OXIDATION-REDUCTION POTENTIALS.
III. THE MERCURIC-MERCUROUS ELECTRODE

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Carter and Robinson[1] were the first investigators to study the oxidation–reduction potential of the mercuric–mercurous electrode, using the perchlorates of mercury. They measured a series of cells of the type

$$Hg \mid Hg_2Cl_2, \ N \ KCl \mid 0.1 \ N \ KCl \ Hg_2(ClO_4)_2, \ Hg(ClO_4)_2 \mid Pt^{+2}$$

assuming that the error due to liquid junction was negligible. The perchlorates of mercury had previously been used by Ley and Heimbucher[3] and later by Linhart[4] and found suitable for electromotive force measurements as they are soluble, easily purified, highly ionized and do not form complex ions to any appreciable extent.

In a previous investigation on the oxidation–reduction potential of the ferric–ferrous electrode,[5] a method has been given for the determination of oxidation–reduction potentials in which the difficulties due to incomplete elimination of liquid junctions and the lack of precise data on the activity of an ion in the presence of other electrolytes have been reduced to a minimum.

In this investigation measurements were made of the cell

$$Pt \mid H_2, \ HClO_4 \mid HClO_4, \ Hg(ClO_4)_2, \ Hg_2(ClO_4)_2 \mid Pt^+$$
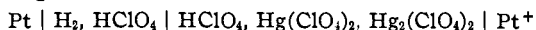
The liquid junction was maintained constant by a Lamb and Larson[6] flowing junction. The reproducibility of such a junction was established by MacInnes and Yeh.[7]

Two sets (A and B) of experimental data are presented. In both sets

[1] Carter and Robinson, J. Chem. Soc., 128, 267 (1927).

[2] All notations and abbreviations employed in this paper are those found in the "International Critical Tables," 1929, Vol. VI, p. 322.

[3] Ley and Heimbucher, Z. Electrochem., 10, 301 (1904).

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

[5] Popoff and Kunz, ibid., 51, 382 (1929).

[6] Lamb and Larson, ibid., 42, 229 (1920).

[7] MacInnes and Yeh, ibid., 43, 2563 (1921).

the concentrations of the perchloric acid were kept the same throughout the cell.

In Set A the ratio of the concentration of the mercuric perchlorate squared to the concentration of the mercurous perchlorate was maintained as near unity as possible. With decreasing concentrations of the mercury salts, within each series, both sides of the cell approach identity, and the liquid junction potential approaches zero. By plotting a function of the potential against the concentration of the mercurous perchlorate and extrapolating to zero concentration of the mercury salt, the liquid junction potentials should also become zero. To obtain the normal oxidation–reduction potential, one must correct for the presence of perchloric acid. By plotting the extrapolated values obtained from the various acidities against the acid concentrations and again extrapolating to zero concentration of perchloric acid, due correction is made for the presence of perchloric acid.

In Set B the concentration of mercuric perchlorate was kept equal to the concentration of the mercurous perchlorate, this procedure enabling one to work with more dilute solutions and to apply the principle of ionic strength. In this set the values of the oxidation–reduction potentials, E' (without any corrections for the activity coefficients), were found to be constant in each acid series although the concentrations of the mercury salts were varied from 0.008 m to 0.0005 m. The values of E' in each acid concentration were plotted against the molality of the perchloric acid and the curve extrapolated to zero. In Set B, series VI and VII, the solutions were dilute enough to use the principle of ionic strength and to calculate approximately the activity coefficients. The oxidation–reduction potentials, E'', thus obtained were plotted against the square roots of the ionic strengths and the line extrapolated to zero ionic strength. The two extrapolated values in Set B were checked mathematically using the method of moments[8,9] and the method of the zero sum.[10] The extrapolated values were found to agree very closely with those obtained by the mathematical methods.

Apparatus and Material

1. **Cell and Equipment.**—Practically the same cell and potentiometric equipment were employed as were used in former studies.[5,11] All e. m. f. measurements were made at 25 ± 0.01°. An Eppley standard cell, No. 30957, the voltage of which was expressed in International volts was used.

[8] H. L. Rietz, "Handbook of Mathematical Statistics," Houghton Mifflin Co., New York, 1924, pp. 68–70.

[9] Karl Pearson, "On the Systematic Fitting of Curves," Biometrica, 1902, Vol. I, pp. 265–303.

