as catalysts has been investigated in many reactions but for the most part only in low concentrations. That the velocity constants for these acids, when used as catalysts, go up faster than their conductivities is well known, but it is not generally recognized that this divergence, for some reactions at least, becomes very great beyond a normal solution. Nor is it common knowledge that there is a large difference in velocities between equivalent concentrations of the common acids in moderately high concentration. It was not until Lewis[1] introduced the concept of the activity of ions and molecules, a property which can be measured over a wide limit of concentrations, that there was any reasonable basis for the explanation of these results.

J. W. Walker and the author[2] showed in 1908 the great difference in hydrolytic products produced where amygdalin was hydrolyzed with concentrated solutions of hydrochloric, sulfuric, oxalic and trichloroacetic acids. The amygdalin

molecule $\underset{\text{III}}{\overset{\overset{\displaystyle I}{\overset{\displaystyle O-G-OG}{\underset{\displaystyle II \mid}{C_6H_5C-H}}}}{\underset{\displaystyle CN}{\mid}}$ has three points where

water may be added. Concentrated hydrochloric acid attacks III readily, I moderately, and II least of all; concentrated sulfuric acid attacks II readily and III very little; concentrated oxalic acid attacks I most readily, then II and III very little, while concentrated trichloroacetic acid does not appear to have an appreciable effect on any of them. It was also pointed out that when the concentration of hydrochloric acid was increased in the ratio of 10 to 13 the velocity increased ten-fold. We believe that these are the first experiments on record which showed conclusively that hydrolysis could not be explained as a function of the hydrogen ion alone.

In 1927[3] we showed that there was a wide difference in velocity constants for hydrogen cyanide hydrolysis with equivalent concentration of hydrochloric and sulfuric acids, the former being much more active. It was pointed out that the velocity constants with hydrochloric acid increased at approximately the same rate as the square of the activity of the hydrogen ion or what Lewis and Randall call the activity of the undissociated molecule. This work was extended by Krieble and Peiker,[4] who pointed out that there was a wide difference between hydrogen chloride and hydrogen bromide and that the addition of

(1) Lewis, *Z. physik. Chem.*, **61**, 129 (1907).
(2) Walker and Krieble, *J. Chem. Soc.*, **85**, 1369 (1909).
(3) Krieble and McNally, THIS JOURNAL, **51**, 3368 (1929).
(4) Krieble and Peiker, *ibid.*, **55**, 2326 (1933).