[10] Campbell, "The Adjustment of Observations," *Phil. Mag.*, **39**, 177 (1929); **47**, 816 (1924).

[11] Popoff, Riddick and Becker, THIS JOURNAL, **52**, 2624 (1930).

2. All water was redistilled from alkaline permanganate in an all-glass still.

3. All perchloric acid was redistilled in an all-glass still under reduced pressure, the first and last fourths being discarded. Air free from carbon dioxide was then passed through the acid to remove any possible trace of free chlorine.

4. Redistilled mercury was passed five times in a fine spray through a mercury purification column containing mercurous nitrate and nitric acid, and then passed three times through a column of distilled water.

5. Mercuric perchlorate was prepared by treating red mercuric oxide with perchloric acid,[12] until the solution was faintly turbid. After filtering, the solution was concentrated in an all-glass vacuum distillation apparatus under about 10 cm. pressure. Glass beads were introduced into the flask to prevent bumping and to serve as a gage to the concentration of the mercuric perchlorate solution. Mercuric perchlorate is very soluble and hence difficult to crystallize. When the density of the solution became such that the glass beads floated, good crystals could be obtained on slow cooling. Crystals produced by fast cooling came out in one solid mass with which it was difficult to work. Slow cooling produced large crystals when a small excess of perchloric acid was present. These crystals could be well drained and were sometimes about 2 cm. in diameter. Several of these large crystals were measured with a contact goniometer giving the angles M M = 120°, and M C = 90°. These indicate crystals in the hexagonal system with the forms $10\overline{1}0$ and 0001. Only the larger crystals could be removed from the solution for examination. Small crystals lose their identity before they can be examined in the air, this being due to the hygroscopic property of the mercuric perchlorate. Crystallization takes place slowly and when complete the glass beads would sink. The supernatant liquid was poured off and the crystals were drained in a centrifuge in special glass centrifuge cups at 800–900 r. p. m. for about twenty minutes. All mercuric perchlorate was at least twice recrystallized.

6. Mercurous perchlorate was prepared by shaking an acidified solution of mercuric perchlorate with an excess of mercury for forty-eight hours at 50°. Subsequent analysis in some of the solutions employed showed that the amount of mercuric perchlorate remaining in the solution was negligible. Both mercuric and mercurous perchlorates were kept in dark bottles under an atmosphere of carbon dioxide. The carbon dioxide was passed through silver sulfate solution and cotton before entering the solution.

7. All other chemicals were of the best quality obtainable.

Analytical Methods

All the data for the analyses are given in Table I. Weight burets were used in all titrations.

1. **Standardization of Perchloric and Hydrochloric Acids.**—The perchloric and hydrochloric acid solutions were standardized against a standard, carbonate-free sodium hydroxide solution, using phenolphthalein as the indicator. The base was standardized against Bureau of Standards potassium acid phthalate. Standardization against potassium acid phthalate had been found to agree closely with the standardization against benzoic acid and against constant boiling hydrochloric acid.[13]

2. **Analysis of Mercuric Salt.**—The stock mercuric perchlorate solution was standardized by three entirely different methods. The mercuric sulfide method was adopted as the standard.

a. **Mercuric Sulfide Method.**—A weighed portion of the mercuric perchlorate solution was acidified with 10 cc. of 0.8 N perchloric acid and diluted to 75 cc. Hydrogen

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[12] Chikashige, *J. Chem. Soc.*, **63**, 1013 (1895).

[13] Popoff and Neuman, *Ind. Eng. Chem., Anal. Ed.*, **2**, 45 (1930).

sulfide was passed for ten minutes. The solution was heated to boiling, cooled, then hydrogen sulfide again was passed until precipitation was complete. The precipitate was filtered through a Gooch crucible, washed with alcohol, carbon disulfide and ether. The carbon disulfide was used to remove any sulfur formed in the oxidation of the hydrogen sulfide. Attempts to employ ammoniacal solutions, etc., as recommended by some, failed to give concordant results. Without the carbon disulfide treatment, the results were very concordant among themselves but higher than the calculated employing pure mercuric chloride as the standard. The precipitate of mercuric sulfide was dried at 105° for one hour. Since the activity product constant of mercuric sulfide is very small (4×10^{-54}), no correction for solubility was made.

b. Potassium Iodide Method.—A solution of potassium iodide was standardized against recrystallized c. p. mercuric chloride. Sodium chloride and perchloric acid were added, the former to retard the formation of mercuric iodide, the latter to give identical conditions in the standardization of the iodide solution as in actual determination of the mercuric ion in the stock solution.

c. Thiocyanate Method.—An approximately 0.1 N solution of potassium thiocyanate was standardized against standard silver nitrate solution using ferric alum as the indicator. Perchloric acid was added for the same reason as in 2b.

The precision of the three methods of determining mercuric ion and the comparison between the three methods are given in Table I, 1 and 2.

Considering the precision of the mercuric sulfide method, one may justify its selection as the standard method, especially after the method was checked using c. p. mercuric chloride as the standard. The other methods were employed as an approximation and a check on a more precise method.

3. Analysis of Mercurous Salt.—The mercurous ion in the stock solution of the mercurous perchlorate was determined by two entirely different methods (see Table I, 3).

a. The Gravimetric Method.—In this method the mercury was precipitated as mercurous chloride with sodium chloride. A correction factor for the solubility and volatility on heating of the mercurous chloride was determined by preparing mercurous chloride, treating a weighed portion of the precipitate under conditions similar to those in the analysis and determining the loss in weight. The filtrate, after the mercurous ion had been precipitated, was treated with hydrogen sulfide, but the amount of the sulfide of mercury obtained was negligible. This method did not give very concordant results in some cases, but the average value agreed with that obtained by the electrometric method.

b. The Electrometric Method.—Mercurous perchlorate was added slowly and with stirring to an excess of sodium chloride solution. The excess sodium chloride was then titrated electrometrically with standard silver nitrate, using a silver–silver chloride electrode. The weight ratio between the sodium chloride and silver nitrate had previously been determined electrometrically. The silver nitrate was standardized against potassium chloride which had been recrystallized three times.

4. Acidity in the Mercury Perchlorate Solutions.—The mercuric and mercurous stock solutions contained free perchloric acid. This acid cannot be determined either electrometrically or colorimetrically employing indicators because of the presence of the mercury salts. The mercury was deposited on mercury cathodes using a current of 0.5 ampere and 3 volts, and the total acid was determined by titration with standard alkali solution. A solution of perchloric acid was electrolyzed using the same kind of electrodes (with free mercury in the solution) as in the analysis for acid in the mercury solution. Since the volume ratios between acid and base (Table I, 4) are the same both before and after electrolysis, it may be concluded that the free acid in the salt solutions can be determined after setting free the mercury on electrolysis by titrating with standard alkali. The acidities of the solutions are given in Table I, 5.

5. Preparation of Solutions of Known Concentration.—The stock solutions of acid and mercury perchlorates were employed for preparing, by weight, the various solutions needed for the cells using the proper buoyancy corrections.

TABLE I

ANALYTICAL METHODS

1. Precision of the Three Methods for Mercuric Ion

HgS method HgS per g. of soln., g.	KI method Weight ratio	KCNS method Weight ratio
0.10858	1.074	0.08319
.10853	1.072	.08315
	1.071	.08323
	1.072	

2. Comparison of the Three Methods for Mercuric Ion

Grams of $Hg(ClO_4)_2$ per gram of solution

HgS method	KI method	KCNS method
0.1864	0.1866	1.1858

3. Mercurous Perchlorate, Grams of $Hg_2(ClO_4)_2$ per gram of solution

Electrometric	Gravimetric
0.06635	0.06615
.06638	.06663
.06631	.06646
.06633	.06636
.06639	.06618
Av. .06635	Av. .06636

4. Volume Ratio of Acid to Base

Before electrolysis	After electrolysis
2.089	2.090
2.087	2.089

5. Acidities of the Mercury Perchlorate Solutions

Solution	Total HClO₄ titer	Mercury titer expressed as HClO₄	Actual HClO₄ titer
$Hg(ClO_4)_2$	0.1099	0.09374	0.01617
$Hg_2(ClO_4)_2$	.06016	.03986	.02030

Experimental Data

Cells of the type

$$Pt \mid H_2, HClO_4 \mid HClO_4, Hg(ClO_4)_2, Hg_2(ClO_4)_2 \mid Pt^+$$
$$E_H \qquad E_1 \qquad\qquad\qquad\qquad E_a$$
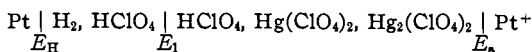
were measured. There are three sources of potential in the cell: E_H, the potential of the hydrogen electrode; E_a, the potential of the mercuric–mercurous electrode; and E_1, the liquid junction potential.

E_H was calculated from the equation

$$-E_H = 0.05915/2 \log (P_{H_2}/P_{760} \times 1/a_H{}^{+2}) \tag{1}$$

P_{H_2} is the pressure of the hydrogen taken as the barometric pressure, corrected for brass scale, minus the vapor pressure of the acid solutions

used. The vapor pressures were computed and taken to be the same as those for hydrochloric acid from the data given in the "International Critical Tables."[14] aH^+ represents the hydrogen-ion activity which was calculated from data of Randall and Young[15] for the mean activity coefficient of hydrochloric acid. Schuhmann[16] states that the mean activity coefficient of perchloric acid may be taken to be the same as that for hydrochloric acid up to one molal. Experimental data, of a somewhat similar nature, show that this conclusion may be correct, at least within the experimental error.

E_a was found from the equation

$$E_a = E_{cell} + E_H \tag{2}$$

E_1 cannot be computed at finite concentrations of mercuric and mercurous perchlorates, but it is kept constant in a given cell by a flowing junction.

1. **Set A.**—In Set A the ratio of the concentration of the mercuric perchlorate squared to that of the mercurous perchlorate was kept equal to one, but the molalities of the mercury salts were varied as shown in Table II. The mercurous ion is considered as a divalent ion.

TABLE II

THE CONCENTRATION OF THE MERCURY SALTS

Cell	Molality of $Hg_2(ClO_4)_2$	Molality of $Hg(ClO_4)_2$
A	0.008100	0.09000
B	.004000	.06324
C	.002000	.04472
D	.001000	.03162

The electromotive force data are given in Table III. The values of E_a in each acid concentration were plotted (Fig. 1) against the molality

TABLE III

ELECTROMOTIVE FORCE DATA (SET A)

Cell	$E_{obs.}$	$-E_H$	E_a	Cell	$E_{obs.}$	$-E_H$	E_a
	Series I. 0.4 m HClO$_4$				Series III. 0.1 m HClO$_4$		
A	0.93257	0.03013	0.9024	A	0.96782	0.06440	0.9034
B	.93247	.03013	.9023	B	.96761	.06440	.9032
C	.93206	.03016	.9019	C	.96674	.06438	.9024
D	.93172	.03016	.9016	D	.96602	.06436	.9017
	Series II. 0.2 m HClO$_4$				Series IV. 0.05 m HClO$_4$		
A	0.94959	0.04760	0.9020	A	0.98643	0.08101	0.9054
B	.94933	.04760	.9017	B	.98626	.08101	.9053
C	.94887	.04748	.9014	C	.98593	.08115	.9048
D	.94851	.04749	.9009	D	.98453	.08114	.9034

[14] "International Critical Tables," 3, 293 (1928).
[15] Randall and Young, THIS JOURNAL, 50, 995 (1928).
[16] Schuhmann, ibid., 46, 58 (1924).

of the mercurous perchlorate and extrapolated to zero concentration of the mercury salt, eliminating the liquid junction potential. The
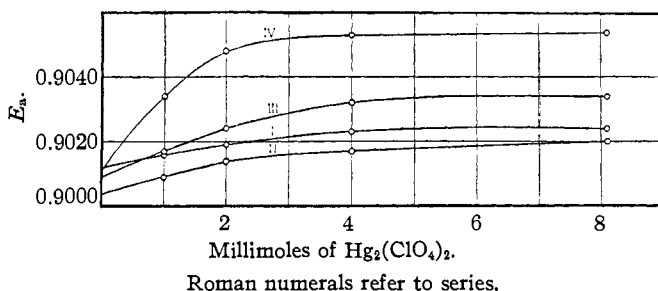

Millimoles of $Hg_2(ClO_4)_2$.

Roman numerals refer to series.

Fig. 1.—The oxidation–reduction potentials at various acidities.

oxidation–reduction potentials, E', obtained at various acidities are given in Table IV. In Fig. 2 the values of E' were plotted against the molality
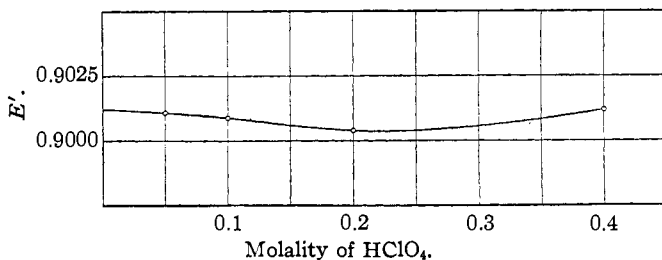

Molality of $HClO_4$.

Fig. 2.—The standard oxidation–reduction potential.

of the perchloric acid and the curve extrapolated to zero concentration of perchloric acid.

TABLE IV

OXIDATION–REDUCTION POTENTIALS AT VARIOUS ACID CONCENTRATIONS

Series	Molality of $HClO_4$	E'
I	0.4000	0.9012
II	.2000	.9004
III	.1000	.9009
IV	.0500	.9011

2. **Set B.**—In Set B the concentration of the mercuric salt was kept equal to the concentration of the mercurous, making it possible to work with a solution in which the ionic strength was as low as 0.023. Table V gives the electromotive force data obtained. E' was calculated from the equation

$$E_a = E' - 0.05915/2 \ (\log C_{Hg_2^{++}}/C_{Hg^{++}^2}) \tag{3}$$

where $C_{Hg_2^{++}}$ represents the concentration of the mercurous ion and $C_{Hg^{++}}^2$ represents the concentration of the mercuric ion squared.

TABLE V

ELECTROMOTIVE FORCE DATA (SET B)

Cell	$C_{Hg^{++}} = C_{Hg_2^{++}}$	$E_{obs.}$	$-E_H$	E_a	E'
		Series I.	1.0 m HClO$_4$		
A	0.004	0.84099	0.00471	0.8363	0.9072
B	.0001	.82329	.00477	.8185	.9072
		Series II.	0.4 m HClO$_4$		
A	0.005	0.86331	0.03016	0.8332	0.9012
B	.002	.85152	.03016	.8214	.9012
C	.001	.84252	.03003	.8125	.9012
D	.0005	.83300	.03016	.8033	.9010
		Series III.	0.2 m HClO$_4$		
A	0.008	0.88644	0.04763	0.8388	0.9008
B	.007	.88465	.04750	.8372	.9009
C	.006	.88275	.04763	.8351	.9008
D	.005	.88014	.04741	.8327	.9007
E	.004	.87722	.04744	.8298	.9007
F	.003	.87371	.04741	.8263	.9009
G	.002	.86828	.04747	.8208	.9006
H	.001	.85949	.04743	.8121	.9008
I	.0005	.85057	.04742	.8031	.9007
		Series IV.	0.12 m HClO$_4$		
A	0.006	0.89565	0.06004	0.8356	0.9013
B	.004	.88999	.05986	.8301	.9010
C	.002	.88113	.06004	.8211	.9009
D	.001	.87224	.05986	.8124	.9011
E	.0005	.86321	.05992	.8033	.9009
		Series V.	0.08 m HClO$_4$		
A	0.006	0.90598	0.06981	0.8362	0.9019
B	.004	.90087	.06981	.8311	.9020
C	.002	.89167	.06960	.8221	.9019
D	.0005	.87379	.06962	.8042	.9018
		Series VI.	0.04 m HClO$_4$		
A	0.007	0.92644	0.08655	0.8399	0.9036
B	.006	.92424	.08635	.8360	.9035
C	.005	.92189	.08648	.8354	.9034
D	.004	.91883	.08635	.8325	.9034
E	.003	.91490	.08642	.8285	.9031
F	.002	.90963	.08635	.8233	.9031
G	.001	.90067	.08637	.8143	.9030
H	.0005	.89175	.08642	.8053	.9030
		Series VII.	0.02 m HClO$_4$		
A	0.001	0.91829	0.10331	0.8150	0.9037
B	.0005	.90961	.10331	.8063	.9039

3. The Activity Coefficients of Perchloric Acid.—Following the procedure of Schuhmann[16] but employing flowing junctions, electromotive force measurements were made using four cells of the type

$$\text{Pt} \mid H_2, HClO_4 \mid HCl, H_2 \mid Pt^+$$
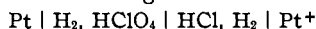
The acid concentrations were varied from 0.02 to 1 molal, but the concentrations of the acids in each cell were kept the same. After making corrections for the small variations in concentration and for the liquid junction potentials employing Lewis and Sargent's[17] formula

$$E_1 = -0.05915 \log \frac{\Lambda_{H^+} + \Lambda_{ClO_4^-}}{\Lambda_{H^+} + \Lambda_{Cl^-}}$$

and the more recent data found in the "International Critical Tables"[18] for the equivalent conductances of the two acids, it was found that any corrections for the unequal activity coefficients of hydrochloric and perchloric acids, would lie within the experimental errors for all concentrations except for the one molal acid, this correction being of the order of 1.2 millivolts.

Final Calculations and Discussion

The standard oxidation–reduction potential of the mercuric–mercurous electrode was finally derived from total concentration and from the principle of ionic strength making use of activity coefficients.

1. From Total Concentration.—It was found convenient in Set A to work with solutions in which the concentration of the mercuric salt squared was equal to the concentration of the mercurous salt. By suitable plottings (Figs. 1 and 2), the standard oxidation–reduction potential was found to be 0.9011 volt. By working with solutions in which the concentration of the mercuric perchlorate was kept equal to that of the mercurous, Set B, it was found that when dilute enough solutions were employed, plotting similar to that in Fig. 1 was unnecessary. The average values of E' which correspond to each acid concentration are given in Table VI. Figure 3 gives the curve obtained. The extrapolated value, 0.9050, was checked mathematically using the methods of moments and the zero sum and it was found to be 0.9045.

TABLE VI

VARIATION OF E' WITH ACIDITY

Molality of acid	E'
1.0	0.9072
0.4	.9012
.2	.9008
.12	.9011
.08	.9019
.04	.9033
.02	.9038

[17] Lewis and Sargent, THIS JOURNAL, 31, 363 (1909).
[18] "International Critical Tables," Vol. VI, 1929, p. 242.

2. From the Principle of Ionic Strength.—In Set B it was possible to work with solutions whose ionic strength was small enough to enable us to use the equation of Brönsted and La Mer[19] for the activity coefficient of a divalent ion given by the equation

$$-\log f = 0.5\ z^2\sqrt{\mu} \qquad (4)$$

This Equation 4 does not hold except in solutions whose ionic strength is of the order of 0.01 or less, but since the calculations involving the
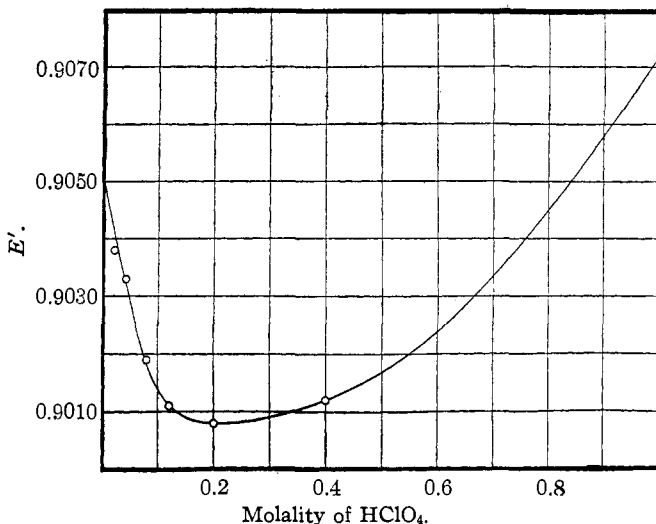

Fig. 3.—The standard oxidation–reduction potential from total concentration.

diameter of the ions, the dielectric constant, the distance of closest approach of the two ions, and others are somewhat uncertain, it was decided to calculate the coefficients by Equation 4 and then to plot the values of E'' (see Table VII), from the equation

$$E_{\mathrm{a}} = E'' - 0.05915/2 \left(\log \frac{C_{\mathrm{Hg_2}^{++}}}{C_{\mathrm{Hg}^{++2}}} \right) -0.05915/2 \left(\log \frac{\gamma_{\mathrm{Hg_2}^{++}}}{\gamma_{\mathrm{Hg}^{++2}}} \right) \qquad (5)$$

against the square root of the ionic strength.   This plot is given in Fig. 4. On extrapolating the straight line, the value for E_0 was found to be 0.9045.

TABLE VII

OXIDATION–REDUCTION POTENTIALS FROM IONIC STRENGTH

μ	f	E''
0.064	0.312	0.9182
.058	.330	.9177
.052	.350	.9167
.046	.372	.9160
.043	.385	.9155
.026	.476	.9133
.023	.498	.9127

19 Brönsted and La Mer, THIS JOURNAL, 46, 555 (1924).

This value was checked mathematically as formerly and was found to be 0.9042.

3. **Effect of Acidity and Concentration of Mercury Salts.**—When the concentration of the perchloric acid was varied from 0.02 to 1 molal, the oxidation–reduction potential of the mercuric–mercurous electrode went through a minimum at about 0.2 m. Since the effect on the potentials of changing the concentration of the mercury salts (keeping the mercuric equal to the mercurous) from 0.008 to 0.0005 m is practically negligible in each acid series, one may conclude that the liquid junction potentials are negligible. This conclusion seems justified since the potential remains the same even in 0.02 m perchloric acid, in which the liquid junction potential should be the largest.

4. **Comparison with Other Investigations.**—The oxidation–reduction potential of the mercuric–mercurous electrode was determined by Carter and Robinson[1] at 18°, using the perchlorates of mercury. They found a value of 0.913 and a much greater variation in the potential with acid concentration. They employed a calomel electrode as the reference electrode, using a potassium nitrate solution as a salt bridge. The use of the bridge in no way eliminates the liquid junction potentials. In all of their calculations they employed the same correction factor, -0.0044 volt, for the activity coefficient regardless of changes in the concentrations of mercury salts. Latimer and Hildebrand[20] give a
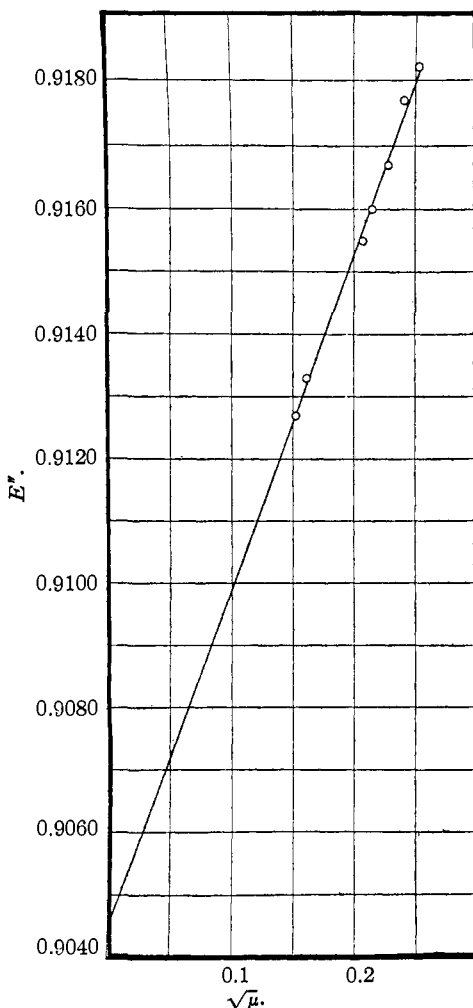

Fig. 4.—The standard oxidation–reduction potential from ionic strength.

[20] Latimer and Hildebrand, "Reference Book of Inorganic Chemistry," Macmillan Co., New York, 1929, p. 368.

value of -0.92 volt, which was calculated from values given by Abegg, Auerbach and Luther.[21]

5. The Standard Potential.—Since practically the same oxidation–reduction potential for the mercuric–mercurous electrode was obtained from either total concentration or ionic strength, one may justify the final value of 0.9050 volt. For analytical purposes the values in various acid concentrations given in Table VI are of special importance.

Conclusions

1. The standard oxidation–reduction potential of the mercuric–mercurous electrode was determined using the perchlorates of mercury.

2. Using suitable mathematical and graphical treatments as well as the activity coefficients of divalent ions from the limiting case of Brönsted and La Mer's equation, the standard oxidation–reduction potential was found to be 0.9050 v.

3. The mean activity coefficients of perchloric acid solutions were found to be practically of the same order as those for hydrochloric acid solutions up to 0.4 m.

4. Methods of analysis involving mercuric and mercurous salts, and acidity in the presence of mercury salts are given.

5. From an analytical standpoint and for all practical purposes, the potentials at various acidities are of greater importance than the standard one and are herein given. The potential goes through a minimum at about 0.2 m perchloric acid.

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[21] Abegg, Auerbach and Luther, "Messungen elektromotorischer Kräfte galvanischer Ketten mit wässerigen Elektrolyten," Halle a. S., Verlag v. Knapp, 1911.